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A TREATISE ON CHEMISTRY



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A

TREATISE ON CHEMISTRY

BY

THE RIGHT HONOURABLE SIR H. E. ROSCOE, F.R.S.

AND

C. SCHORLEMMER, F.R.S.

VOLUME II

THE METALS

PART I

"Chymia, alias Alchemia et Spagirica, est ars corpora vel mixta, vel composita, vel aggregata etiam in principia sua resolvendi, aut ex principiis in talia combinandi." STAHL, 1723

NEW EDITION COMPLETELY REVISED BY
B. MOUAT JONES AND OTHERS

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PREFACE TO VOL. II

(FIRST EDITION)

THE aim which the Authors have set before themselves in treating of the Metals and their Compounds is the same as that which they proposed in the discussion of the Non-Metallic Elements. Owing, however, to the large number of the Metals and their Salts, the description of these latter could not, within practicable limits, be made so complete as is possible in the case of the Non-Metallic Compounds. Hence the Authors, whilst giving the characteristic properties of each metal, have been obliged to restrict their notice to those compounds which possess the greatest interest either of a theoretical or practical kind.

Due attention has been paid to the more important technical processes connected with Metallurgy, and no pains have been spared to assist the description of such processes by Drawings of the most modern forms of apparatus and plant.

As an illustration of this the Authors would refer to the Chapter on the Soda and Glass Manufactures in Part I., and to the Metallurgy of Iron in Part II.

At the end of the volume will be found short Chapters on the Classification of the Elements; on Spectrum Analysis, so far as the detection of terrestrial matter is concerned.

January, 1878.

PREFACE TO THE THIRD EDITION

During the nineteen years which have elapsed since the publication of the first Edition of this volume of the Treatise much important work on the chemistry of the Metals and their Compounds has been done. So much indeed that a completely New Edition has been prepared, in which the Metallic Elements and their Compounds have been rearranged and all new matter of importance added. I again have to thank my friends Drs. Colman and Harden for the valuable help which they have given me in this as in the last volume.

H. E. ROSCOE.

September, 1897.

PREFACE TO THE FOURTH EDITION

MUCH new and important matter with regard to the Metals and their Compounds has come to light in the ten years since the last edition of this work appeared, and in the present volume care has been taken to include all the more important points connected with the recent discoveries. The subject of crystallography, which formerly appeared in the first volume, has now been included in the second, and here I must express my thanks to Professor Miers for permitting the use of the illustrations from his own work and for reading the proof of this chapter. Several contributors have assisted in the work of revision; amongst them I must mention Mr. C. O. Bannister, who has written upon Metallurgy and Alloys, Mr. Harry Baker, Dr. Colman, Dr. Marshall Watts, and Mr. Young, who have all assisted in various departments.

H. E. ROSCOE.

September, 1907.

PREFACE TO THE FIFTH EDITION

In preparing the fifth edition of the metals I have to thank several friends for assistance. By their contributions the subject has been brought up to date.

Whilst the general character of the work is preserved, several important alterations and additions will be found in this volume. Thus Dr. J. C. Philip has revised and improved the introductory and physical portions, whilst by his reading the whole of the final proofs accuracy has been maintained throughout. Mr. T. V. Barker has rearranged the chapter on crystallography and has inserted the recent work done in that subject. Dr. Makower has succeeded in placing in clear light the results of the new and important researches in the wide field of radioactivity.

Mr. Bannister, who once more has undertaken the metallurgical portion, Dr. Spencer (Rare Earths), Mr. Baker (Alkali Manufacture), Drs. Keane and Mollwo Perkin (Metallic Compounds) have ably assisted me in their several departments.

It is to be noted that unless a specific statement to the contrary is made all atomic weights are referred to $O = 16$.

H. E. ROSCOE.

July, 1913.

PREFACE TO THE SIXTH EDITION

In the ten years which have elapsed since the publication of the fifth edition of this book much new knowledge has been obtained of the chemistry of the metals and of their compounds. An endeavour has been made to incorporate the most important of this new material in the present edition while bringing the rest of the volume up to date. Great advances have been made in our fundamental ideas of atomic and molecular structure, of valency and of chemical affinity and in the interpretation of the Periodic Law. This has been largely a result of the rapid development of the science of radioactivity and the "new physics" and of the introduction of two new methods of investigation—positive ray analysis and X-ray spectroscopy. So rapid has been this advance, and so much new data is being acquired daily, that in a work of this kind, devoted mainly to a systematic account of the metals and their compounds, anything like a complete account of the new theories would be out of place. Only the outstanding results of the "new chemistry" have therefore been referred to, while the general style and character of the book have been maintained.

The introductory chapter on valency, the classification of the elements, atomic members, isotopes, atomic structure and spectrum analysis, has been revised by

Mr. L. J. Hudleston, and Mr. T. V. Barker has again dealt with the section on crystallography. Groups I. and II. have been brought up to date by Professor H. V. A. Briscoe; Alkali Manufacture by Professor J. R. Partington ; Groups III. and V. by Dr. H. F. V. Little; The Rare Earths and the Titanium group by Professor J. F. Spencer; Group VI. by Mr. A. A. Eldridge; the Germanium group and Manganese by Mr. C. R. Bury; Group VIII. by Dr. O. R. Howell; while Professor C. O. Bannister has once more revised the metallurgical portions and Dr. Makower the section on the Radioactive elements.

For the purpose only of convenience in handling and binding, the book has been divided into two parts, the pagination being continuous.

B. MOUAT JONES.

April, 1923.

THE FOLLOWING ARE THE CHIEF CONTRACTIONS EMPLOYED IN THIS VOLUME

Abbreviated Title	Journal
Amer. Chem J . . .	American Chemical Journal.
Amer. J. Sci. . .	American Journal of Science.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Physik . .	Annalen der Physik.
Ann. Chim. Phys. .	Annales de Chimie et de Physique.
Ann. Mines . .	Annales des Mines
Arch. Néerland. . .	Archives Néerlandaises des Sciences exactes et naturelles
Arch. Pharm. . .	Archiv der Pharmazie.
Atti R. Accad. Lincei .	Atti della Reale Accademia dei Lincei.
Ber. . .	Berichte der deutschen chemischen Gesellschaft.
Biochem. Zeit.	Biochemische Zeitschrift
Brit Assoc. Reports	Reports of the British Association
Bull. Acad. roy. Belg. .	Académie royale de Belgique—Bulletin de la Classe des Sciences
Bull. Geol. Soc. Amer .	Bulletin of the Geological Society of America.
Bull. Soc chim. .	Bulletin de la Société chimique de Paris.
Chem. Centr. .	Chemisches Centralblatt.
Chem. News .	Chemical News.
Chem. Zeit. . .	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Academie des Sciences.
Gazz. . .	Gazzetta chimica italiana.
Geol. Mag. .	Geological Magazine.
Jahrb. Min . .	Neues Jahrbuch fur Mineralogie, Geologie und Palaeontologie.
J. Amer. Chem. Soc	Journal of the American Chemical Society.
J. Chim. phys . . .	Journal de Chimie physique.
J. Iron Steel Inst. . .	Journal of the Iron and Steel Institute.
J. Pharm.	Journal de Pharmacie.
J. Physical Chem. .	Journal of Physical Chemistry
J. pr Chem. . . .	Journal fur praktische Chemie.
J. Roy. Agric. Soc. . .	Journal of the Royal Agricultural Society.
J. Russ. Phys. Chem. Soc. .	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind. . .	Journal of the Society of Chemical Industry.
Journ. Chem. Soc. .	Journal of the Chemical Society.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Mem. Manch. Phil. Soc. .	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Min. Mag.	Mineralogical Magazine.
Monatsh.	Monatshefte fur Chemie und verwandte Theile anderer Wissenschaften.
Pflüger's Archiv . . .	Archiv fur die gesammte Physiologie des Menschen und der Thiere.
Pharm. J.	Pharmaceutical Journal.
Phil. Mag.	Philosophical Magazine.

Abbreviated Title	Journal
Phil. Trans.	Philosophical Transactions of the Royal Society.
Pogg. Ann.	Poggendorff's Annalen der Physik und der Chemie.
Proc. Chem. Soc. . . .	Proceedings of the Chemical Society.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings [English Version].
Proc. Roy. Soc. . . .	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin. . .	Proceedings of the Royal Society of Edinburgh.
Quart. J. Geol. Soc. . .	Quarterly Journal of the Geological Society.
Rec. trav. chim. . . .	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Sitzungsber. K. Akad. Wiss. Berlin	Sitzungsberichte der koniglich preussischen Akademie der Wissenschaften zu Berlin.
Zeit. anal. Chem. . . .	Zeitschrift fur analytische Chemie.
Zeit. angew. Chem. .	Zeitschrift fur angewandte Chemie.
Zeit. anorg. Chem. . .	Zeitschrift fur anorganische Chemie.
Zeit. Chem. . . .	Zeitschrift fur Chemie.
Zeit. Elektrochem. .	Zeitschrift fur Elektrochemie.
Zeit. Kryst. Min. . .	Zeitschrift fur Krystallographie und Mineralogie
Zeit. physikal. Chem. . .	Zeitschrift fur physikalische Chemie, Stochiometrie und Verwandtschaftslehre.
Zeit. physiol. Chem. . .	Hoppe-Seyler's Zeitschrift fur physiologische Chemie.

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CHEMISTRY

THE FOLLOWING ARE THE ATOMIC WEIGHTS OF THE ELEMENTS USED IN THIS VOLUME.

1922.

International Atomic Weights.

		0 = 16.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39 9
Arsenic	As	74·96
Barium	Ba	137 37
Bismuth	Bi	208·0
Boron	B	10·9
Bromine	Br	79·92
Cadmium	Cd	112 40
Cæsium	Cs	132 81
Calcium	Ca	40 07
Carbon	C	12 005
Cerium	Ce	140·25
Chlorine	Cl	35 46
Chromium	Cr	52·0
Cobalt	Co	58 97
Columbium	Cb	93·1
Copper	Cu	63 57
Dysprosium	Dy	162·5
Erbium	Er	167·7
Europium	Eu	152 0
Fluorine	F	19 0
Gadolinium	Gd	157·3
Gallium	Ga	70 1
Germanium	Ge	72·5
Glucinum	Gl	9 1
Gold	Au	197 2
Helium	He	4 00
Holmium	Ho	163 5
Hydrogen	H	1 008
Indium	In	114 8
Iodine	I	126 92
Iridium	Ir	193·1
Iron	Fe	55 84
Krypton	Kr	82·92
Lanthanum	La	139 0
Lead	Pb	207·20
Lithium	Li	6 94
Lutecium	Lu	174 0
Magnesium	Mg	24·32
Manganese	Mn	54 93
Mercury	Hg	200·6
Molybdenum	Mo	96·0
Neodymium	Nd	144 3
Neon	Ne	20 2
Nickel	Ni	58 68
Niton (radium emanation)	Nt	222 4
Nitrogen	N	14 008
Osmium	Os	190 9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31 04
Platinum	Pt	195 2
Potassium	K	39 10
Praseodymium	Pr	140 9
Radium	Ra	226 0
Rhodium	Rh	102·9
Rubidium	Rb	85 45
Ruthenium	Ru	101 7
Samarium	Sa	150 4
Scandium	Sc	45·1
Selenium	Se	79 2
Silicon	Si	28 3
Silver	Ag	107 88
Sodium	Na	23 00
Strontium	Sr	87 63
Sulphur	S	32·06
Tantalum	Ta	181 5
Tellurium	Te	127 5
Terbium	Tb	159 2
Thallium	Tl	204 0
Thorium	Th	232 15
Thulium	Tm	168 5
Tin	Sn	118 7
Titanium	Ti	48 1
Tungsten	W	184·0
Uranium	U	238 2
Vanadium	V	51 0
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	173·5
Yttrium	Yt	89 33
Zinc	Zn	65·37
Zirconium	Zr	90·6

CHEMISTRY

THE METALS

1 THE metals gold, silver, copper, iron, tin, and lead were known to the ancients. We find them mentioned in the writings of the Old Testament, as well as in those of the early Greek authors. The name of mercury is first found in the writings of Theophrastus, but the existence of most of the remaining metals became known only in comparatively recent times. Antimony appears to have been obtained in very early times, although the reputed Basil Valentine describes its preparation as a novelty, but neither zinc nor bismuth became generally known until the sixteenth century.

An historical notice of each metal will be found under its own heading. We have here simply to consider the progress of our knowledge concerning the properties of the metals as a class.

2 The Latin writer who adopted the name of Geber (Vol. I., p. 6) is the first author in whose writings we find a distinct definition of the word metal: "Metallum est corpus miscibile, fusibile, et sub malleo ex omni dimensione extendibile." According to this definition, mercury, which had been looked upon as metallic by the Greek alchemists, is not included amongst the metals. Geber likewise distinguished gold and silver as the noble metals, because they did not undergo any change in the furnace, whereas the others were termed base metals. This definition was accepted throughout the whole of the middle ages, so that when the brittle metals antimony, bismuth, and zinc came to be well known, they were classed as bastard or semi-metals. Thus, for instance, Paracelsus says: "Zinc, which is a metal and yet no metal, and bismuth and the like being partly malleable . . . . are bastards of the metals."

Opinion was divided respecting the position of mercury, until its solidification by extreme cold, and its malleability in this condition, had been observed in 1759. From this time forward it was universally admitted to be a metal.

The brilliant experiments and reasoning of Lavoisier towards the close of the eighteenth century finally established the elementary nature of the metals, which hitherto had been looked upon by the followers of Stahl as compounded of a calx united with phlogiston (Vol. I., p. 14). In Lavoisier's classification of substances, drawn up in 1787, the metals are grouped together as one of the five classes into which he divided the elements, the distinction between metals and semi-metals being abandoned.

The decomposition of the alkalis by Davy in 1807 made chemists acquainted with substances of an entirely new character. Although the bases of soda and potash agreed "with metals in opacity, lustre, malleability, conductive powers as to heat and electricity, and in their qualities of chemical combination," [1] and were classed by Davy himself with the metals, yet, inasmuch as they were lighter than water, they were not considered by many chemists to be metals proper. In 1808 Erman and Simon attempted [2] to revive the old distinction between true metals and substances resembling metals by proposing for the new substances the name of metalloids (μέταλλον a metal, εἶδος similar). This proposal, however, was not generally accepted, and the elements were from this period classed in two groups, the non-metals and the metals, the newly coined term, metalloid, being applied, or rather perhaps misapplied, by Berzelius in 1811 to designate the former of the two classes, in which sense it is still sometimes employed. It soon became evident that the separation of the elements into these two groups was not a logical one, since no satisfactory basis of classification could be obtained. With the discovery of the alkali metals a high specific gravity had ceased to be characteristic, and the property of metallic lustre soon shared its fate. Thus tellurium, discovered in 1782, was grouped with the metals because of its lustre and specific gravity. Its close chemical analogy with sulphur, however, which was pointed out by Berzelius in 1832, clearly indicated that these two elements belonged to the same class.

[1] Davy, *Phil. Trans.*, 1808, **98**, 31.
[2] Gilbert's *Annalen*, 1808, **28**, 347.

In the same way, every property supposed to be characteristic of a metal has been found to be shared by some one or other non-metallic substance, or to be absent from some otherwise well-characterised metal. Thus opacity, and the power of conducting electricity well, were long deemed essential properties of a metal; but we now know that, in very thin layers, metals such as gold and silver are transparent, whilst several non-metals, such as graphite, and selenium, in one of its modifications, conduct electricity like metals.

3 The relations of the so-called non-metals to the metals are well seen when the elements are arranged according to the periodic system (p. 50), which has now superseded the old classification. Thus the elements of the nitrogen group exhibit in a striking manner the gradual transition from a distinctly non-metallic to a distinctly metallic element. Nitrogen itself is undoubtedly a non-metallic body, whilst phosphorus in certain of its allotropic modifications approaches the metals, one of these modifications, indeed, being termed metallic phosphorus. Arsenic, the third member of the nitrogen family of elements, was formerly classed as a semi-metal. At a later period it was considered to be a metal proper, and even now some chemists rank it amongst the metals, whilst others, looking to its striking similarity with phosphorus, place it amongst the non-metals. Antimony and bismuth are elements which belong to this same group, and these substances are always considered to be metals from their close analogy to other distinctly metallic substances. It will be noticed that the members of this group of elements approach more and more closely to a true metal as the atomic weight increases. The same peculiarity is observed in other groups. The elements titanium and zirconium are, on the one hand, closely connected with the non-metal silicon, whilst, on the other, they exhibit the most marked analogies with tin, and are classed accordingly amongst the metals. We must, however, be careful not to draw the conclusion that the elements which possess the highest atomic weights are necessarily metals, and those which possess the lowest are non-metals. Lithium, which after hydrogen and helium possesses the smallest atomic weight, is a well characterised metal, and hydrogen itself exhibits in its chemical relations far more analogy with the metals than with the non-metals; whilst, on the other hand, xenon, with the atomic weight 130, shows none of the characteristics of a metal.

Although the division into metals and non-metals is thus seen to be one which does not admit of exact definition, it is none the less true that the metals as a class do possess certain generic properties which most of the non-metals either do not possess at all, or exhibit only in a very slight degree. Amongst these properties that of metallic lustre may especially be mentioned. This property is characteristic of all metals, and if it is not noticeable when the metals are in a state of fine division, in which case they frequently appear in the form of black powders, it can readily be observed when the powder is rubbed with a hard body.

Another generic difference which may be noticed is that whilst the characteristic oxides of the non-metals belong to the class of acid-forming oxides, those of the metals are basic in character, only the higher oxides of certain of the metals, as a rule, being capable of forming acids.

DETERMINATION OF THE ATOMIC WEIGHTS OF THE METALS.

4 Although by the year 1819 chemists were in possession of the three principles, laid down respectively by Avogadro, Dulong and Petit, and Mitscherlich, by which they are now guided in the selection of the atomic weights of the elements, yet nearly half a century was to elapse before the establishment of a consistent and generally accepted method of applying these principles.

Avogadro's theory (Vol. I., p. 75), proposed in 1811, a few years only after the introduction of the idea of combination between atoms of characteristic weights, rendered necessary a division of the particles even of elementary substances. The chemists of the period were not, however, prepared to admit the validity of these views, and hence they endeavoured to obtain some other foundation upon which to erect a system of atomic weights. Berzelius (1818) found this in the assumption of the identity of volume and atom in the case of the elementary gases, ascribing to water the formula H_2O, and to oxygen the relative atomic weight 16. In deciding upon the atomic weights of the other elements, especially the metals, Berzelius was forced,[1] like Dalton, to have recourse to purely arbitrary assumptions.

[1] *Essai sur la théorie des proportions chimiques, etc.*, Paris, 1819.

When the important discoveries of Dulong and Petit, and Mitscherlich (Vol. I., p. 42), were made, Berzelius at once saw the simplification which would be effected by the adoption of the theories of these chemists, and in his next table of atomic weights he introduced them consistently, thus arriving at numbers which, with a few exceptions, differ from the modern ones only by small amounts due to the errors of the analytical processes then employed. The chief of these exceptions, potassium, sodium, and silver, were due to the close chemical analogy between the strongly basic oxides of these metals and those of calcium, zinc, etc.; this led Berzelius, in spite of the known specific heat of silver, to formulate them all on the same type RO, the atomic weights assigned to the three metals being therefore twice as great as those now employed.

Dumas, on the other hand, at first based his system of atomic weights on Avogadro's theory, but was seduced from his allegiance to this by a false application of it, which had, however, received the countenance of Avogadro himself. Because the molecules of hydrogen, nitrogen, oxygen, and chlorine were each supposed, according to this theory, to be made up of two atoms, Dumas concluded that the same should be true of the molecules of the vapour of any elementary substance whatever. On this basis he calculated the vapour density of sulphur, but found that the experimental density was three times as great as the theoretical. A somewhat similar inconsistency was observed in the case of phosphorus, and Dumas was thus led to abandon Avogadro's theory, whilst Berzelius was induced by the same experiments to modify his theory of the identity of volume and atom in the case of simple substances, and to confine it to the simple permanent gases.

The discovery of dimorphism in 1823 had rendered the application of Mitscherlich's theory of isomorphism to the selection of atomic weights somewhat uncertain, so that at this time, about 1830, doubts were cast on the possibility of obtaining any satisfactory method of ascertaining the relative weights of the atoms, and it was proposed that chemists should content themselves with employing the equivalent weights directly determined by analysis.

The equivalent system had been proposed in England by Wollaston[1] at a very early date (1814), and had found very general acceptance amongst his countrymen; it had, moreover,

[1] "A Synoptic Scale of Chemical Equivalents," *Phil. Trans.*, 1814, **104**, 1.

been adopted by Gmelin in his great *Handbook of Chemistry* (1817), and had thus come into very general use. The tendency to abandon the idea of the chemical atom, as distinct from the equivalent, was moreover strengthened by Faraday's discovery (1834) that the electrolytic equivalents of the metals, that is the relative amounts deposited during a given time by a given current of electricity, are identical with their chemical equivalents.

The rapid development of organic chemistry which occurred in the years 1830–1855 made chemists acquainted with many reactions, such as the formation of mixed ethers (Williamson), acid anhydrides (Gerhardt), and esters, the production of mixed salts of polybasic acids, etc., which could not easily and consistently be formulated on the basis of the equivalent system. Numerous modifications of the system were therefore introduced by individual investigators, until it became quite impossible to interpret a chemical formula without special information as to the sense in which the symbols were employed by the particular author in question.

A most important proposal was put forward by Gerhardt, who, along with Laurent, had resuscitated Avogadro's theory, and applied it consistently to all volatile compounds. He regarded all the basic oxides of the metals as derived from water by the replacement of the hydrogen by two atoms of the metal, the general formula of the oxides being R_2O. Silver, potassium, and sodium thus received the atomic weights which are now recognised, whilst the atomic weights of metals such as lead, zinc, calcium, etc., had only one-half of the modern values.

In 1858, the various conflicting systems were finally co-ordinated by Cannizzaro [1] in his *Sketch of a Course of Chemical Philosophy*. In this admirable paper, which is one of the classics of chemical literature, he pointed out in detail how a complete and consistent system of formulæ could be obtained by the recognition both of Avogadro's theory, and the theory of atomic and molecular heats as founded by Dulong and Petit, Neumann, and Joule. In the case of metals which form compounds volatile without decomposition, Cannizzaro was able to show that the

[1] Sunto di un corso di filosofia chimica fatto nella Reale Università di Genova del Professore S. Cannizzaro, Nuovo Cimento (1858), VII. An English translation of this paper has been published as No. 18 of the *Alembic Club Reprints*. Reference may be made also to the Cannizzaro Memorial Lecture, by Sir William Tilden, *Journ. Chem. Soc.*, 1912, **101**, 1677.

atomic weight deduced from specific heat was in agreement with the value deduced from vapour density. The atomic weights suggested by Cannizzaro were gradually adopted by chemists as soon as they realised the simplicity and consistency of the system, and they are the ones still employed. One of the immediate results flowing from the adoption of Cannizzaro's numbers was the periodic system of classification of the elements introduced by De Chancourtois, Newlands, Mendeléeff, and Lothar Meyer (see p. 46).

5 The determination of the atomic weight of an element involves, as has already been pointed out (Vol. I., p. 77), two processes :—(1) The determination of the proportion by weight in which the element combines with other elements, or, as it is called, the chemical equivalent of the element; (2) the selection of that multiple of the equivalent which represents the smallest amount of the element found in a molecule, and which is known as its *atomic weight*.

I. Determination of the Equivalent.

6 In expressing the chemical equivalents of the elements, it is convenient to have some one element as the standard of reference, and formerly hydrogen was chosen for this purpose. Since, however, comparatively few of the metals form well-defined compounds with hydrogen, the equivalent of a metal referred to hydrogen had in nearly all cases to be calculated from an analysis of the compounds of the metal with oxygen or chlorine. Accordingly, it is generally agreed that oxygen should be taken as the standard element (Vol. I., p. 78). On this basis the equivalent of an element is defined as the number of parts by weight of the element which combine with 8 parts by weight of oxygen. Our knowledge of the quantitative relation between hydrogen and oxygen (Vol. I., p. 284) on the one hand, and hydrogen and chlorine (Vol. I., p. 213) on the other, permits an extension of the definition in the following terms : the equivalent of an element is the number of parts by weight of the element which combine with 1·003 parts by weight of hydrogen or 35·46 parts by weight of chlorine. Elements which combine with any of the standards in several different proportions have, of course, a corresponding number of different equivalents.

The equivalent of an element can be most directly determined

by the analysis or synthesis of its oxide, a process which gives immediately the proportion by weight in which the element combines with oxygen. Thus the equivalents of nickel and iron have been determined by reducing a weighed amount of the oxide to the corresponding metal, whilst the inverse process of converting the metal into an oxide has been employed in determining the equivalents of antimony and of bismuth. In most cases, however, this direct process cannot be applied, and recourse is then had to indirect methods of analysis or synthesis. Thus the chlorides of the metals cannot, as a rule, be directly analysed or synthesised with great quantitative accuracy; it is therefore usually more convenient and accurate to bring a weighed amount of the chloride into reaction with a salt of silver, and ascertain either the amount of silver required to combine with the whole of the chlorine present, or the weight of silver chloride produced, or both of these quantities. When this is known, the amount of chlorine present, and therefore the composition of the chloride, can be calculated, provided that the ratio in which silver unites with chlorine, *i. e.*, the composition of silver chloride, be known.

Stas found, for example, that 85·031 parts of sodium chloride required 156·862 parts of silver for the complete precipitation of its chlorine in the form of silver chloride. Since 107·12 parts of silver were found by him to be equivalent to 1 of hydrogen, and to combine with 35·18 of chlorine to form silver chloride, it follows that the amount of sodium chloride which is required to react with 107·12 parts of silver, and therefore contains 35·18 parts of chlorine, is $\frac{85{\cdot}031 \times 107{\cdot}12}{156{\cdot}862} = 58{\cdot}06$. Hence $58{\cdot}06 - 35{\cdot}18 = 22{\cdot}88$ parts of sodium are equivalent to 107·12 parts of silver, or 1 part of hydrogen. This conclusion, if re-stated on the basis of the oxygen standard, would run: 23·06 parts of sodium are equivalent to 107·98 parts of silver or 8 parts of oxygen.

In a similar way, the equivalent of an element may be indirectly ascertained by estimating the amount of any substance required for, or produced in, a reaction in which a weighed amount of the element or one of its compounds takes part. The equivalents of a very large number of the metals have accordingly been ascertained by the conversion of an oxide into a salt, of a salt into an oxide, or of one salt into another. Thus, for example, Erdmann and Marchand found that 100 parts of calcium carbonate yield 136·05 parts of calcium sulphate. From

the known composition and properties of carbonic acid gas and sulphur trioxide, it follows that an increase of weight of 35·80 in this reaction corresponds with 43·67 parts of carbonic acid gas in the original carbonate, and, further, that this is combined with such a quantity of an oxide as contains 15·88 parts of oxygen. Hence 100 parts of calcium carbonate, which gain 36·05 in the reactior, contain $\frac{43{\cdot}67 \times 36{\cdot}05}{35{\cdot}80} = 43{\cdot}99$ parts of carbonic acid gas, combined with 56·01 parts of calcium oxide, and this contains $\frac{15{\cdot}88 \times 36{\cdot}05}{35{\cdot}80} = 16$ parts of oxygen, and 40·01 of calcium. Hence, according to this particular experiment, the equivalent of calcium is $\frac{40{\cdot}01 \times 8}{16} = 20{\cdot}005$. The equivalent of calcium can also be similarly deduced from the results obtained by the same chemists for the calcination of calc-spar, 13·6031 grams of which were found to yield 7·6175 grams of quicklime on ignition.

In other cases the amount of hydrogen which is evolved when a weighed amount of a metal is dissolved in an acid or alkali (aluminium, zinc), the amount of a metal precipitated by a weighed amount of another metal from a solution of one of its salts, the amount of metal deposited by the electrolysis of a weighed amount of a salt (copper), the amount of an acid required to neutralise a weighed amount of a given base, may be used for the determination of the equivalent, provided that the necessary knowledge of the equivalents of the various other substances involved is available.

In all these indirect processes, in addition to the unavoidable experimental error of the actual estimation, there is also the experimental error involved in each of the equivalents employed in the calculation. The investigator, therefore, in selecting methods for the determination of the equivalent of an element, will, if possible, choose such as involve substances of which the equivalents are known with the greatest accuracy. The experimental error of the actual estimation cannot be entirely removed, but its effect is diminished by taking the average result of a large number of experiments, and by arranging that the amount of material employed shall be sufficiently large to make this inevitable error bear as small a ratio as possible to the number which is to be determined. A further precaution, which should always be taken when it is practicable, is to

determine the equivalent by as many distinct processes as possible, since in this way the special experimental error which is peculiar to each process is to some extent eliminated.

The experimental foundation which is thus seen to be necessary for the construction of a system of equivalents is due in great part to the classical labours of Stas,[1] who carried the processes of analytical chemistry to a degree of accuracy quite unknown to his predecessors, Dalton, Berzelius, and Dumas. Stas chose silver as the substance which was most convenient for experimental purposes, and determined its equivalent on the one hand to oxygen, and on the other to chlorine, bromine, iodine, sulphur, and potassium, very great precautions being taken to avoid error. The equivalent of silver to chlorine, bromine, and iodine was determined by the direct synthesis of the corresponding compound. In the case of chlorine, the silver and the silver chloride obtained from it were weighed; on the other hand, the compositions of the bromide and iodide were determined by a series of complete syntheses, the metallic silver, the bromine or iodine, and the silver bromide or iodide being all weighed. The equivalent of silver to oxygen was ascertained by the reduction of silver chlorate, bromate, and iodate to the chloride, bromide, and iodide. The difference in weight between the oxygenated salt which was taken and the halogen compound which was obtained gives the ratio of oxygen to silver chloride, etc., and the composition of the latter having been ascertained as just described, the ratio of silver to oxygen can be calculated. In another series of experiments designed for the same purpose, potassium chlorate was converted into potassium chloride by heat, and the ratio of potassium chloride to oxygen thus obtained. The amount of silver necessary to combine with the chlorine of a weighed amount of potassium chloride was then determined, and the ratio silver : potassium chloride : oxygen thus ascertained. A similar series of experiments was carried out with the sulphide and sulphate of silver. In this way, then, the equivalents of silver, chlorine, bromine, iodine, sulphur, and potassium, relatively to oxygen, were all obtained, and these were used by Stas for the determination of the equivalents of sodium, lithium, lead, and nitrogen.

The probable error in the mean equivalent of silver deduced

[1] Nouvelles recherches sur les lois des proportions chimiques; sur les poids atomiques et leur rapports mutuels (Bruxelles, 1865).

from these five sets of experiments amounts to only 0·0034 per cent. More recent investigations, however, tend to show that, in spite of the great care exercised by Stas, certain errors were not avoided, and that the numbers obtained by him require correction. The fundamental ratios have been subjected to very careful revision by a number of workers, and the result has been that the values adopted by Stas have been altered to a slight extent. The most probable value, for example, of the ratio Ag : AgCl is now taken as 100 : 132·87, instead of 100 : 132·85, found by Stas. The adoption of corrected values for the fundamental ratios has rendered necessary alterations in those atomic weights which have been calculated with the aid of the ratios. The changes which have been agreed on are all incorporated in the table of atomic weights on p. 2, and a summary of the work which has led to the adoption of these changes will be found in the Reports of the International Committee on Atomic Weights.[1]

The special methods adopted for the determination of the equivalents of the various metals will be found under their several headings.

II. Selection of the Atomic Weight.

7 The methods already described (Vol. I., p. 77) for the determination of the atomic weight of an element by ascertaining the molecular weights of a number of its compounds by the vapour density method, and then finding out by comparison the smallest amount of the element which is ever present in a molecule, may be applied without alteration to such of the metals as form volatile compounds. Many metals, however, form such a small number of volatile compounds that the determination of the atomic weight by this method becomes unsatisfactory, and, of course, it cannot be applied at all to such of the metals as do not form volatile compounds. The molecular weights both of the metals themselves and of their compounds in solution in various solvents may in certain cases be ascertained either by the cryoscopic method of Raoult, or by the boiling point method (Vol. I., p. 132).

In cases to which none of these methods can be applied

[1] *Proc. Chem. Soc.*, 1906, **22**, 8; 1907, **23**, 7; 1908, **24**, 5; 1909 **25** 3; *Journ. Chem. Soc.*, 1909, **95**, 2219; 1910, **97**, 1865; 1911, **99**, 1870; 1912, **101**, 1882; 1913, **103**, 1743; 1914, **105**, 2577; 1915, **107**, 1282; 1916, **109**, 777; 1919, **115**, 879; 1920, **117**, 885.

chemists are guided by the specific heat of the metal and its compounds, its general relations with the other elements, and the isomorphism of its compounds.

Molecular Weights of the Compounds of the Metals.

8 The most volatile among the compounds of the metals are the organo-metallic derivatives, which may be looked upon as compounds of the metals with the alcohol radicles. They are usually obtained by the action of a metal on an organic iodide, zinc-methyl, for example, being prepared by the action of zinc on methyl iodide:

$$2Zn + 2CH_3I = ZnI_2 + Zn(CH_3)_2.$$

These compounds are usually liquids which boil at comparatively low temperatures, and their vapour densities can therefore be determined by the ordinary methods, except that, as they are very readily oxidised and are usually spontaneously inflammable, the determinations must be carried out in an atmosphere of an indifferent gas, such as nitrogen. In addition to these compounds of the metals with the alcohol radicles, the remarkable compounds of nickel and iron with carbonic oxide, and the metallic derivatives of acetylacetone, serve for the same purpose. Volatile organic compounds, the vapour densities of which have been determined, are formed by the following metals: Zn, Hg, Al, Sn, Pb, Sb, Bi, Ge, Mn, Cr, Co, Mo, Fe, and Ni.

Further, many metals form halogen compounds which volatilise at moderate temperatures, and the vapour density of which can therefore be determined. In a few cases, the vapour density of the metal itself has been found to be of value in deciding upon the atomic weight.

The experimental methods of ascertaining the vapour density of substances which are volatile only at high temperatures differ somewhat from those ordinarily employed. The older determinations of Deville and Troost, Roscoe, and others were carried out by Dumas's method, a bulb of porcelain, which can be sealed by means of the oxy-hydrogen jet, being used for temperatures above that at which glass softens. The great difficulty inherent in this process is the determination of the temperature, which must be known with considerable accuracy. This was determined either calorimetrically, by the aid of a weighed mass of platinum, or by the use of a second similar

bulb containing iodine or mercury, the temperature being calculated from the amount of vapour left in this second bulb under the conditions of the experiment. This process has now been superseded by that of Victor Meyer, which was originally introduced for this purpose, and presents the great advantage that a knowledge of the temperature of the experiment is not involved in the calculation of the results. An apparatus constructed of, or lined with, porcelain, platinum, or iridium, is employed, and is heated to the requisite temperature either by the vapour of some substance of high boiling point, or by a gas- or electric-furnace. It is of course essential that the temperature of the apparatus be maintained constant throughout the duration of the experiment. The air in the apparatus is usually displaced by nitrogen, to prevent the oxidation which would otherwise occur in many cases at the high temperature employed. A modification of Victor Meyer's method, suitable for temperatures about 2000°, and involving the use of very small quantities of material, has been devised by Nernst.[1]

The interpretation of the experimental results is often rendered difficult by the complete or partial dissociation of the compound, either into two similar or two dissimilar molecules. The occurrence of this is rendered evident by the fact that the vapour density varies with the temperature at which it is determined. Several cases of this kind are discussed in connection with the subject of valency.

Atomic Heat.

9 The specific heat of a body is the ratio of the quantity of heat required to raise the temperature of the body 1° to the quantity required to raise that of an equal weight of water 1° (Maxwell). The amount of heat needed to raise a kilogram of water through 100° is thirty-one times as large as that required to raise the same weight of platinum through the same interval of temperature, or, in other words, the amount of heat which raises one kilogram of water through 100° will raise thirty-one kilograms of platinum over the same range; hence the specific heat of platinum is said to be $s^{1}_{1} = 0{\cdot}032$. The specific heat of the same substance varies considerably under different physical conditions and according as the substance is solid, liquid, or gaseous.

[1] *Zeit. Elektrochem.*, 1903, **9**, 622.

A careful determination of the specific heat of thirteen of the solid elements by Dulong and Petit in the year 1819[1] showed that a simple relation existed between the chemical equivalent and the specific heat of these substances. When the numbers representing these two quantities for each element were multiplied together, the products were found either to be equal, or to stand in a very simple ratio. By a supposition analogous to that made by Avogadro with respect to the combination of gases by volume, Dulong and Petit concluded that the specific heat of the metals varied inversely as the atomic weight, and proposed to adopt as the relative atomic weights of the metals those numbers which, multiplied by the specific heat, gave a constant product. Having thus modified the atomic weights which were current at that time, the French experimentalists formulated the proposition that *the atoms of different elements possess the same capacity for heat*, or *all the elements have the same atomic heat*. Although chemists at the time acknowledged the importance of this generalisation, they did not regard it as established beyond doubt, inasmuch as the alterations in the atomic weights introduced by Dulong and Petit, although admissible in some cases, led in other respects to very improbable conclusions. Moreover, a few of the elements investigated by the French chemists were very impure, so that the specific heats which they obtained were inexact. Berzelius very properly insisted that further investigation was necessary, and added,[2] "If we attempt to apply this idea to compound bodies, and if the result of such an examination confirms the views of Dulong and Petit, this discovery will rank as one of the most important parts of theoretical chemistry."

The next step in the direction thus indicated by Berzelius was made by F. Neumann,[3] who showed that equivalent quantities of similarly constituted compounds require equal quantities of heat to raise their temperature by the same amount, and that this equality is independent of difference in crystalline form; thus calc-spar and aragonite possess the same specific heat. Neumann, however, did not connect this discovery of the relation between the specific heats of the compounds with that of Dulong and Petit respecting the specific heats of the elements. Only by degrees, and in the hands of numerous

[1] *Ann. Chim. Phys.*, 1819, **10**, 395.
[2] Berzelius's *Jahresb.*, 1822, **1**, 19.
[3] *Pogg. Ann.*, 1831, **23**, 1.

observers, was this connection established. The researches which have mainly contributed to the development of the subject are those of Hermann, 1834, Regnault, 1840, De la Rive and Marcet, 1840, Joule, 1844, Woestyn, 1845, Garnier, 1852, Cannizzaro, 1858, H. Kopp, 1864 [1] (whose memoir contains an historical introduction to the whole subject), Tilden, 1900, Dewar, 1905, Nernst and Lindemann, 1910.

It is especially to the researches of Regnault and Kopp that we are indebted for the corroboration of the results of the earlier experiments proving that the rule of Dulong and Petit is applicable with a very considerable degree of accuracy to about forty of the elementary bodies, when the mean specific heats of the solid elements between 0° and 100° are employed. We may, therefore, regard those weights of the elements as their atomic weights which, when multiplied into the specific heats of the elements, give a constant number. This number represents the capacity of the atom for heat, or the *atomic heat* of the element, and its value for most of the elements lies near 6·3. This is clearly seen if we multiply the specific heats of a few metals by their corresponding atomic weights, for example :—

	Specific heat.		Atomic weight.		Atomic heat.
Lead . .	0·0310	×	207·2	=	6·4
Platinum . .	0·0323	×	195·2	=	6·3
Silver . .	0·0562	×	107·88	=	6·1
Tin . . .	0·0551	×	118·7	=	6·5
Zinc . . .	0·0935	×	65·37	=	6·1

This relationship may therefore be employed for the purpose of controlling the determinations of atomic weight in doubtful cases. Amongst those elements which conform to the theory are in the first place the metals, and then certain non-metals, such as bromine, iodine, selenium, tellurium, and arsenic.

The following table shows within what limits the atomic heat of the different elements varies. The first column contains the names of the elements, the second their mean specific heats for the range of temperature given in the third, the fourth the atomic weight, the fifth the product of the atomic weight into the specific heat, and the sixth the names of the observers :—

[1] *Annalen*, 1864, Suppl. 3, 1.

I.	II.	III.	IV.	V.	VI.
Lithium . .	0·9408	27° to 99°	6·94	6·5	Regnault.
Sodium . .	0 2934	— 28 „ 6	23·00	6·7	„
Magnesium .	0 2460	18 „ 99	24·3	6·0	Voigt.
Aluminium .	0·2189	15 „ 185	27·1	5·9	Tilden.
Phosphorus .	0 202	13 „ 36	31·0	6·3	Kopp.
Sulphur . .	0 1844	15 „ 97	32·1	5·9	Regnault.
Potassium .	0 1662	— 78 5 „ 23	39·1	6·5	Schuz.
Calcium . .	0 149	0 „ 100	40·1	6 0	Bernini.
Titanium .	0 1125	0 „ 100	48·1	5·4	Nilson and Pettersson.
Vanadium .	0·1153	0 „ 100	51·0	5 9	Mache.
Chromium .	0 1208	0 „ 100	52 0	6 3	„
Manganese .	0 1217	14 „ 97	54·9	6 7	Regnault.
Iron . . .	0·1162	23 „ 100	55·8	6·5	Trowbridge.
Cobalt . .	0 1030	15 „ 100	59 0	6 1	Tilden.
Nickel . .	0 1084	15 „ 100	58 7	6·4	„
Copper . .	0 0936	20 „ 100	63·6	6·0	Schmitz.
Zinc . . .	0 0935	0 „ 100	65·4	6·1	Bunsen.
Gallium . .	0 079	12 „ 23	70·1	5 5	Berthelot.
Germanium .	0 0737	0 „ 100	72 5	5·3	Nilson and Pettersson.
Arsenic . .	0 0830	21 „ 68	75 0	6·2	Bettendorf & Wullner.
Selenium .	0 0840	22 „ 62	79 2	6·7	„ „
Bromine . .	0·0843	— 78 „ —20	79 9	6 7	Regnault.
Zirconium .	0 0660	0 „ 100	90 6	6 0	Mixter and Dana.
Molybdenum	0 0647	20 „ 100	96 0	6·2	Stucker.
Ruthenium .	0 0611	0 „ 100	101·7	6 2	Bunsen.
Rhodium .	0 0580	10 „ 97	102 9	6·0	Regnault.
Palladium .	0 0593	10 „ 100	106·7	6 3	„
Silver . .	0 0562	15 „ 100	107 9	6 1	Bartoli and Stracciati.
Cadmium .	0 0548	0 „ 100	112·4	6·2	Bunsen.
Indium . .	0 0569	0 „ 100	114·8	6 5	„
Tin . . .	0 0551	20 „ 109	118·7	6 5	Spring.
Antimony	0 0495	0 „ 100	120 2	5 9	Bunsen.
Tellurium .	0 0483	— 15 „ 100	127·5	6 2	Tilden.
Iodine . .	0 0541	9 „ 98	126 9	6 9	Regnault.
Cæsium . .	0 048	0 „ 26	132·8	6·4	Erkardt and Graefe.
Lanthanum .	0 0448	0 „ 100	139 0	6·2	Hillebrand.
Cerium . .	0 0448	0 „ 100	140·2	6 3	„
Tantalum .	0 0363	16 „ 100	181·5	6 6	von Bolton.
Tungsten .	0 0336	0 „ 100	184·0	6·2	Mache.
Osmium . .	0 0311	19 „ 98	190 9	5 9	Regnault.
Iridium . .	0 0323	18 „ 100	193 1	6·2	Behn.
Platinum .	0 0323	0 „ 100	195·2	6·3	Bunsen.
Gold . . .	0 0316	0 „ 100	197·2	6·2	Violle.
Mercury . .	0 0319	— 78 „ —40	200·6	6·4	Regnault.
Thallium .	0 0326	20 „ 100	204·0	6·6	Schmitz.
Lead . . .	0 0310	18 „ 100	207 2	6 4	Behn.
Bismuth . .	0 0304	17 „ 99	208 0	6·3	Voigt.
Thorium .	0 0276	0 „ 100	232 2	6 4	Nilson.
Uranium .	0 0280	0 „ 98	238·2	6·7	Blumcke.

10 The following elements, the atomic heats of which are less than 5, have been omitted from the foregoing table :—

I.	II.	III.	IV.	V.	VI.
Glucinum .	0 4246	0° to 100°	9·1	3 9	Nilson and Pettersson.
Boron . .	0·3066	0 „ 100	10 9	3·4	Moissan and Gautier.
Diamond .	0·1461	0 „ 99 8	12 0	1 8	Weber.
Graphite .	0·1904	0 „ 99	12 0	2 3	„
Wood charcoal	0·1935	0 „ 99	12·0	2 3	„
Gas carbon .	0·2040	24 „ 68	12 0	2 4	Bettendorf & Wullner.
Silicon . .	0·1730	14 „ 97	28 3	4 9	Regnault.

These elements therefore possess at temperatures between 0° and 100° smaller atomic heats than correspond to Dulong and Petit's rule. Weber,[1] however, showed that the specific heats of carbon, boron, and silicon increase rapidly with the temperature, and that at high temperatures their atomic heats become nearly constant and approximate to the mean value obtained for other elements. Thus diamond has a specific heat of 0·1128 at 10·7°, 0·2218 at 140°, 0·4408 at 606·7°, and 0·4589 at 985°, at which temperature it has an atomic heat of 5·51. Graphite with an atomic heat of 1·37 at — 50·3°, reaches the value of 5·60 at 980°.

Similar results were obtained in the case of silicon. The specific heat of this element increases from 0·1360 at — 39·8° to 0·2029 at 232°, above which it appears to remain constant, the atomic heat then being 5·7. Boron also exhibits the same phenomenon, the specific heat increasing from 0·1965 at — 39·6° to 0·3663 at 233°, and probably becoming constant at 500–600°.

Humpidge[2] showed that glucinum exhibited a similar behaviour, the atomic heat reaching the nearly constant value of 5·65 at 500°.

Weber further showed that the allotropic modifications of a substance at low temperatures possess different specific heats, but that this difference diminishes as the temperature rises, and at last altogether disappears. For example, Regnault concluded from his experiments that the specific heat of amorphous carbon was different from that of the two other modifications. Weber has, however, distinctly shown that this is not the case, but that carbon exists in only two thermal modifications, (1) opaque, (2) transparent. These thermal differences occur

[1] *On the Specific Heat of the Elements Carbon, Boron, and Silicon* (Stuttgart, 1874).

[2] *Proc. Roy. Soc.*, 1885, **38**, 188; 1885, **39**, 1.

only at low temperatures, and when a high temperature is reached no variation is observed.

11 From the table (p. 18) we see that the atomic heats of the elements differ from one another considerably, even within the limits of temperature at which these values have been obtained. Thus, for instance, whilst the value for the majority lies between 6·1 and 6·6, in others the number sinks so low as 5·3, and in the case of iodine exceeds 6·7. These differences may perhaps in some instances be explained by the fact that the substances under investigation were impure. It must also be remembered that the specific heat of most substances varies with the temperature, and the researches of Pionchon,[1] Behn,[2] Tilden,[3] and others,[4] have shown that this variation, even for the metals, is often very considerable. This is well seen in the following table, in which the true specific and atomic heats of a number of metals are given for a series of temperatures :— [5]

Absolute temperature	Aluminium		Nickel.		Silver.		Tellurium.	
	Specific heat.	Atomic heat.	Specific heat.	Atomic heat.	Specific heat	Atomic heat.	Specific heat.	Atomic heat.
100°	0 1226	3 32	0 0575	3·37	0·0467	5 04	0 0462	5 89
200	0 1731	4 69	0 0878	5 15	0 0528	5·70	0 0471	6 00
300	0·2053	5 56	0·1054	6·18	0 0558	6·02	0·0480	6 12
400	0·2254	6 11	0 1168	6 85	0 0572	6·17	0 0489	6 23
500	0 2384	6 46	0 1233	7·24	0 0581	6 27	0·0498	6 35
600	0·2471	6 70	0 1275	7·48	0 0587	6 33	0·0507	6 46
700	0·2531	6 86	0 1301	7 63	0·0590	6 37	0 0516	6 58
800	—	—	0 1321	7 75	—	—	—	—
900	—	—	0 1338	7 85	—	—	—	—

In general the differences between the atomic heats of the elements become more marked the lower the temperature at which the specific heats are determined. Indeed Dewar has shown that at 50° Abs. the atomic heat is a periodic function of the atomic weight. As the result of numerous experiments at very low temperatures, particularly those of Nernst and his collaborators, it is established that as the temperature decreases

[1] *Compt. rend.*, 1886, **102**, 1122.

[2] *Ann. Physik*, 1901, [4], **1**, 257.

[3] *Phil. Trans.*, 1900, **194**, 33; 1903, **201**, 38; 1904, **203**, 143.

[4] Wigand, *Ann. Physik*, 1907, **22**, 99; Magnus, *ibid.*, 1910, **31**, 597; Richards and Jackson, *Zeit. physikal. Chem.*, 1910, **70**, 414; Schimpff, *ibid.*, 1910, **71**, 257.

[5] Tilden, *Journ. Chem. Soc.*, 1905, **87**, 555. Here, as in other tables of this section, the values of the atomic heat have been recalculated on the basis of the revised figures for the atomic weights of the elements.

the specific heats of all elements fall, at first rapidly, then more slowly, tending to vanish at the absolute zero. The following table illustrates this for a few of the elements :—

Silver.		Lead.		Copper.		Aluminium.		Diamond.	
Abs. temp	Atomic heat.	Abs. temp.	Atomic heat.	Abs temp	Atomic heat.	Abs. temp.	Atomic heat.	Abs temp	Atomic heat.
173°	5 46	198°	6·27	173°	4 98	173°	4 54	262°	1 14
86	4·40	123	5 89	88	3 38	88	2 62	222	0 76
66	3 66	63	5 65	33	0·54	83	2 41	205	0 62
45	2·47	37	4·40	28	0·32	35	0·33	88	0 03
35	1 58	23	2 96	24	0·22	32	0 25	30	0 00

The original statement of Dulong and Petit as to the identity of the atomic heats of the elements can therefore be regarded as only a rough approximation, applicable mainly to the metals between 0° and 100°.[1]

We must bear in mind that when we speak of specific heat, we really refer to a complex quantity, comprising not only the heat which actually goes to raise the temperature of the heated body, but also that which is expended in performing external or internal work, such as expansion, or diminution of the cohesion of the particular body. This last amount of heat is different for different substances, whilst the first amount is theoretically the same for a molecule of any substance.

The above generalisation does not apply to liquid or gaseous elements with the single exception of mercury, which possesses almost the same atomic heat in the liquid as in the solid state.

The most important evidence for the applicability of Dulong and Petit's rule is the fact that the results deduced from it agree with those deduced from Avogadro's theory for those metals which form volatile compounds, and with which, therefore, such a comparison can be instituted.

A theoretical basis for the rule has been developed by Einstein,[2] Nernst and Lindemann,[3] and Debye.[4]

[1] Compare Lewis, *J. Amer. Chem. Soc*, 1907, **29**, 1165, Nernst, *Zeit. Elektrochem*, 1911, **17**, 265.

[2] *Ann. Physik*, 1907, [4], **22**, 180; 1911, **35**, 679.

[3] *Ann. Physik*, 1911, [4], **36**, 395; *Sitzungsber. K. Akad. Wiss. Berlin*, 1911, 494.

[4] *Ann. Physik*, 1912, [4], **39**, 789. See also W. C. McC. Lewis, *Quantum Theory* (Longmans), Chap. III, for a general theoretical treatment of atomic heats.

Molecular Heat of Compounds.

12 The law that the molecular heat of a compound is equal to the sum of the atomic heats of its elements, or that the atomic heat of an element does not undergo change when that element enters into combination, was first laid down by Joule,[1] but its experimental verification is chiefly due to Kopp. The following examples will illustrate this :—

		Specific heat.	Molecular heat. Found.	Molecular heat. Calculated.
Potassium bromide	KBr	0·1070	12·7	13·2
Mercuric iodide . .	HgI_2	0·0423	19·2	20·2
Lead iodide . . .	PbI_2	0·0427	19·7	20·2
Lead bromide . .	$PbBr_2$	0·0533	19·6	19·8

This agreement, moreover, is maintained at varying temperatures, so that the specific heat of each of the elements in a compound varies with the temperature in the same way as it does when the element itself is heated. This is shown in the following table for nickel telluride, NiTe, the calculated figures being obtained by adding together the atomic heats of nickel and tellurium given on p. 20.[2]

Absolute temperature.	Molecular heat. Observed.	Molecular heat. Calculated.
100°	8·44	9·26
200	11·43	11·15
300	12·50	12·30
400	13·01	13·08
500	13·24	13·59
600	13·37	13·94
700	13·45	14·21

Hence if the atomic heat of a solid element has not been determined, it may be calculated from the molecular heat of its compounds with other elements the atomic heats of which are known. In this way the atomic heats of rubidium, strontium, barium, and titanium have been determined at various times, and the values so found agree with the rule which comprises all the other metals.

Kopp has shown also that the elements which are gases at

[1] *Phil. Mag.*, 1844, [3], **25**, 334.

[2] Tilden, *Journ. Chem. Soc.*, 1905, **87**, 557.

the ordinary temperature possess a constant atomic heat in their various solid compounds. On this basis the atomic heat of chlorine has been found to be 5·9, that of nitrogen 5·3, of fluorine 5·0, of oxygen 4·0, and of hydrogen 2·3. The following examples illustrate this point :—

		Specific heat.	Molecular heat. Found.	Molecular heat. Calculated.
Silver chloride . .	$AgCl$	0·089	12·7	12·0
Zinc chloride . . .	$ZnCl_2$	0·136	18·5	17·9
Potassium platini-chloride. . . .	K_2PtCl_6	0·118	57·4	54·7
Ice	H_2O	0·478	8·6	8·6
Mercuric oxide . .	HgO	0·048	10·4	10·4
Calcium carbonate .	$CaCO_3$	0·206	20·6	20·7
Potassium sulphate .	K_2SO_4	0·196	34·2	34·9
Hexachloroethane .	C_2Cl_6	0·177	41·9	39·2

Kopp has moreover proved that the elements boron, silicon, and carbon possess, in combination, the same atomic heat as in the free state, at temperatures below 100°. This renders it probable that, if we could obtain the specific heat of oxygen and hydrogen compounds at a high temperature, the atomic heats of these elements would exhibit the same sort of alteration which has been proved to occur in the case of carbon, silicon, and boron.

In the case of oxygen such a change has actually been deduced from experiments on the specific heats of the metallic oxides by Tilden, who has calculated from the temperature variation of the specific heat of alumina, Al_2O_3, that the atomic heat of combined oxygen is 1·9 at 100° Abs., 3·3 at 300°, 3·8 at 500°, and 4·0 at 700°. These results lead to the value 3 for the atomic heat of combined oxygen at about 0° C., and hence it follows, since the specific heat of ice between — 78° and 0° is 0·47, that the atomic heat of combined hydrogen is 2·7. These numbers differ somewhat from those of Kopp given above.

13 Taking into consideration the results thus deduced from the molecular heats of compounds, it appears that the elements which possess an exceptionally small atomic heat at temperatures below 100° have low atomic weights and, with the exception of glucinum, are non-metals (see p. 19). All the non-metals the

atomic weights of which are high, as well as the remaining metals, agree approximately with Dulong and Petit's rule below 100°.

14 As instances of the employment of the atomic heat in selecting the atomic weight, the following may be quoted.

Thallium shows many analogies on the one hand with the alkali metals, and on the other with lead, and it was for some time a matter of doubt whether the lower chloride should be formulated as $TlCl_2$, in which case the atomic weight would be 405·2, or as TlCl, the atomic weight being then 202·6. Regnault found the specific heat of thallium to be 0·0335, and thus decided the question in favour of the latter view, since $0·0335 \times 202·6 = 6·8$.

A similar instance occurs in the case of indium, the chloride of which contains 38·3 parts by weight of metal to 35·46 parts by weight of chlorine. Indium has a very considerable resemblance to zinc and cadmium, and for this reason the chloride was supposed to have the formula $InCl_2$, giving an atomic weight of 76·6 to the metal. In 1870 Bunsen [1] ascertained by means of his ice calorimeter that the specific heat of indium is 0·057. Now $0·057 \times 76·6 = 4·4$, or only two-thirds of the atomic heat of the other metals. Hence we must assume that the true atomic weight of the metal is $76·6 \times \frac{3}{2} = 114·8$. This gives the formula for the chloride, $InCl_3$, which has been confirmed by the vapour density.

The example of uranium may also be quoted. At one time this metal was supposed to have an atomic weight of about 119, and to resemble iron in its chemical characteristics, its oxides being assigned the formulæ UO and U_2O_3. At a later period, however, it was found that the chemical relations of the metal agreed better with the atomic weight 236·7, according to which its oxides would be UO_2 and UO_3. This conclusion was confirmed by Zimmermann, who found its specific heat to be 0·0276, its atomic weight therefore being about 238.[2]

Isomorphism.

15 An account of the general phenomena of isomorphism will be found under "Crystallography." As briefly mentioned in the historical introduction (Vol. I., p. 42), Mitscherlich was the first to perceive that substances which are similar in crystalline form are similar also in chemical composition; he concluded

[1] *Phil. Mag.*, 1871, [4], **41**, 161, 392. [2] *Annalen*, 1885, **232**, 299.

from his observations that the same number of atoms combined in the same way produces the same crystalline form, this latter being independent of the chemical nature of the atoms and depending only on their number and relative position. He pointed out soon afterwards that this relation might be employed for the determination of the relative combining weights of two elements or compounds. Thus, having found that potassium sulphate and potassium selenate, which crystallise in the rhombic system, are isomorphous, he concluded that selenic acid (the anhydride) would, like sulphuric acid, contain three times as much oxygen as the base with which it was combined in the salt in question, this conclusion being afterwards confirmed by analysis.

At the time when Mitscherlich first stated his theory of the relation between atomic composition and crystalline form, the only available means of ascertaining the atomic weights of the metals was that provided by Dulong and Petit's rule, which had been applied only to some thirteen elements. The rule, moreover, had not at that time been extended to the molecular heat of compounds, and hence the atomic weights of a large number of metals could be determined only by analogy, or by arbitrary assumptions. Under these circumstances Mitscherlich's theory of isomorphism proved of great importance, and was at once applied by Berzelius to the determination of the atomic ratios of such elements as chromium, titanium, etc. Thus the ratio of the amounts of oxygen in chromium sesquioxide and chromic anhydride per unit of chromium was known to be 1 : 2, the simplest expression of which, according to the Daltonian system, would be by the formulæ CrO and CrO_2, although Berzelius formulated them for other reasons as CrO_3 and CrO_6. Chromium sesquioxide, however, is isomorphous with ferric oxide, iron being an element the atomic weight of which had been determined by the specific heat method, and hence the formula Cr_2O_3 was given to it. Chromic anhydride thus became CrO_3, which is in full agreement with the fact that the chromates are isomorphous with the sulphates, sulphuric anhydride having been formulated by Berzelius on independent grounds as SO_3.

At present the isomorphous relations of the compounds of an element only supply additional confirmation of the atomic weight, which has now been deduced for every element either from the molecular weight of its compounds, from the atomic

heat of the element itself, from the molecular heat of its compounds, or from the ratio of the specific heat of the element at constant pressure to that at constant volume (Vol. I., p. 135).

The elements may be grouped into the following series,[1] the members of which form isomorphous compounds. Elements which form several series of compounds are often found in a corresponding number of isomorphous series, the isomorphous relations of one type of compound being different from those of another.

(1) (*a*) K, Rb, Cs, Tl, (NH_4).
(*b*) Li, Na, Ag.
(2) (*a*) Gl, Mg, Zn, Cd, Mn, Fe, Co, Ni, Os, Ru, Pd, Pt, Cu.
(*b*) Ca, Sr, Ba, Pb, Ra.
(3) La, Di, Yt, Ce, Er.
(4) Al, Fe, Cr, Co, Mn, Ir, Rh, Ga, In, (Ti).
(5) Cu, Hg, Pb, Ag, Au.
(6) Si, Ti, Ge, Zr, Sn, Pb, Th, Mo, Mn, U, Ru, Rh, Ir, Os, Pd, Pt, Fe.
(7) N, P, As, V, Sb, Bi.
(8) Cb, Ta.
(9) S, Se, Cr, Mn, Mo, W, As, Sb, Fe, Te (?).
(10) F, Cl, Br, I, Mn, (CN).

No cases of isomorphism have as yet been observed among the compounds of the following elements:

H, B, Sc, C, and O.

The details of the isomorphous compounds of the metals included in the above series will be found under the several metals.

The Molecular Weights of the Metals.

16 The metals as a rule boil at exceedingly high temperatures, and up to the present it has for this reason been found possible to obtain definite results with the vapour densities of

[1] Arzruni, *Physikalische Chemie der Krystalle* (Vieweg, 1895). Sonderabdruck aus Graham-Otto's *Ausfuhrliches Lehrbuch der Chemie*, 1 Band, 3 Abtheilung. See also Groth, *Einleitung in die chemische Krystallographie*, pp. 48–53 (Engelmann, Leipzig), or the English translation of this volume, *Introduction to Chemical Crystallography*.

zinc, cadmium, mercury, silver, antimony, bismuth, lead, and thallium only.[1] The results obtained indicate that the molecules of these metals are monatomic, although it should be noted that the values obtained for the vapour densities of the four last metals are all somewhat higher than would be expected on that basis. The vapour densities of potassium and sodium have been determined only approximately, since the vapours of these metals attack the material of which the apparatus is constructed. The results, however, point to the conclusion that these two metals form monatomic molecules.

The molecular weights of many of the metals have been determined also by the cryoscopic and vapour-pressure methods of Raoult (Vol. I., pp. 132–5). These experiments render it probable that in nearly all cases the molecules of the metals are identical with their atoms. When tin is used as a solvent for the metals Ni, Ag, Au, Cu, Tl, Na, Pd, Mg, Pb, Zn, Cd, Hg, Bi, and Ca, the solutions which are formed behave on cooling in the same manner as dilute solutions of non-electrolytes in water (*loc. cit.*). Atomic proportions of these metals, when added to a fixed amount of tin, so as to form a dilute solution of the metal, all lower the freezing point of tin to the same extent. Further, the amount of the depression agrees with that calculated from theoretical considerations, on the assumption that the molecular weights of the dissolved metals are identical with their atomic weights.[2] Some metals, such as indium and aluminium, appear to be exceptional: but the apparent association in such cases may be explained by the formation of compounds with the solvent, or by the formation and separation of solid solutions. The freezing points and vapour pressures of solutions of the metals in mercury have also been examined, and lead to similar conclusions, although the results obtained are not so regular as when tin is the solvent.[3]

17 The identity of atom and molecule has been confirmed in the case of mercury vapour by the determination of the ratio of the specific heat at constant pressure to that at constant volume (see Vol. I., p. 135). In the same way it has been shown that

[1] Biltz and Meyer, *Zeit. physikal. Chem*, 1889, **4**, 264; Biltz, *ibid*, 1896, **19**, 385; Wartenberg, *Ber*, 1906, **39**, 381; *Zeit. anorg. Chem*, 1907, **56**, 320. See also W. E. S. Turner, *Molecular Association* (Longmans), 1915, for a summary of the data.

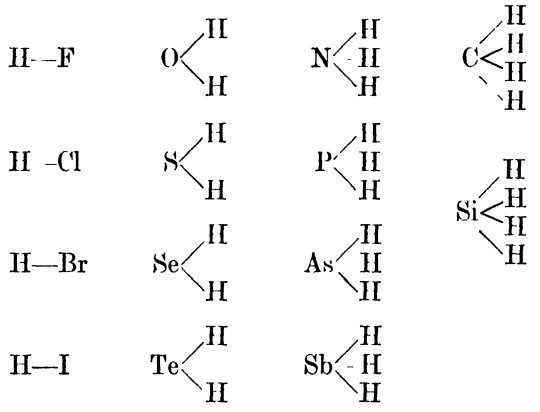
[2] Heycock and Neville, *Journ. Chem. Soc.*, 1890, **57**, 376.

[3] Tammann, *Zeit. physikal. Chem.*, 1889, **3**, 441; Ramsay, *Journ. Chem. Soc.*, 1889, **55**, 521; Turner, *loc. cit.*

the molecules of sodium and potassium in the state of vapour are monatomic.[1]

VALENCY OF THE ELEMENTS.

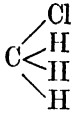
18 In connection with the non-metallic elements it has already been pointed out (Vol. I., p. 145) that the atoms of these elements differ in the number of hydrogen atoms with which they can combine. This varying combining power of the elements is known as *valency* or *quantivalence*, and the elements are described as monovalent, divalent, trivalent, or tetravalent (univalent, bivalent, tervalent, or quadrivalent), or as monads, dyads, triads, or tetrads, according as they combine with one, two, three, or four atoms of hydrogen. This is expressed also by saying that each of these elements has one, two, three, or four *units of affinity* or *bonds*, and in combination with hydrogen each of these is satisfied by combining with the single unit of affinity of the latter. This is graphically expressed in the following formulæ, the mutual bond of affinity being represented by the straight line connecting the two atoms:



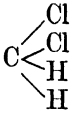
The further investigation of the non-metallic elements has shown that similar relationships are to be found in their compounds with elements other than hydrogen. Thus, in the compounds mentioned above, the hydrogen may be replaced by other elements, and it has been found that those elements which combine with only one atom of hydrogen are able to replace only one atom of that element, whilst the divalent elements

[1] Robitzsch, *Ann. Physik*, 1912, **38**, 1027.

are able to replace two atoms, the trivalent three, and so forth. Thus, if we take the compound of carbon and hydrogen, CH_4, we can replace one or more atoms of hydrogen by an equal number of chlorine atoms, two or four atoms by one or two atoms of oxygen, and three atoms by an atom of nitrogen, the graphic formulæ of the compounds obtained being given below :—



Methyl chloride.



Methylene chloride.



Formaldehyde.



Carbon dioxide.

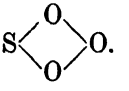


Hydrocyanic acid.

From these and many other similar facts, the conclusion was at first drawn by some chemists that the valency of an element is a constant property, and remains the same in all compounds which it forms. As the number of the compounds the true molecular weights of which were ascertained became larger, it was found, however, that this view could not be maintained without modification. Thus phosphorus, which forms the hydride PH_3, yields two chlorides, PCl_3 and PCl_5, and as, in the latter, it is combined with five monovalent atoms, it must in this case be pentavalent, whilst in PCl_3 and PH_3 it is trivalent. Upholders of the theory of constant valency denied that phosphorus pentachloride was a true compound, and regarded it as a *molecular compound* of PCl_3 and Cl_2, analogous to a salt containing water of crystallisation, basing this view on the fact that when phosphorus pentachloride is volatilised it decomposes into these two portions. It was then shown that by suitable means the pentachloride may be volatilised without decomposition, and that its vapour density then corresponds with the formula PCl_5. Further, a phosphorus pentafluoride has been discovered which is gaseous at the ordinary temperature, and has the molecular formula PF_5. The valency of phosphorus, therefore, towards the halogens cannot be regarded as constant.

Again, the two chief oxides of sulphur have the formulæ SO_2 and SO_3, and on the assumption that sulphur and oxygen are both divalent the constitutional formulæ were written :—



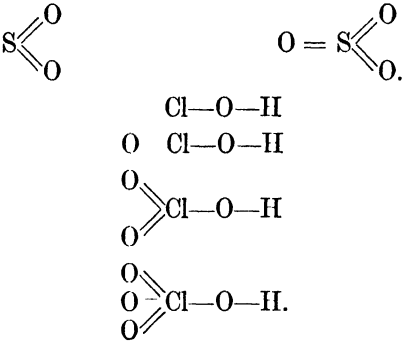


Among the oxygen compounds of chlorine we are acquainted

with four oxy-acids having the formulæ $HClO$, $HClO_2$, $HClO_3$, and $HClO_4$, the constitutions of which were represented as follows :—

H—O—Cl
H—O—O—Cl
H—O—O—O—Cl
H—O—O—O—O—Cl.

In all these cases, however, another interpretation is possible, namely, that the divalent oxygen is connected directly with the sulphur or chlorine atom, the valency of the latter varying in the different cases, as shown in the following formulæ :—



In such cases, it must be remembered (see Vol. I., p. 147), it is only after the *constitution* of a compound has been ascertained that the valency of the component atoms can be deduced.

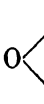
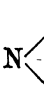
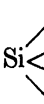
No definite proof has hitherto been obtained of the correctness of either view, but the balance of evidence is strongly in favour of the latter, as it is found that those compounds which can be proved to contain oxygen atoms directly combined together in the manner shown in the first series of formulæ, such as hydrogen peroxide, are extremely unstable. It is, moreover, probable that the longer the chain of oxygen atoms, the less would be the stability of the compound, whereas, in reality, the stability of the oxy-acids of chlorine increases with the number of oxygen atoms in the molecule. Sulphur, again, is undoubtedly a hexad in the hexafluoride, SF_6, which is a very stable gas, whilst in the highest compound which has been obtained with chlorine, SCl_4, it is a tetrad. Oxygen, moreover, which is usually a dyad, is probably a tetrad in the salts which many organic oxygen compounds form with acids,

and which are termed oxonium salts. It is now, therefore, generally supposed that the valency of an element is not a constant, but a variable, property.

It will, however, be noticed that in the above cases there is a certain regularity in the variation, the valency of an element being always represented by either an odd or even number, and in the great majority of the compounds of the non-metallic elements the same rule holds. Even to this there are a few notable exceptions, such as nitric oxide, NO, in which nitrogen behaves as a dyad instead of as a triad or a pentad, whilst in chlorine peroxide, the formula of which has been proved [1] to be ClO_2, chlorine is a tetrad.

19 When we consider the compounds of the metals, it is found that the relations become still more complex than is the case with the non-metals. It is only in recent years that any very definite conclusions could be drawn on this point, as until then the true molecular weights of very few metallic derivatives were known, these having for the most part such high boiling points that the vapour density of very few of them had been determined. The improved methods of determining vapour densities at high temperatures, due chiefly to Victor Meyer and his pupils,[2] have, however, considerably enlarged the material at our disposal, and the results have necessitated some modification of the older views.

No metal combines with hydrogen to form a stable volatile compound, and hence the valency towards this element cannot be determined. Many metals, however, form volatile compounds with the monovalent alcohol radicles (p. 14). These compounds may be regarded as substituted metallic hydrides, and serve also for the determination of the valency of such metals as form them. The table below gives the constitutional formulæ of some of the compounds of non-metals with hydrogen and alcohol radicles, and of a number of the metallo-organic compounds the vapour densities of which have been ascertained:—

Hydrogen chloride.	Water.	Ammonia.	Silicon hydride.
			

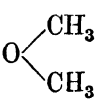
[1] Pebal and Schacherl, *Annalen*, 1882, **213**, 113.

[2] *Pyrochemische Untersuchungen*, 1884 (Vieweg); and numerous papers, *Ber.*, 1880–1890.

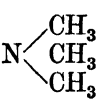
Methyl chloride.



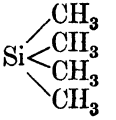
Methyl oxide.



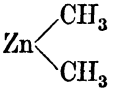
Trimethylamine.



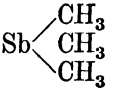
Silicon tetramethyl.



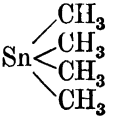
Zinc methyl.



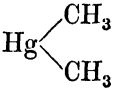
Antimony methyl.



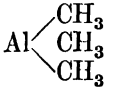
Tin tetramethyl.



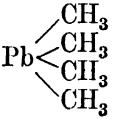
Mercury methyl.



Aluminium methyl.



Lead tetramethyl.



The vapour densities of a number of metallic chlorides, as well as of a few iodides, have now been determined. The molecular formulæ based on the vapour densities are given below :—

I	II.	III.	IV.	V.	VI.
NaCl	$GlCl_2$	$AlCl_3$	$TlCl_4$	$CbCl_5$	WCl_6
KCl	$CrCl_2$	$CrCl_3$	VCl_4	$TaCl_5$	
KI	$FeCl_2$	$FeCl_3$	$GeCl_4$	$MoCl_5$	
RbCl	Cu_2Cl_2	$GaCl_3$	$SnCl_4$	WCl_5	
CsCl	$ZnCl_2$	$InCl_3$	$ZrCl_4$		
CsI	$GaCl_2$	$SbCl_3$	UCl_4		
AgCl	$SnCl_2$	$BiCl_3$			
InCl	$InCl_2$				
TlCl	$HgCl_2$				
	$PbCl_2$				

20 A definite conclusion as regards the molecular formula of a compound can be drawn from its vapour density only when the latter remains constant through a considerable range of temperature. In many instances the vapour density diminishes gradually with rise of temperature, and attains a constant value only at temperatures considerably above the boiling point. The same fact has been observed with substances boiling at comparatively low temperatures, such as acetic acid. This appears to indicate the presence in the vapour of a certain proportion of heavier molecules which gradually decompose as

the temperature rises. Thus the first determination of the vapour density of ferric chloride, made by V. and C. Meyer,[1] agreed approximately with the formula Fe_2Cl_6. Subsequently, V. Meyer and Grunewald showed [2] that the vapour density of ferric chloride is, even at 448°, rather lower than corresponds to the formula Fe_2Cl_6, and that, as the temperature rises, the density gradually becomes less, until at 750° the value agrees closely with the formula $FeCl_3$, and remains constant up to 1,077°.

At temperatures above 448° a certain amount of the ferric chloride is dissociated into ferrous chloride and chlorine, but at 448° no decomposition of this character takes place, and even here the vapour density is smaller than that required by the formula Fe_2Cl_6; hence, at temperatures not far above the boiling point, a number of the molecules must have a smaller molecular weight than the above, *i. e.*, they must have the formula $FeCl_3$.

Another instance of a similar kind is furnished by aluminium chloride; the older experiments of Deville and Troost in 1857 gave the vapour density at 9·3, corresponding to the formula Al_2Cl_6. Nilson and Pettersson,[3] in repeating this determination in 1887 at higher temperatures, obtained the following numbers: –

Temperature.	Vapour density.
440°	7·789
758	4·802
835	4·542
943	4·557
1,177	4·269
1,244	4·247
1,260	4·277

The calculated value for the formula Al_2Cl_6 is 9·2, and for $AlCl_3$, 4·6.

The conclusion to be drawn from these results is that the chlorides of variable vapour density have the simpler formulæ at high temperatures, but that as the temperature falls combination or association occurs between the molecules. It is not improbable that in many cases the molecules of the fused or solid substance are more complex than those of the gas. This has already been shown experimentally for some liquids (Vol. I.,

[1] *Ber.*, 1879, **12**, 1195. [2] *Ber.*, 1888, **21**, 687.
[3] *Zeit. physikal. Chem.*, 1887, **1**, 463.

p. 118), and the extension of the same method to fused salts has led to analogous results.[1]

21 The application to aqueous salt solutions of the methods for ascertaining the molecular weight of substances in solution by the depression of the freezing point and elevation of the boiling point (Vol. I., p. 132) is complicated by the fact that most salts undergo electrolytic dissociation in aqueous solution. The general result obtained, when allowance is made for this by the determination of the electrical conductivity (Vol. I., p. 124), is that in most cases salts have a molecular formula identical with the empirical formula. When salts are dissolved in liquids in which ionisation does not occur, or occurs only to a very small extent, the results obtained point also, as a rule, to the simple formulæ, but in many cases evidence is obtained of molecular association, or combination between two or more molecules, and the results are found to vary with the solvents employed.[2]

The identity of the molecular and empirical formulæ of many chlorides has also been confirmed by the determination, by the vapour pressure method, of their molecular weights when dissolved in boiling bismuth chloride; in this solvent very little electrolytic dissociation occurs, owing to the fact that the chlorine atom is common to both the solvent and the dissolved substance. All the chlorides examined had under these circumstances at 447° the simple formula containing only one atom of metal in the molecule. This holds for the chlorides of Li, Na, K, Rb, Cs, Ca, Ba, Sr, Zn, Cd, Ag, Pb, Mn, and Co, together with ferrous, palladious, and platinous chlorides, and the two chlorides of copper.[3] In all cases where a comparison is possible, these results agree with those deduced from the vapour density at high temperatures, except in the single instance of cuprous chloride.

It appears from the foregoing that in the compounds formed by the metals, the linking together of two atoms of a metal to form a molecule which is stable at a high temperature does not often occur. In certain cases, however, it must be assumed that this sort of combination exists. Tin, for example, forms a volatile compound $Sn_2(C_2H_5)_6$, and Ogg [4] has proved that the

[1] Bottomley, *Journ. Chem. Soc.*, 1903, **83**, 1421; Lorenz and Kaufler, *Ber.*, 1908, **41**, 3727.

[2] See on this point Werner, *Zeit. anorg. Chem.*, 1897, **15**, 1; Beckmann, *Zeit. physikal. Chem.*, 1903, **46**, 857; Turner, *Journ. Chem. Soc.*, 1911, **99**, 899

[3] Rügheimer and Rudolfi, *Annalen*, 1905, **339**, 311.

[4] Ogg, *Zeit. physikal. Chem.*, 1898, **27**, 285.

mercurous salts in aqueous solution yield the divalent ion $Hg_2^{\cdot\cdot}$ and not the simple ion $Hg^{\cdot}$, and that they therefore have most probably the double formula Hg_2X_2. In the case of cuprous chloride, the molecule Cu_2Cl_2 certainly exists at 1700°, although in solution in bismuth chloride at 447° only the simple molecules CuCl are present. Moreover, as already stated, the simple molecules capable of existing in the state of gas at high temperatures may form more complex molecules as the temperature falls.

These facts render it difficult to draw definite conclusions as to the valency of the metals in these compounds. Copper in cuprous chloride, for example, must be regarded as monovalent if the formula be CuCl, whilst if the formula be Cu_2Cl_2, it may be looked upon as divalent, the constitution of the chloride being then written Cl . Cu . Cu . Cl. Similarly, aluminium must be regarded as trivalent in its chloride if the molecular formula be $AlCl_3$, whereas it becomes tetravalent if the molecular formula be Al_2Cl_6:



In the present condition of knowledge, it is best to consider the valency of the metals only for the simplest form of each molecule which has been proved to be capable of existence.

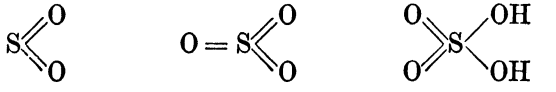
The examination of the list of chlorides (p. 32) shows then not only that the valency of the same metal does vary in different compounds, but that it does not even vary in a regular manner, such as remaining either odd or even. Thus in the case of indium, three volatile chlorides are known, having the formulæ InCl, $InCl_2$, $InCl_3$, in which the metal is a monad, dyad, and triad respectively. Iron is a dyad in ferrous chloride, and a triad in ferric chloride, whilst tungsten acts as a tetrad, a pentad, and a hexad.

In considering the compounds of the metals with oxygen, the available material is not so copious, inasmuch as the actual molecular weights have been determined in but few cases. In most instances the formulæ of the oxides (and of the salts they form with either acid or basic oxides) are taken as the simplest possible, or in some cases as analogous to those of the oxides of elements of the same group the vapour density of which has been determined. The valency deduced from these formulæ

frequently differs from that obtained from the vapour density of the chloride of the metal; thus the only volatile chloride of vanadium has the formula VCl_4, whilst in its general deportment this element is analogous to nitrogen and phosphorus, behaving as a triad and pentad. Again, the only volatile chloride of molybdenum has the formula $MoCl_5$, but in many other compounds, such as molybdic acid and the molybdates, the metal acts as a hexad.

22 The valency of an element can no longer, therefore, be regarded as always varying in a regular manner, but appears to vary irregularly according to the nature of the other elements with which it combines. At the same time, an element almost always shows what may be termed a characteristic valency, *i. e.*, a valency which remains constant throughout a large and important series of compounds. Thus, for example, the alkali metals are monovalent in the great majority of their compounds, although a few halogen derivatives have recently been prepared in which they behave as triads and pentads; the metals of the alkaline earths almost always behave as dyads, and nitrogen, phosphorus, and arsenic either as triads or pentads. Carbon in particular shows a very constant tetrad valency, almost the whole of its immense number of compounds containing the element in the tetravalent state. These general regularities find their best expression in the periodic classification of the elements, and will be further considered in discussing the latter.

23 *Werner's Theory of Principal and Supplementary Valencies.*—The molecules formed by the combination of two or more elements are usually not devoid of the power of combining with further atoms or molecules. Thus, for example, sulphur dioxide, SO_2, readily combines with oxygen to form sulphur trioxide, SO_3; this unites with a molecule of water to form sulphuric acid, H_2SO_4, and this again with a further quantity of water to form the crystalline hydrate, $H_2SO_4,4H_2O$. According to the ordinary theory of valency, sulphur dioxide is an unsaturated compound in which sulphur acts as a tetrad; in sulphur trioxide the sulphur is a hexad, and the oxygen a dyad:

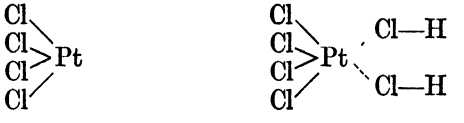


The introduction of water into this molecule can be explained

by a rearrangement of the valencies of the elements of the two compounds, which leads to a constitutional formula for sulphuric acid in accordance with its chemical behaviour. The further introduction of four molecules of water into this molecule cannot be simply represented on the lines of the ordinary theory. It is apparent that some power of combination is still left in such molecules, and this is usually ascribed to the *residual affinity*, either of the molecules as a whole, or of certain of the atoms contained in them.

Very little is known about the mode of combination in such cases, but many theories have been proposed in order to include compounds of this character, among which are to be numbered almost all the double and complex salts of the metals, the ammoniacal metallic compounds, the hydrates, and similar substances.

The most successful attempt in this direction has been made by Werner,[1] whose views are based more especially upon the composition and properties of the ammoniacal metallic derivatives and the complex salts of the metals. According to this theory the atom possesses two kinds of valency, viz., *principal valency*, which is concerned in the combination of atoms or radicles which can exist as ions, or are equivalent to ions; and *supplementary valency*, which is concerned with the combination of radicals which cannot exist as ions. Thus the atoms or groups —Cl, —Na, $-NO_2$, $-ClH_3$, &c., combine by virtue of their principal valencies; groups such as $-OH_2$, $-NH_3$, —ClK, $-CrCl_3$, &c., by means of their supplementary valencies. Platinum, for example, combines with four atoms of chlorine by principal valency forming the molecule $PtCl_4$, the highest chloride of platinum which can be obtained. This molecule readily combines, however, with two molecules of hydrogen chloride by the supplementary valencies of the platinum and chlorine atoms, forming chloroplatinic acid, H_2PtCl_6:



The constitution of these molecules is represented above according to Werner's theory, principal valencies being represented

[1] *Annalen*, 1902, **322**, 261. See also Werner's *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*; an English translation of this volume has been published under the title: "New Ideas on Inorganic Chemistry."

by unbroken lines, and supplementary valencies by dotted lines.

The number of atoms which can combine directly with a single atom appears to be to some extent independent of the nature of the particular atoms concerned. The atoms of most elements can unite in this way with six other atoms or groups, which may be regarded as being situated in the primary sphere of action of the central atom, and are said to be *co-ordinated* with it. These six may be united to the central atom either by principal or by supplementary valency, and if any of the principal valencies of this atom remain unsaturated, the radical thus formed has a corresponding power of combining with further atoms, which, however, must remain in the secondary sphere of action of the central atom.

The trivalent atom of cobalt, Co, can, for example, co-ordinate six molecules of ammonia by supplementary valencies, forming a radical $Co(NH_3)_6$, in which the trivalent cobalt atom is still capable of combining with three monovalent atoms of chlorine by principal valency, forming the well-known compound, $[Co(NH_3)_6]Cl_3$, hexammine-cobaltic chloride (luteo-cobalt chloride). In this substance the six molecules of ammonia are regarded as being situated in the primary sphere, and united with the cobalt atom by supplementary valencies, whilst the three chlorine atoms are situated in the secondary sphere of action, and are united with the cobalt by principal valencies.

On the other hand, in the co-ordination radical, $[CoCl_3(NH_3)_3]$, both the chlorine atoms and the molecules of ammonia are situated in the primary sphere, the chlorine atoms being united with the cobalt by principal, and the ammonia molecules by supplementary, valency. The trivalent cobalt atom is therefore saturated and incapable of further combination. This substance is known as triammine-cobaltic chloride, and when dissolved in water does not undergo electrolytic dissociation, because the chlorine atoms form part of the complex radical. The solution, therefore, does not yield a precipitate of silver chloride when silver nitrate is added. On the other hand, the hexammine-cobaltic chloride molecule, in which the chlorine is not part of the complex radical, dissociates in aqueous solution into the ions $[Co(NH_3)_6]'''$ and $3Cl'$, and the whole of the chlorine is precipitable by silver nitrate.

The maximum number of atoms or groups which can unite directly with a central atom is therefore six, plus the valency

of the central atom. In some cases the co-ordination number is four (carbon, boron, and nitrogen), and it is possibly as high as eight in some instances (molybdenum), but for the great majority of elements it is six.

This theory has proved of great value in the classification of the complex derivatives of the metals, and numerous applications of it will be found under the separate metals. The more recent development of the theory has taken the form of prediction of the existence of isomerides, and the predictions have been verified in a striking manner. The representation of the six co-ordinated groups or atoms as arranged in space round the central atom in the relative positions of the angles of an octahedron, leads to conclusions as to the existence of *cis-* and *trans-*isomerides in certain cases, and of optical isomerides in others. Such isomerides have now been isolated,[1] and this fact gives strong support to Werner's views.

24 *Electrochemical Theory of Valency. Corpuscular Theory of the Constitution of the Atom.*—Concerning the nature of valency very little is at present known. One important relation has, however, been established by the classical researches of Faraday. When a salt of a metal is dissolved in water and the solution is electrolysed, the amount of the metal deposited in a given time depends on the valency which the metal possesses in that salt. Thus when solutions of salts of a univalent and divalent metal, such as the sulphates of silver and zinc, are electrolysed by the same current, two atomic proportions of silver are deposited for each atomic proportion of zinc, the same amount of oxygen being liberated at the anode in each case. Since the same amount of electricity has been conveyed by the ions of the metal in the two cases, it follows that the electrical charge conveyed by each silver ion is only half as great as that conveyed by each ion of zinc. A similar relation is found in other cases, and it may be stated as a general law that the electrical charge which is conveyed by the ion of a metal in the electrolysis of a solution of a salt is directly proportional to the valency of the ion.

These facts have led many chemists to the conclusion that chemical combination is essentially an electrical phenomenon, and occurs always between a positive and a negative radical. This was, indeed, the fundamental principle of the dualistic system of Berzelius, but was rendered truly applicable to the

[1] See Werner, *Ber.*, 1911, **44**, 2449, 3231.

facts of chemical combination only by Faraday's discovery of the quantitative laws of electrolysis.[1]

This idea receives much support from recent developments in our knowledge of the structure of atoms. It has been shown that substances of all kinds must contain electrons, negatively charged particles, and Millikan[2] has shown that the charge on all of these is identical whatever the source. Further, the ratio of the charge to the mass of electrons has been determined and also found to be identical in all cases (provided only that the electron is not moving with a velocity approaching that of light, in which case its mass is increased by virtue of its motion). On combining the two results it is found that the mass of an electron is only 1/1830 that of a hydrogen atom. These electrons, then, form a constituent of all atoms, but experiments by various methods have shown that the number present is only one half (approximately) that expressing the weight of the atom on the scale O = 16, so that they constitute only an insignificant fraction (about one-twentieth of one per cent.) of the total weight. Positive charges, on the other hand, have never been obtained except in association with mass equal to, or greater than, that of a hydrogen atom per unit charge, so that the mass of an atom is probably supplied by the positive charges which it must contain (since atoms are neutral and have been proved to contain negative charges—electrons). These have been investigated by Rutherford[3] and others by means of α-particles, which are produced in some radioactive changes (q.v.), have a mass four times that of a hydrogen atom and bear a charge that exactly neutralises two electrons. In fact they have been shown to be helium atoms minus two electrons. On passing a stream of these through gases, or thin sheets of solid materials like gold-foil, it can be calculated from the observed scattering that the positive charge on an atom is concentrated in a volume which is very small compared to that of the atom as a whole. On these lines has been established Rutherford's Nuclear Theory, according to which an atom consists of a positively charged nucleus around which a corresponding number of electrons are grouped at distances relatively great compared to the dimensions of the nuclei and electrons themselves.

The difference between the atoms of the various elements

[1] See on this point Helmholtz, The Faraday Lecture, *Journ. Chem. Soc.*, 1881, **39**, 277.

[2] Millikan, *The Electron.*

[3] *Phil. Mag.*, 1911, **21**, [6], 669.

consists in differences in the charge on the nucleus and therefore in the number of electrons surrounding it. Exactly how these electrons are arranged is as yet a matter for hypothetical conjecture which is better considered after the periodic law has been discussed (p. 77); but the hypotheses which are most fruitful in explaining valency involve the assumption that these electrons occupy positions, or oscillate around mean positions, fixed with regard to the nucleus. Probably where the central positive charge, and therefore the number of surrounding electrons in the neutral atom, is greater than eight, they arrange themselves as though on the surfaces of a series of concentric spheres, the number and arrangement of the electrons in the outermost of these being all important in determining the chemical behaviour of the atom.

Considerations of symmetry suggest that for each of the spheres some one particular number and arrangement of electrons will be most stable, though the configuration affording the greatest degree of stability may vary from sphere to sphere. In the neutral atom the total number of electrons to be arranged is determined solely by the positive charge on the nucleus, so the atoms of some elements may have the requisite number to supply all the spheres formed with exactly as many electrons as will afford the maximum configurational stability, whilst others must perforce have too many or too few in one or more of their spheres.

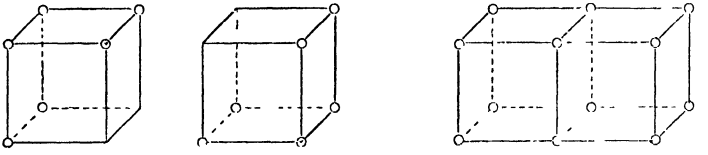
On these lines G. N. Lewis [1] has brought forward a very interesting theory of valency. He suggests that the atoms of all elements are built up in such a way that the series of spheres surrounding the nucleus all have the exact number of electrons consistent with maximal configurational stability except the outermost one, which has the same number as that of the group in the periodic table (q.v.) to which the element belongs. Further he supposes that this outermost sphere for all elements (except hydrogen) requires eight electrons for the highest stability and that there are definite forces tending to produce this arrangement.

Eight electrons symmetrically disposed correspond to the eight corners of a cube, and this figure may therefore be taken as a diagrammatic representation of the atom. To take the case of oxygen as an example, since this is one of the elements of the sixth group it would have only six of the eight corners of the cubic model occupied by electrons. Another oxygen atom could, however, be brought into juxtaposition with the first in such

[1] *J. Amer. Chem. Soc.*, 1916, **38**, 762.

a manner that two of the electrons of each occupy the vacant spaces in the other, as shown in the diagram below.

In this case, without disturbing the electrical neutrality of the whole, each atom has its configurational forces satisfied, and these supply the valence bond. This corresponds to what is called a non-polar linking, the characteristics of which are that the atoms are held in fixed positions relative to each other, as the facts of stereochemistry seem to require, and dissociation into ions occurs but slightly so that the electrical character of the linking is not obvious. Nevertheless oxygen can be ionised and, as can be seen from the symmetry of the above arrangement, if the molecule were broken up, say by collision with an α-particle, the constituent parts might not separate in their original forms, but one atom might break off with seven, or even eight, electrons in its outer sphere, thus forming a singly or doubly charged negative ion, leaving the other with too few electrons, and therefore positively charged. The ions, however, especially



the latter, would not be very stable, and recombination would readily occur under the influence, first of the electrostatic, and then of the configurational forces.

As an extreme modification of this, the combination between sodium and chlorine may be considered. Sodium belongs to the first group, so that its outer sphere has only one electron, whilst chlorine, belonging to the seventh, has seven. Hence, though the chlorine atom can complete its full configuration by means of the single electron from the sodium, yet the latter cannot possibly complete its group of eight by sharing with a single atom. Consequently the sodium parts altogether from its outside electron and exposes the next sphere which, by hypothesis, is configurationally complete. The two ions thus formed are held together purely by electrostatic forces, since the electron has passed over altogether and is not shared. This corresponds to a linking of the extreme polar type which is characterised by the readiness with which it forms ions and by the related fact that it can be broken by the passage of an electric current. Since the bond is purely electrostatic it would be expected that,

when the compound is dispersed in a medium of high dielectric constant like water, the force uniting the parts should be weakened and dissociation occur under the stresses of thermal agitation, thus giving a reasonable explanation of ionic dissociation. Further, since configurational forces do not come into play, any dissociated sodium ion should be able to recombine with any chlorine ion so that there should be a continual exchange of partners. This has been shown to be the case with compounds of this type by G. von Hevesy and L. Zeckmeister.[1] Again, in the crystalline solid Bragg [2] has shown that the sodium and chlorine ions are arranged in interpenetrating space lattices such that each ion is symmetrically surrounded by six oppositely charged ions, and cannot be said to be combined with any one of these more than with any other, an arrangement in perfect harmony with the electrostatic view of the valence bonds.

Between these two extreme types of combination all intermediate grades may be met with, as would be anticipated on this theory. Since all degrees of strength of linkage by configurational forces must occur, the ease with which the atoms may be torn apart as ions must vary through all stages. It is interesting to note, too, that Werner's co-ordination number can be related to the number of electrons which an atom is capable of sharing with other atoms.

Since this theory is still largely hypothetical it is to be expected that great modifications in detail, such as in the exact configurations which are stable, may have to be made (p. 77), but the fundamental principles seem important enough to justify the space spent on their consideration. The nature of the forces tending to produce stable configurations are as yet uncertain, but Parsons has suggested that electrons, instead of being point charges, are magnetons, that is, annular discs of electricity rotating about their own centres. If this prove to be the case, the strong magnetic fields set up would possibly provide the necessary forces, although no satisfactory theory has yet been evolved.

CLASSIFICATION OF THE ELEMENTS.

25 The number of substances at present described as elementary is 87 (see this vol., p. 2), and of these about 70 have

[1] *Ber*, 1920, **53**, [*B*], 410. [2] Bragg, *X-Rays and Crystal Structure.*

been subjected to close investigation, and their properties and those of their compounds definitely ascertained. Their atomic weights have also been determined with a moderate degree of accuracy, and it has been shown that these numbers really represent atomic weights, and not simply the equivalents of the elements (see pp. 13–27).

The question naturally arises whether these substances are in reality incapable of further decomposition, or whether by suitable means they might not in turn be resolved into still simpler substances. Indeed, very soon after the enunciation of Dalton's atomic theory, speculations as to the compound nature of the so-called elements were published. Thus, in the year 1815, Prout suggested[1] that the elements were in reality all composed of hydrogen, basing his supposition on the numbers at that time adopted for the atomic weights compared with hydrogen, which were in most cases whole numbers. The extreme simplicity of the hypothesis attracted many adherents, but the later careful determination of the atomic weights by Berzelius did not confirm it. It was somewhat modified by Dumas,[2] who assumed that the unit weight of hydrogen was itself composed of two or even four atoms, in which case the atomic weights would all be multiples of either 0·5 or 0·25. The very careful experiments of Marignac, and especially of Stas (p. 12), which were carried out with extraordinary care for the purpose of testing Dumas's hypothesis, showed that the atomic weights of many elements are multiples neither of 1, nor of 0·5, nor of 0·25, and this conclusion has been confirmed by more recent investigations. At the same time, it is worth while noting that of the 87 elements in the atomic weight table no fewer than 43 have atomic weights within one-tenth of a unit above or below an integral number. It appears that the probability against such a condition being fortuitous is 20,000 millions to one.[3]

The inquiries made to investigate the validity of Prout's hypothesis brought to light a number of relationships which exist between the atomic weights of analogous elements. Even before the enunciation of the atomic theory, and before the

[1] Anonymously published in Thomson's *Annals of Philosophy*, 1815, vol. vi., "On the Relations between the Specific Gravities of Bodies in their Gaseous State and the Weight of their Atoms."

[2] *Ann. Chim. Phys.*, 1859, [3], **55**, 129.

[3] See Ramsay, B.A. Reports, 1911, 10.

true nature of the alkalis and alkaline earths was known, Richter [1] had pointed out that those quantities of the alkaline earths which neutralise a given weight of an acid could be arranged as members of the arithmetical progression $a + nb$, in which the value of n was 0 for alumina, 1 for magnesia, 3 for lime, 9 for strontia, and 19 for baryta. In 1817 Dobereiner directed attention to the fact that the atomic weight of strontium is the mean of those of the two closely allied elements calcium and barium, and later on the same was found to be approximately true in the case of other groups of three elements, or *triads*, as they were called. In 1850 Pettenkofer [2] brought forward the view that, in the case of analogous elements, the difference in the atomic weights is either a constant or a simple multiple of that constant; thus, using the whole number nearest to the atomic weight, the following series were given:

		Difference.			Difference.
Li	= 7		O	= 16	
		16			16
Na	= 23		S	= 32	
		16			3 × 16
K	= 39		Se	= 80	
					3 × 16
			Te	= 128	

This idea was further developed by Kremers, Gladstone, and especially by Dumas, and attention was directed to the analogy existing between such a group of elements and the homologous hydrocarbon radicles. Thus, if we take the radicles of the C_nH_{2n+1} and C_nH_{2n} series, we have:

		Difference.			Difference
CH_3	= 15		C_2H_4	= 28	
		14			14
C_2H_5	= 29		C_3H_6	= 42	
		14			14
C_3H_7	= 43		C_4H_8	= 56	

When the more exact modern numbers are employed, it is found that the differences between the atomic weights of Cl

[1] *Ueber die neuern Gegenstande der Chymie*, 1797, **8**, 21.

[2] *Munchene Gelehrten Anzeigen*, 1850, **30**, 261, quoted in *Annalen*, 1858, **105**, 187.

elements are not quite so regular as when the above approximate numbers are taken, but even then the approximation to Pettenkofer's rule seems far too close to be due to chance. Further investigation showed that a very large number of the elements could be divided into groups showing similar relationships, and, in 1864, Lothar Meyer [1] tabulated a large number of such groups, and arranged a certain number of the elements in the order given in the table on p. 47, according in the first place to the magnitude of their atomic weights, and in the second place to their valency.

Natural Arrangement of the Elements.

26 The discovery of any system which should embrace the whole of the elements was rendered possible only by the adoption of the consistent atomic weights proposed by Cannizzaro in 1858. Previous to this date, the attempts at classification consisted only in the division of the elements into groups, and did not bring out the relations which exist between them as a whole. This was first achieved in what is usually known as the *natural arrangement of the elements.*

The first attempt at such an arrangement was made by de Chancourtois [2] in 1862, in whose system the elements were arranged in order of their atomic weights along a spiral line drawn round a vertical cylinder, the surface of which was divided into sixteen vertical strips by straight lines. The points occupied by the various elements on this surface were termed "characteristic points," or "geometrical characters." De Chancourtois enunciated the fundamental theorem of his system as follows:—"The relations between the properties of different bodies are manifested by simple geometrical relations between the positions of their characteristic points. For instance, oxygen, sulphur, selenium, tellurium, and bismuth,[3] fall approximately on the same vertical generating line, while magnesium, calcium, iron, strontium, uranium, and barium fall on the opposite generating line. On either side of the first of

[1] *Die modernen Theorien der Chemie*, 1864, 1st edition, p. 137.

[2] *Compt. rend.*, 1862, **54**, 757, 840, 967; 1862, **55**, 600; 1863, **56**, 263, 479; 1866, **63**, 24; see also Hartog, "A First Foreshadowing of the Periodic Law," *Nature*, 1892, **41**, 186.

[3] Probably a misprint, as bismuth does not fall on the same line in the table.

——	Tetrad.	Triad	Dyad.	Monad.	Monad.	Dyad.
	—	—	—	—	Li = 7·03	(Gl = 9·3 ?)
Difference =	—	—	—	—	16·02	14·7
	C = 12·0	N = 14·04	O = 16·00	F = 19·0	Na= 23·05	Mg = 24·0
Difference =	16·5	16·96	16·07	16·46	16·08	16·0
	Si = 28·5	P = 31·0	S = 32·07	Cl = 35·46	K = 39·13	Ca = 40·0
Difference =	$\frac{89\cdot1}{2}$ = 44·55	44·0	46·7	44·51	46·3	47·6
	—	As = 75·0	Se = 78·8	Br = 79·97	Rb= 85·4	Sr = 87·6
Difference =	$\frac{89\cdot1}{2}$ = 44·55	45·6	49·5	46·8	47·6	49·5
	Sn = 117·6	Sb = 120·6	Te = 128·3	I = 126·8	Cs = 133·0	Ba = 137·1
Difference =	89·4 = 2 × 44·7	87·4 = 2 × 43·7	—	—	71 = 2 × 35·5	—
	Pb = 207	Bi = 208	—	—	(Tl= 204 ?)	—

these lines we find hydrogen and zinc on the one hand, bromine, iodine, copper, and lead on the other; parallel to the second line we find lithium, sodium, potassium, manganese, etc."

On Fig. 1, p. 49, will be found the representation of the first two turns of de Chancourtois' helix, the surface of the cylinder being developed on the plane surface of the paper, and it will be seen that the elements which lie on the same generating line do belong to the same family.

27 Very shortly afterwards (1864) several similar attempts at a classification of the elements as a whole were made independently by Newlands,[1] who arranged the elements in order of their atomic weights, and finally placed them in seven horizontal series, each consisting of eight members, as shown in the following table:

H	F	Cl	Co, Ni	Br	Pd	I	Pt
Li	Na	K	Cu	Rb	Ag	Cs	Os
Gl	Mg	Ca	Zn	Sr	Cd	Ba	Hg
B	Al	Cr	Yt	Ce	U	Ta	Tl
C	Si	Ti	In	Zr	Sn	W	Pb
N	P	Mn	As	Di	Sb	Cb	Bi
O	S	Fe	Se	Rh, Ru	Te	Au	Th

According to Newlands, the properties of an element in any vertical group are analogous to those of the elements in the corresponding position in the other groups. From analogy with the musical notes, he gave to this relationship the name of the "Law of Octaves."

Both these proposals, however, received very little attention from chemists; indeed, they seem to have been almost entirely forgotten. In fact, a systematic arrangement of the elements according to their atomic weights appeared to some chemists almost as absurd and unnatural as an alphabetical arrangement. In the year 1869, however, the same system of classification, but on a wider basis, was proposed by the Russian chemist Mendeléev,[2] without any previous knowledge of the work of the above-named chemists. His classification not only included the elements then known, but also left room for many elements at that time undiscovered. He showed that when the elements

[1] *Chem. News*, 1864, **10**, 59, 94; 1865, **12**, 83, 94; 1866, **13**, 113, 130. See also Newlands, *On the Discovery of the Periodic Law*, 1884. (E. and F. N. Spon.)

[2] *Zeitschr. Chem.*, 1869, 405; *Annalen*, Suppl., 1872, **8**, 133.

are arranged in the order of their atomic weights, they may be divided into groups, in each of which a similar gradation of

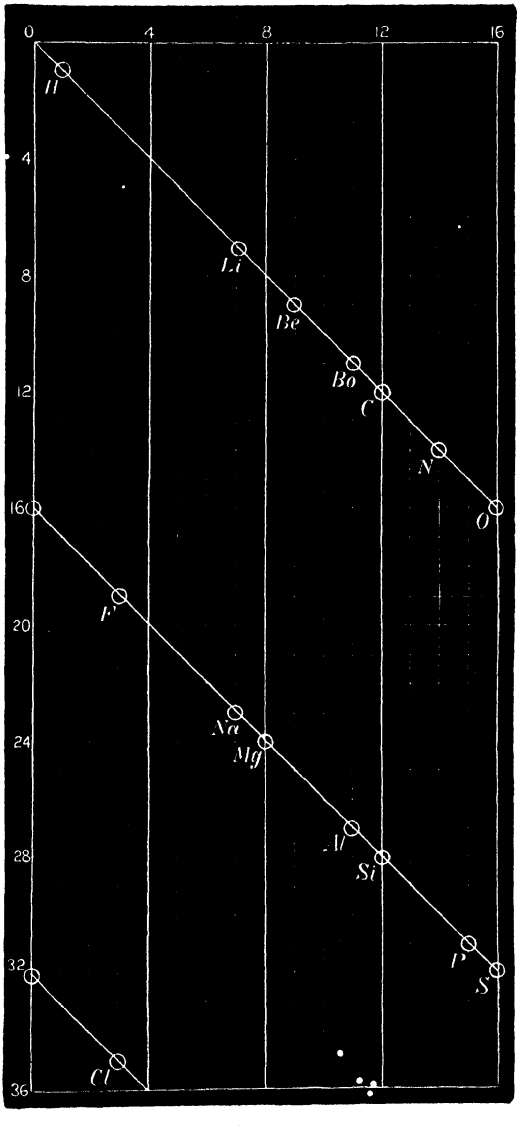


FIG. 1.

properties from element to element occurs, the properties of the elements thus appearing as periodic functions of the atomic weight.

At a slightly later date, Lothar Meyer,[1] continuing his investigation of the relations between the elements, which had already led to the publication of the table given on p. 45, independently put forward views which were almost identical with those of the Russian chemist, and it is to these two investigators that the chief developments of the natural classification of the elements are due.

The Periodic System.

28 In his original paper,[2] Mendeléev sums up his conclusions as follows:

(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 either have nearly the same value (*e.g.*, platinum, iridium, osmium), or 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, glucinum, boron, carbon, nitrogen, oxygen, and fluorine.[3]

(4) The elements which are 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 body.

(6) We must expect the discovery of many yet *unknown* elements, *e.g.*, elements analogous to aluminium and silicon, the atomic weights of which 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.

[1] *Annalen*, Suppl., 1870, **7**, 354.

[2] *J. Russ. Phys. Chem Soc.*, 1869, **1**; quoted in Faraday Lecture, *Journ. Chem. Soc*, 1889, **55**, 634.

[3] Barium and iron are printed by mistake in the English original (*loc. cit.*) instead of boron and fluorine.

In the table given on pp. 52–53 the elements are arranged according to the system of Mendeléev and Lothar Meyer, with the addition of a group numbered zero, containing the helium family of elements,[1] and it will be seen that they fall into nine groups, each group occupying one of the vertical columns in the table, whilst there are twelve horizontal series or periods. The members of each group show in most cases a close connection with each other, which is most noticeable in the case of elements belonging to alternate horizontal series. In the table, therefore, the elements in each group are arranged on alternate sides of the column, each group becoming thus divided into two sub-groups, the members of one of which are situated in the *even* horizontal series, whilst the others fall in the *odd* series. Thus in the second group we have the two sub-groups, Gl, Ca, Sr, Ba, Ra, situated in the even horizontal series, and Mg, Zn, Cd, Hg in the odd. The eighth group is somewhat anomalous, as it appears to occur only in the even periods or series, and, unlike the other groups, always contains three members, the atomic weights of which are more nearly equal than is usually the case.

An inspection of the table shows that the first group contains all the alkali metals, the second group those of the alkaline earths, and also the metals glucinum, magnesium, zinc, cadmium, and mercury. In the third group we find the family, aluminium, gallium, and indium; in the fourth, carbon, silicon, titanium, zirconium, and tin; in the fifth, nitrogen, phosphorus, vanadium, arsenic, antimony, and bismuth; in the sixth, oxygen, sulphur, selenium, and tellurium; and in the seventh, the halogens. The eighth group includes, in addition to the closely allied metals, iron, cobalt, and nickel, the whole of the elements known as the platinum metals. In almost all these cases, the elements mentioned had been classed as members of the same family before Mendeléev's work was published, and their continued occurrence in the same group is strong evidence in favour of the general correctness of his views.

Cases will be observed, however, in which there is no very evident connection between members of the two sub-groups comprised in the same group, as, for example, in the case of silver, copper, and gold on the one hand, and the alkali metals on the other, in the first group; a considerable number of

[1] Ramsay, *Ber.*, 1898, **31**, 3111; Mendeléev, *Principles of Chemistry* (1905), vol. ii., p. 20.

Group.	O.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
					MH_4	MH_3	MH_2	MH	Volatile Hydrogen compounds.
Series 1		H 1 008							
„ 2	He 4 00	Li 6 94	Gl 9 1	B 10 9	C 12 005	N 14 008	O 16 00	F 19 0	
„ 3	Ne 20·2	Na 23 00	Mg 24 32	Al 27 1	Si 28 3	P 31 04	S 32 06	Cl 35 46	
„ 4	A 39 9	K 39 10	Ca 40 07	Sc 45 1	Ti 48 1	V 51 0	Cr 52 0	Mn 54·93	Fe 55 84 Co 58 97 Ni 58 68
„ 5		Cu 63 57	Zn 65 37	Ga 70 1	Ge 72 5	As 74 96	Se 79 2	Br 79 92	
„ 6	Kr 82·92	Rb 85 45	Sr 87·63	Yt 89 33	Zr 90 6	Cb 93 1	Mo 96 0	—	Ru 101·7 Rh 102 9 Pd 106·7

„ 7		Ag 107 88	Cd 112 40	In 114 8	Sn 118 7	Sb 120 2	Te 127 5	I 126 92	
„ 8	Xe 130 2	Cs 132 81	Ba 137 37	La 139 0	Ce 140 25	—	—	—	
„ 9		—	—	—	—	—	—	—	
„ 10	—	—	—	—	—	Ta 181 5	W 184 0	—	Os 190 9 Ir 193 1 Pt 195 2
„ 11		Au 197 2	Hg 200 6	Tl 204 0	Pb 207 20	Bi 208 0	—	—	
„ 12	Nt 222 4	—	Ra 226 0	(?) Ac	Th 232 15	(?) Bv	U 238 2	—	
		M_2O	MO	M_2O_3	MO_2	M_2O_5	MO_3	M_2O_7	MO_4 { Highest salt-forming oxides.

resemblances can indeed be traced, but these are not so prominent as to have led previously to these elements being classified together. In the sixth group also there is very little obvious connection between chromium, molybdenum, and tungsten on the one hand, and the elements of the sulphur group on the other, nor in the seventh group between manganese and the halogens. It will, however, be noticed that in all these cases the elements in question come either just before or just after the occurrence of the eighth group, and it is probable that their somewhat peculiar relationship is connected with the existence of this group.

Mendeléev suggested an alternative method of tabulation which overcomes certain of these difficulties, and, with some modifications and additions, this is given on page 55. The elements forming series 2 and 3 (pp. 52–53), *i.e.*, those which have the lowest atomic weights, and which differ in many respects from the members of the same groups having higher atomic weights, are regarded as typical elements, and the remainder are arranged in double periods, each consisting of an odd and an even series of the first table. The two sub-groups into which each group in the table pp. 52–53 is divided are thus separated, the even series coming at the commencement of the long period, the odd series at the end, and the elements of group VIII in the centre.

The typical elements are probably best regarded as being common to both the sub-divisions of the group to which they belong. Thus Li and Na are common to the sub-groups headed by K and Cu; Gl and Mg to those headed by Ca and Zn, etc.[1]

At either end of the typical series its members are much more closely related to one of the sub-groups than to the other, whilst towards the middle of the series this difference is not so striking. Thus Li and Na are more analogous to K, Rb, and Cs (even series, pp. 52–53) than to Cu, Ag, and Au; F and Cl, on the other hand, are more closely related to Br and I (odd series, pp. 52–53) than to Mn, whilst C and Si show considerable analogy both to Ti and Ge.[2]

A comparison of the first two double periods (Nos. 3 and 4

[1] A table in which these relations are very clearly demonstrated has been published by Orme Masson, *The Classification of the Chemical Elements* (Neville, Mullen, and Slade, London and Melbourne). See also Richards, *Amer. Chem. J.*, 1898, **20**, 543.

[2] Abegg, *Ber.*, 1905, **38**, 1386.

Natural Arrangement of the Elements. Second Table.

								H										
(1)	He	Li	Gl	B	C	N	O	F	} Typical Periods.									
(2)	Ne	Na	Mg	Al	Si	P	S	Cl										
(3)	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
(4)	Kr	Rb	Sr	Yt	Zr	Cb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
(5)	Xe	Cs	Ba	La	(Ce?)	—	—	—	—	—	—	—	—	—	—	—	—	—
(6)	—	—	—	—	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—
(7)	Nt	—	Ra	—	Th	—	U	—	—	—	—	—	—	—	—	—	—	—

} Double Periods.

Even series in table, pp. 52–53. Eighth group in table, pp. 52–53. Odd series in table, pp. 52–53.

in the table, p. 55), which contain only one space to be filled by a missing element, shows the very complete analogy which exists between them. In the later double periods so many elements are at present missing that the relations are not so apparent, although in numerous cases they are still distinctly seen. This arrangement, moreover, corresponds more closley with the periodic variation in the physical properties of the elements (p. 58).

As the atomic weight becomes higher, the change of properties in passing from any element to the one with the next higher atomic weight becomes less marked, and among those having the highest atomic weights, considerable resemblance is frequently noticed between two successive elements. Thus gold in many properties resembles both platinum and mercury, and lead is nearly related to thallium on the one hand, and to bismuth on the other.

Chemical Properties in Relation to the Periodic System.

29 The periodic variation of both physical and chemical properties as we pass from group to group must now be considered, taking first the chemical properties.

Group 0 is occupied by the monatomic gases of the helium family, which form no compounds.

The most strongly electropositive elements known, the oxides of which act almost exclusively as bases, or at most as neutral substances, occur in groups I and II (table, pp. 52–53), whilst the strongly electronegative elements, the chief oxides of which form strong acids, occur in the sixth and seventh groups. The third, fourth, and fifth groups occupy an intermediate position, the members of the third group yielding oxides which, with the exception of those of the elements having the lowest atomic weights, have for the most part basic properties, but frequently act as acids towards stronger bases; in the fourth and fifth groups the acidic nature of the oxides is most prominent in the case of members of lower atomic weight, whilst the higher members show an increasing tendency to form basic oxides. Those members of the sixth and seventh groups which fall towards the centre of the double periods form both basic and acidic oxides, the acid-forming oxides being those containing the most oxygen, and generally corresponding in formula with the acid-forming oxides of the other elements of the same vertical

group. The members of the eighth group usually form basic oxides, but the higher oxides of ruthenium and osmium are strong acid-forming oxides.

Considering the arrangements in short and long periods (p. 55), it is seen that the elements of the helium group, which must be regarded as electrochemically indifferent, fall between the strongly electronegative halogens and the strongly electropositive alkali metals. Towards the centre of the long periods, on the other hand, a more gradual change in chemical properties occurs, through the medium of the metals of group VIII.

It is a remarkable fact that, excluding the first two series, only the elements of the odd series (pp. 52-53) form organometallic derivatives of the type M_xR_y, in which M is a metal and R a hydrocarbon radicle. The composition of these compounds corresponds with that of the volatile hydrogen compound formed by the typical elements of the group. Thus the compounds $Zn(C_2H_5)_2$, $Sn(C_2H_5)_4$, and $Sb(C_2H_5)_3$ are known, whilst no such substances have been obtained from calcium, titanium, or vanadium.

VALENCY.

30 It has already been stated that the valency of an element cannot be regarded as constant, but that it varies according to the nature of the elements with which combination occurs. There is nevertheless, in general, a regularity in the valency of the elements in the majority of their compounds, and we usually speak of them as monovalent, divalent, etc., according to their behaviour in the most characteristic of their compounds. This typical valency shows in a marked manner a periodic variation with the atomic weight.

The group numbered zero contains the remarkable monatomic elements of the helium group, which, so far as is at present known, form no compounds whatever, and must therefore be presumed to have zero valency. Group I contains the whole of the metals which are usually monovalent towards hydrogen, the halogens, and the alkyl radicles, and also to oxygen, the typical formulæ of the compounds being M^IR (R = H,CH_3,Cl, etc.) and M_2^IO. The metals of the second group act in most cases as divalent elements towards the halogens and alkyl radicles, and also to oxygen, the typical formulæ being $M^{II}R_2$ and $M^{II}O$. In the third group we find the elements which are usually trivalent in their compounds both with hydrogen, or other monovalent radicles, and with oxygen. the typical formulæ

of these being $M^{III}R_3$ and $M_2^{III}O_3$. In the fourth, we have the general formulæ $M^{IV}R_4$ and $M^{IV}O_2$, but, in addition, compounds are formed by these elements having the same general formula as those of group II. In all these cases it is found that among the members having the highest atomic weights the regularity is less marked; thus gold is more frequently trivalent than monovalent, thallium forms compounds in which the metal is monovalent, and lead in its most characteristic compounds is divalent.

Passing on to the fifth group, it is found that the characteristic valency in the hydrogen compounds differs from that in the oxygen compounds, the members being trivalent in the hydrides and pentavalent in the highest oxides, the general formulæ being $M^{III}H_3$ and $M_2^{V}O_5$. They also form characteristic compounds with oxygen in which the metal is trivalent, and behave towards the halogens in the same manner as towards oxygen. In the sixth group the characteristic valency again becomes less towards hydrogen, the typical formula being $M^{II}H_2$, whilst with oxygen they form the characteristic acid-forming oxides $M^{VI}O_3$, and with halogens the compounds $M^{VI}Cl_6$. With oxygen and halogens they form, in addition, compounds having the same general formulæ as those of the elements of groups II and IV. The members of the seventh group are, like those of the first, monovalent towards hydrogen, but they are heptavalent towards oxygen in their highest oxides, which have the general formula $M_2^{VII}O_7$. Many of them also form oxides corresponding to those of the first, third, and fifth groups.

In the eighth group no very characteristic valency is noticeable, but it is only in this group that oxygen compounds containing an octavalent element are found; only two of these are at present known, namely RuO_4 and OsO_4. A characteristic of many members of this group is the formation of stable complex cyanides, such as the ferrocyanides, in which the metal is contained in the acid radical, and also of the remarkable series of compounds derived from ammonia, such as the cobaltammonium and platinammonium salts.

Physical Properties of the Elements in Relation to the Periodic System.

31 As with the chemical properties, so it is found that almost all the physical properties of the elements are periodic functions of the atomic weight.

(1) Specific Gravity and Atomic Volume.

One of the most characteristic properties of the elements is their specific gravity in the solid or liquid state, which has been determined with considerable accuracy in the majority of cases. The following table gives the specific gravities at the ordinary temperature (water = 1).

Specific Gravity of the Elements.

Aluminium	2·70	Mercury (liquid)	13·55
Antimony	6·62	Molybdenum	9·0
Arsenic	5·72	Neodymium	6·96
Barium	3·8	Nickel	8·8
Bismuth	9·80	Osmium	22·48
Boron	2·45	Palladium	11·5
Bromine (liquid)	3·14	Phosphorus (yellow)	1·83
Cadmium	8·64	„ (red)	2·20
Cæsium	1·88	Platinum	21·4
Calcium	1·55	Potassium	0·86
Carbon (amorphous)	1·7 –1·9	Praseodymium	6·47
„ (graphite)	2·1 –2·3	Rhodium	12·1
„ (diamond)	3·5 –3·6	Rubidium	1·52
Cerium	6·8	Ruthenium	12·26
Chlorine (liquefied)	1·44	Samarium	7·75
Chromium	6·7	Selenium	4·3 – 4·8
Cobalt	8·6	Silicon	2·0 – 2·5
Columbium	8·4	Silver	10·42–10·53
Copper	8·93	Sodium	0·97
Gallium	5·92	Strontium	2·54
Germanium	5·46	Sulphur	1·92– 2·07
Glucinum	1·93	Tantalum	16·6
Gold	19·2 –19·4	Tellurium	6·25
Indium	7·2	Thallium	11·85
Iodine	4·94	Thorium	11·0
Iridium	22·4	Tin	7·28
Iron	7·86	Titanium	4·5
Lanthanum	6·15	Tungsten	19·1
Lead	11·34	Uranium	18·7
Lithium	0·53	Vanadium	5·5
Magnesium	1·74	Zinc	6·86– 7·2
Manganese	7·39	Zirconium	6·4

The following are the densities (water = 1), at their boiling points, of elements which are gaseous under atmospheric conditions :—

Argon	1·405	Krypton	2·155
Chlorine	1·56	Nitrogen	0·81
Fluorine	1·14	Oxygen	1·118
Helium	0·12	Xenon	3·52
Hydrogen	0·07		

The specific gravity of a given element often varies slightly, not only with the temperature, but also with the physical condition. Thus cast metals, or metals deposited electrolytically, become denser when rolled and hammered, electrolytic copper having a sp. gr. of 8·952, which rises to 8·958 when rolled, and cast zinc a sp. gr. of 7·0, whilst that of rolled zinc is 7·2. The different allotropic modifications of the same element also have as a rule different specific gravities, but in all these cases the difference is usually small compared with the differences between the numbers for the different elements.

The periodic variation of the specific gravity at once becomes manifest if the numbers are placed under the symbols of the elements in the periodic table. Thus, taking the second typical period and first double period, we have the following : —

	Na	Mg	Al	Si	P	S	Cl
Sp. gr.	0·97	1·74	2·70	2·5	2·0	1·9	1·4

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
0·86	1·6	—	4·5	5·5	6·7	7·4	7·9	8·6	8·8

Cu	Zn	Ga	Ge	As	Se	Br
8·9	7·0	5·9	5·5	5·7	4·4	3·1

The specific gravity is low at the beginning of both periods, increases regularly to a maximum in the middle, and then decreases until it has again become very low at the end of the periods. It has already been noted that the difference between the atomic weights of the successive elements forming the centre of the double period is smaller than the average, and it will be observed that the variation of specific gravity also is less for these elements.

32 These relations become more strongly marked if, instead of the specific gravities, we take the atomic volumes, *i.e.*, the

numbers of cubic centimetres which would be occupied by the atomic weights of the elements in grams. If these are arranged, as suggested by Lothar Meyer, so that the ordinates represent the atomic volumes, and the abscissæ the atomic weights, and the points denoting the atomic volumes are then joined, we obtain a line [1] which exhibits the periodic relations in a graphic manner.

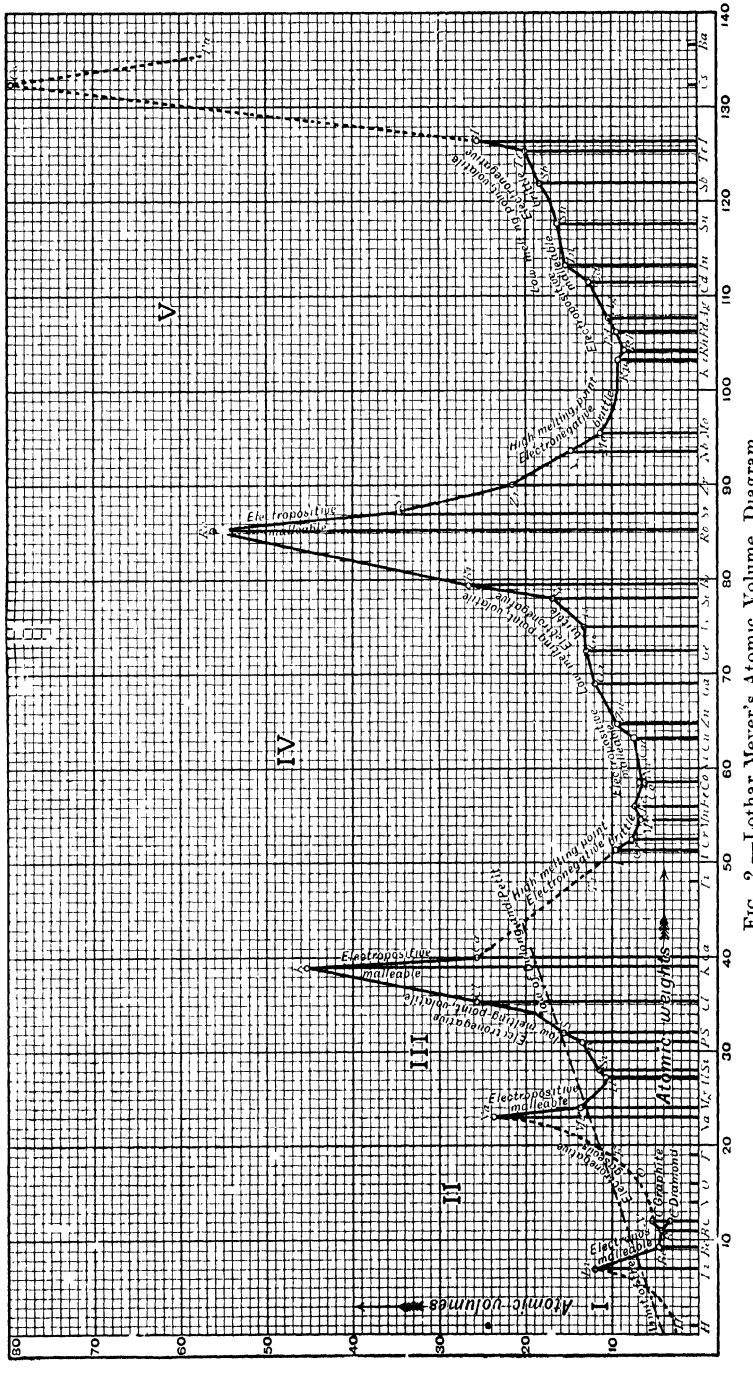
This diagram is shown on p. 62, up to and including barium: after this metal the number of gaps due to incompletely investigated or missing elements becomes so large that the diagram is very incomplete, and this portion has therefore been omitted.

It will be seen that the atomic volume reaches a maximum at the commencement of each of the two typical periods and then at the commencement of the double periods, falling to a minimum at the middle and then again rising to the end of the period, and from the last member of each period a further rise is observed to the initial member of the next. This diagram, moreover, brings out relationships which are not otherwise so readily perceived. Thus elements the atomic volumes of which are very nearly equal possess very different properties according as they are on an ascending or a descending portion of the line, or, in other words, according as they have a smaller or larger atomic volume than the element having the next higher atomic weight. This is exemplified in the cases of aluminium and phosphorus, chlorine and calcium, molybdenum and cadmium, etc. Elements which are characterised by the properties of ductility or brittleness always occur in corresponding positions in the diagram, the ductile elements being found at a maximum or minimum, or immediately following the latter. The periodic variation in these properties is clearly indicated in the diagram.

The work of Richards [2] has shown that the line representing

[1] Mendeléev points out that this diagram is open to the objection that it does not indicate that there is only a limited and definite number of elements in each period, but might be taken to imply that any number of elements might occur in each period; thus, for example, it might be assumed that an element of atomic weight 25 might exist between Mg and Al, having an atomic volume of about 13 and properties intermediate between those of the two metals named; for such an inference there is in reality no ground, and it must therefore be borne in mind that the line joining the points representing the atomic volumes is not a true curve, such as, for example, those representing the solubilities of salts, but is simply drawn to render the periodic variation more evident to the eye.

[2] See *Journ. Chem. Soc.*, 1911, **99**, 1214.


Atomic volumes
Atomic weights
I
II
III
IV
V
Electropositive
malleable
Electronegative
brittle
Low melting point
High melting point

the variation of compressibility of the solid elements with their atomic weight runs parallel to the atomic volume line, and this suggests that atomic volume and compressibility are fundamentally connected. According to Richards' theory of compressible atoms, this connection is a natural one, for it is to be expected that the atoms with a large volume should be more compressible than those which have a small volume and are therefore presumably under great cohesive pressure.

(2) Melting Point of the Elements.

33 Another characteristic property of most elementary substances is the melting point, although this has not been accurately determined in the case of so many elements as the specific gravity, chiefly owing to the difficulties of obtaining correct results for those elements which melt either at a very high or a very low temperature. The following list gives the melting points and boiling points of the elements, so far as definite values are available (Landolt and Börnstein).[1]

Melting and Boiling Points of the Elements.

	Melting point.	Boiling point.
Helium	—	— 268·7° C.
Hydrogen	— 258·9° C.	— 252·6
Oxygen	— 227	— 182·5
Fluorine	— 233	— 187
Nitrogen	— 210·5	— 195·5
Argon	— 187·9	— 186·1
Krypton	— 169	— 151·7
Xenon	— 140	— 109·1
Chlorine	— 101·5	— 33·7
Mercury	— 38·8	357
Bromine	— 7·3	58·6–63·0
Cæsium	26·5	670
Gallium	30·1	—
Rubidium	38·5	696
Phosphorus	44·3	287·3
Potassium	62·5	757·5
Sodium	97·6	877·5
Iodine	113·0	184·3

[1] See also Harker, *Proc. Roy. Institution*, 1912.

	Melting point.	Boiling point.
Sulphur	112·8° C. / 119·2	444·6° C.
Indium	155	—
Lithium	179	—
Selenium	217	690
Tin	231·9	ca. 2270
Bismuth	270	1420–1435
Thallium	303	—
Cadmium	321	778
Lead	327	1525–1580
Zinc	419	918
Tellurium	455	1390
Cerium	623	—
Antimony	630	ca. 1440
Magnesium	650	ca. 1120
Aluminium	657	ca. 1800
Calcium	800	—
Strontium	ca. 800	—
Lanthanum	810	—
Neodymium	840	—
Barium	850	—
Praseodymium	940°	—
Germanium	ca. 958	—
Silver	961	ca. 2000°
Gold	1064	—
Copper	1083	—
Manganese	ca. 1240	ca. 1900
Nickel	1452	—
Cobalt	1490	—
Iron	ca. 1520	ca. 2450
Palladium	1549	—
Chromium	ca. 1550	ca. 220
Vanadium	ca. 1680	—
Platinum	1750	—
Columbium (Niobium)	ca. 1950	—
Molybdenum	ca. 2110	—
Tantalum	ca. 2250	—
Iridium	ca. 2300	—

The boiling points of certain metals have also been determined in a high vacuum by Krafft,[1] with the following results :

Mercury . . .	155° C.	Zinc	550° C.
Potassium . .	365	Bismuth . . .	993
Sodium . . .	418	Silver . . .	1360
Cadmium . .	450		

It has, moreover, been shown by Moissan [2] that all the metals, without exception, can be boiled under atmospheric pressure in the electric furnace, the temperature of which is probably not greater than 3500° C.

Carnelley has published a series of important papers,[3] dealing with the melting points of the elements, and has shown that, like the specific gravities, these also are periodic functions of the atomic weight. This is readily seen from the following table (p. 66) taken from one of Carnelley's papers,[4] with some modifications of the numbers, rendered necessary by more recent determinations of the melting points of some elements. The numbers are in many cases only approximate, and all are given in absolute temperatures, taking — 273° C. as zero.

If the melting points are mapped out in the same manner as the atomic volumes, a periodic curve is obtained, in which, however, the maxima occur in the centre of the second and third periods, and afterwards in the centre of the double periods, whilst the minima occur at the ends.

Carnelley has further shown that the melting points of analogous compounds of the elements exhibit the same periodic variation with the atomic weight as those of the elements themselves.

(3) Conductivity of Metals.

34 The conductive power of the metals for heat and electricity, which is almost invariably far greater than that of the non-metals and all chemical compounds, varies considerably also in the different metals, and even in the same metal, according to its physical condition and chemical purity. The order of conductive power of the metals is the same for both heat and

[1] *Ber.*, 1905, **38**, 262.

[2] *Compt. rend.*, 1906, **142**, 189, 425, 673.

[3] Published in *Journ. Chem. Soc.*, *Proc. Roy. Soc.*, and *Phil Mag.* from 1876 onwards.

[4] *Phil. Mag.*, 1879, [5], **8**, 315.

0	I.	II.	III	IV	V.	VI	VII.	VIII
	H 14°							
He <H	Li 452°	Gl <1230°	B v. h	C v. h	N 62·5°	O 46°	F 40°	
Ne <A	Na 371°	Mg 923°	Al 930°	Si c. 1690°	P yel. 317° red c. 620°	S 386°	Cl 171°	
A 85°	K 335°	Ca 1073°	Sc ?	Ti v. h.	V c. 1953°	Cr c. 1820°	Mn c. 1513°	Fe c. 1793° Co 1763° Ni 1725°
	Cu 1356°	Zn 692°	Ga 303°	Ge c. 1231°	As ?	Se 490°	Br 266°	
Kr 104°	Rb 311°	Sr c. 1073°	Yt ?	Zr >Si	Cb c. 2223°	Mo c. 2380°	—	Ru >2200° Rh >2000° Pd 1822°
	Ag 1234°	Cd 594°	In 428°	Sn 505°	Sb 903°	Te 728°	I 386°	
Xe 133°	Cs 300°	Ba 1123°	La 1083°	—	—	—	—	— — —
	—	—	—	—	—	—	—	
—	—	—	—	—	Ta c. 2523°	W >Mo	—	Os v. h. Ir c. 2570° Pt 2023°
	Au 1337°	Hg 234°	Tl 576°	Pb 600°	Bi 543°	—	—	
Nt	—	Ra	—	Th ?	—	U >Fe	—	— — —

v. h. = very high

c = about.

electricity, a fact first pointed out by Forbes[1] in 1833. Generally speaking, the soft metals conduct best, and the conductivity of all metals becomes lower as the temperature rises. Dewar and Fleming[2] have shown that, as the temperature is lowered, the conductivity of all metals tends to become more nearly equal, and the curves representing the conductivity at different temperatures indicate that at the absolute zero the conductivity of all of them would become perfect, or, in other words, at that temperature the resistance would be *nil*.

These properties, as well as almost all the other physical properties of the element, such as volatility, magnetic and diamagnetic properties, heats of formation of compounds, thermal expansion, formation of coloured ions, and even elasticity and breaking strain, indicate the same general periodic variation as has already been shown for the specific gravity, compressibility, and melting point; space will not permit the discussion of these here, but for details reference may be made to Lothar Meyer's *Modern Theories of Chemistry*, translated by Bedson and Williams (Longmans).[3]

35 There is, however, one important physical property which does not exhibit this periodic variation, viz., the atomic heat. As already shown (p. 16), this is approximately constant, and the fact is made use of in determining the true atomic weight of an element from its equivalent. The exceptions to this rule are found among those elements of low atomic weight which fall below an oblique line drawn across Lothar Meyer's diagram from the commencement to the vertical line representing an atomic weight of 40 (see Fig., p. 62), whilst those above the line follow the law. Without reference to the diagram, this may be expressed by saying that of the elements having an atomic weight of less than 40, only those agree with Dulong and Petit's rule at the ordinary temperature the sp. gr. of which in the solid state is less than 1·75. However, for all elements the specific heat is a function of the temperature approximating to zero before the absolute zero of temperature is reached.

[1] *Phil. Mag*, 1833, **4**, 27.

[2] *Ibid.*, 1893 [5], **36**, 271.

[3] See also Rudorf, *The Periodic Classification and the Problem of Chemical Evolution* (London and New York, Whittaker & Co, 1900); Richards, Faraday Lecture, *Journ. Chem. Soc.*, 1911, **99**, 1201.

Correction of Doubtful Atomic Weights.

36 The periodic arrangement of the elements has proved of great value in checking doubtful atomic weights. In 1869, when Mendeléev first promulgated his theory, the atomic weights then accepted for many elements did not allow of their being placed in a position corresponding to their properties, and Mendeléev boldly concluded that in such cases either the equivalent had been wrongly determined, or an incorrect multiple of the latter had been taken for the atomic weight. In almost every instance subsequent research has justified this conclusion. Thus, for example, the atomic weight of molybdenum was given by some chemists as 92, and by others as 96, and, as the former figure placed the metal before the pentavalent columbium, Mendeléev adopted the number 96, which placed it in the same group as chromium; this is now the accepted value. Again, the atomic weights of the four elements, gold, platinum, iridium, and osmium, were at that time taken as Au 195·2, Pt 195·7, Ir 195·7, and Os 197·6, whereas according to the requirements of the periodic system the order should be reversed, osmium having the lowest and gold the highest atomic weight; this also has been proved by the redeterminations made by Lothar Meyer and Seubert, Thorpe and Laurie, and Kruss, the numbers now adopted being Os 190·9, Ir 193·1, Pt 195·2, and Au 197·2.

The atomic weight of indium was at first taken as 75·2, and the formula of the chloride as $InCl_2$, but for an element of this atomic weight no place was available in the periodic system; if, however, the formula of the chloride is taken as $InCl_3$, the atomic weight becomes 112·8, and the element then falls naturally between cadmium and tin, and in the same group as aluminium. Determinations of the specific heat of the metal and the vapour density of the chloride have subsequently proved the correctness of the supposition. Uranium was formerly supposed to have an atomic weight of 60, and later, of 120, neither of these numbers fitting into the periodic system. The metal, however, falls in naturally if the atomic weight be about 240, and this was confirmed by Roscoe's determination of the vapour density of uranium chloride, UCl_5, and by Zimmermann's determination of the specific heat of the metal. Another element the atomic weight of which was doubtful was glucinum, which was regarded by some as a divalent metal of atomic weight 9, and by others as a trivalent metal of atomic weight 13·5. The

determination of the vapour density of glucinum chloride has now shown that this has the formula $GlCl_2$; the atomic weight must therefore be 9, which agrees with the demands of the periodic system.

37 In the table given above (pp. 52–53) the sequence of atomic weights has been broken in three places in order to maintain certain elements in the groups to which their chemical and physical properties assign them; argon (39·9) precedes potassium (39·10); tellurium (127·5) precedes iodine (126·92); and cobalt (58·97) precedes nickel (58·68). The chemical properties of argon and tellurium are so well marked that there seems no doubt that these elements have been correctly placed, and there is at least a possibility that more extended investigation may show that their atomic weights are not so high as they are at present thought to be. Cobalt is usually placed before nickel, both on account of its physical and chemical relations to iron and nickel, and because of the close analogy which many of its compounds present to those of rhodium and iridium. These reasons cannot, however, be considered as having the same weight as those which apply to argon and tellurium.[1]

Existence of Unknown Elements.

38 The arrangement of the elements according to the periodic system leaves, as already seen, a number of blanks, which Mendeléev assumed were to be filled by elements then undiscovered, and he suggested that, from the properties of the elements with the next higher and lower atomic weights, and from those of the other members of the same group, it was possible to predict very closely the properties such elements would have when discovered. Thus, for instance, were selenium unknown, its properties could be largely predicted from those of arsenic and bromine on the one hand, and of sulphur and tellurium on the other, these elements being termed by Mendeléev the "atom analogons" of the element in question. At that time there were three gaps for elements with atomic weights less than 75, namely, one having an atomic weight of 44, corresponding to boron, one of atomic weight about 69, corresponding to aluminium, and one of atomic weight 72, corresponding to

[1] For a discussion of the evidence bearing on the atomic weight of tellurium, see vol i., p. 485.

silicon. To these hypothetical elements Mendeléev gave the names Ekaboron, Ekaluminium, and Ekasilicon (from the Sanskrit, *Eka*, one), and, proceeding in the manner indicated, he gave in considerable detail the properties such elements would possess. In less than twenty years his predictions were completely verified by the discovery of gallium by Lecoq de Boisbaudran in 1875, of scandium by Nilson in 1879, and of germanium by Winkler in 1887. The first is Mendeléeff's ekaluminium, the second ekaboron, and the third ekasilicon, and the striking manner in which the forecast was fulfilled in each case may be seen from the following table, in which the predicted properties and those actually observed are arranged in parallel columns.

Ekaboron.	Scandium.
At. wt. 44.	At. wt. 44·1.
Oxide Eb_2O_3, sp. gr. 3·5.	Sc_2O_3, sp. gr. 3·86.
Sulphate $Eb_2(SO_4)_3$.	$Sc_2(SO_4)_3$.
Double sulphate not isomorphous with alum.	$Sc_2(SO_4)_3,3K_2SO_4$—slender prisms.
Ekaluminium.	**Gallium.**
At. wt. 68, sp. gr. 6·0.	At. wt. 69·9, sp. gr. 5·92.
Ekasilicon	**Germanium.**
At. wt. 72, sp. gr. 5·5.	At. wt. 72·5, sp. gr. 5·46.
Oxide, EsO_2, sp. gr. 4·7.	Oxide, GeO_2, sp. gr. 4·7.
Chloride, $EsCl_4$, liquid, boiling slightly below 100°, sp. gr. 1·9.	Chloride, $GeCl_4$, liquid, boiling at 86°, sp. gr. 1·887.
Ethide, $Es(C_2H_5)_4$, liquid, boiling at 160°, sp. gr. 0·96.	Ethide, $Ge(C_2H_5)_4$, liquid, boiling at 160°, sp. gr. slightly less than that of water.
Fluoride, EsF_4, not gaseous.	Fluoride, $GeF_4,3H_2O$, white, solid mass.

39 From the above it will be seen that the periodic system of classification rests on a very firm basis, the successful prediction of the properties of undiscovered elements forming very strong evidence in favour of the general plan. In certain respects the system will doubtless undergo modification as our knowledge increases, for difficulties occur which cannot at present be explained. Thus there are elements sometimes in the same group between which only a limited amount of analogy can be traced,

and, on the other hand, elements which have a good deal in common are sometimes separated widely.

It is now realised that just as, according to the scheme on p. 55, the two first short periods are followed by two longer periods, so after this must come even longer periods, containing thirty-two elements instead of the eighteen in the preceding ones. In general, it is probable that a period consists of the elements between two inert gases, and this interval becomes longer as we pass down the table. According to this, the old difficulties that were met with in trying to find places for the elements of the rare earths disappear, as it is no longer expected that elements in the middle of a period should correspond very closely with the middle members of a shorter period.

A further difficulty is found in the anomalous position of hydrogen, which forms the sole member of the first series at present known, and which in its properties differs to so great an extent from all other known elements. It resembles the alkali metals inasmuch as it is monovalent and strongly electro-positive, but differs very greatly from them in other respects. On the other hand, it has been maintained [1] that hydrogen as a monovalent, diatomic gas falls naturally at the head of the halogen group, and the great similarity in properties of the hydrocarbons to their halogen substitution derivatives is adduced as evidence of chemical analogy between hydrogen and the halogens. This relation, moreover, appears to accord better with the sequence of atomic weights, the difference between hydrogen and fluorine being 18, whilst that between hydrogen and lithium is 6, a number much lower than is observed elsewhere between two members of a vertical group.

Mendeléev himself regarded hydrogen as standing at the head of group I., and as being one of a series consisting of two elements only, the missing element being a member of the helium family, of atomic weight less than 0·4. Mendeléev further suggested [2] that this element may be identical with the unknown element coronium, to which certain lines of the spectrum of the outermost region of the solar corona have been ascribed. He also put forward the surmise that the ether itself may in reality be composed of atoms of an element of about one-millionth of the atomic weight of hydrogen, which he places in a zero series preceding that containing hydrogen.

[1] Orme Masson, *Chem. News*, 1896, **72**, 283.

[2] *Principles of Chemistry*, vol. II, Appendix III. (Longmans, Green & Co., London, 1905).

Many attempts have been made to modify Mendeléev's table, so as to reduce the number of anomalies and bring out more clearly the relations between the elements, but none of these proposals has as yet been generally accepted.[1]

Atomic Numbers.

40 The inner meaning of the periodic law has recently become more clear as the outcome of, chiefly physical, research. It has already been stated that experiments on the scattering of α-rays have shown that the positive charge of an atom is concentrated in a volume extremely minute compared to that of the atom as a whole, as estimated on the kinetic theory of gases and in other ways, so that it must be supposed that the negative electrons which balance this positive charge are grouped around it as a nucleus in such a way as to occupy a volume more nearly equal to that of the atom as ordinarily determined.

Evidence has now been found suggesting, almost to the point of certainty, that successive elements in the periodic table differ from each other by one unit charge on the nucleus and therefore by one electron in the surrounding layers of these. This is indicated approximately by determinations of the number of electrons present in the atoms of various elements by the scattering of X-rays,[2] and β-rays [3] and also by determining the positive charge directly by the scattering of α-rays,[4] but, at first, none of these methods was very precise. Very clear and precise evidence for this postulate was afforded, however, by Moseley's [5] study of the characteristic X-rays emitted by different elements when excited by bombardment with cathode rays. Moseley found that the square roots of the frequencies of these characteristic X-rays formed, to a very high degree of accuracy, a uniform arithmetical series as successive elements were taken in turn and, to account for this, theory required that the charge

[1] See on this point, Rudorf, *The Periodic Classification and the Problem of Chemical Evolution* (Whittaker & Co., London and New York, 1900), where references to the literature up to 1900 will be found; Werner, *Ber.*, 1905, **38**, 914; Armstrong, *Proc. Roy. Soc.*, 1902, **70**, 86; Reynolds, *Journ. Chem. Soc.*, 1902, **81**, 612; Zengelis, *Chem. Zeit.*, 1906, **25**, 294; Schmidt, *Zeit. physikal. Chem*, 1911, **75**, 651; Baur, *ibid.*, 1911, **76**, 569; Sanford, *J. Amer. Chem. Soc*, 1911, **33**, 1349.

[2] Barkla, *Phil. Mag.*, 1922, **21**, [6], 648.

[3] Crowther, *Proc. Roy. Soc*, 1910, [*A*], **84**, 226.

[4] Rutherford, *Phil. Mag*, 1911, **21**, [6], 669.

[5] *Phil. Mag.*, 1913, **26**, [6], 1024; 1914, **27**, [6], 703.

on the nucleus should increase by unity on passing from each member to the next higher one.

Very strong confirmatory evidence for this is found in the facts of radioactivity (*q.v.*). Whenever a radioactive change occurs either an α-particle, which has two positive charges, or a β-particle, which is a negative charge, is expelled, and the energy changes associated therewith compel the supposition that they come from the *nucleus* itself. Consequently, the former change must reduce the positive charge on the nucleus by two units and the latter increase it by one. Now it is found as a perfectly general law, known as Soddy's law, that the change associated with the expulsion of an α-particle gives rise to a product which must be classified in the next lower group but one to the parent substance, whilst in those changes where a β-particle is expelled the product appears to belong to the next higher group in the periodic table—a result in perfect harmony with that obtained by Moseley.

If the elements are written out in the order in which they occur in the periodic table and numbered so that hydrogen is 1, sodium 11, aluminium 13, and so on, these figures, at the suggestion of van den Broek,[1] are called the *atomic numbers* of the elements, and it is natural to suppose that these atomic numbers give the actual number of positive charges on the nucleus of the atoms. That this is so has been confirmed by the more accurate work on the scattering of α-particles by Chadwick.[2] The atomic numbers of all the known elements between sodium and lead, with the exception of the inert gases, have been determined by this method or modifications thereof, and in particular de Broglie[3] has studied some of the elements of higher atomic weight, including thorium and uranium, and in all cases the atomic numbers obtained experimentally conform to those obtained by numbering the elements in the order in which they appear in the periodic table, assuming only five unknown elements. Two of these, of atomic numbers 43 and 75 respectively, occur under manganese in group 7A, where there are known vacancies in the periodic table; another, of atomic weight 75, occurs before osmium where there is a vacancy under iodine; another, of atomic number 87, occurs where there is a vacancy under cæsium in group 1A; and the last, of atomic number 61, appears amid the rare earths.

[1] *Phys. Zeit.*, 1913, **14**, 32. [2] *Phil. Mag.*, 1920, **40**, [6], 734.
[3] *Compt. rend.*, 1916, **165**, 87, 352.

The rare earths are particularly interesting from this point of view, as it is now known that barium has the atomic number 56 and tantalum 73, so there is room for only sixteen elements between them, fifteen of which are known. This knowledge is of great use, since the difficulties of separating the rare earths are such that previously it could not be determined how many there might be and much time might have been wasted in endeavouring to isolate new elements that did not exist.

In the three anomalies of the periodic table (p. 69), the atomic numbers determined experimentally confirm the order of the table and not that of the atomic weights. Thus the atomic number of chlorine is 17, of potassium 19, and of calcium 20, leaving 18 for argon and thus bringing it before potassium in spite of the lower atomic weight of the metal. Similarly, the atomic number of cobalt is 27 and that of nickel 28, in spite of the atomic weight of the latter being lower. Hence it must be supposed that atomic numbers are more fundamental than atomic weights, a conception that is confirmed by the facts considered in the next paragraph.

Isotopes.

41 Since, in radioactive changes, both α- and β-particles are expelled and it must be supposed that both these come from the nucleus, it follows that, in some cases at least, the nucleus must be complex, containing both positive and negative charges, and the atomic number gives the *net*, not the absolute, number of positive charges on the nucleus. Consequently, it should be possible to have different complex nuclei with the same *net* positive charge giving rise to atoms of the same atomic number but of different masses.

The case arises frequently and obviously among the radioactive elements where the expulsion of an α-particle is followed by that of two β-particles, thus restoring the net nuclear charge, but reducing the mass by that of the α-particle, that is, by four units. Soddy introduced the term *isotopes* for all elements having the same atomic number, but with nuclei which, except for their net charge, differed in any way. In their purely chemical properties, isotopes were found to behave identically, indicating that these were determined by the number and arrangement of the electrons surrounding the nucleus, but the radioactive properties, which are dependent upon the constitution of the

nucleus itself, are different, as would also be any properties dependent primarily, or even partly, upon mass.

Chemical properties, therefore, depend, not upon the mass of the atom, but on the atomic number, and it is only the fact that the atomic weights of elements, as ordinarily determined, are approximately proportional to the atomic numbers that enabled the periodic law to be discovered in the way that it was.

An interesting case of isotopy arises from branching radioactive decompositions. Thus radium C_1 decomposes in two ways: (1) by loss of an α-particle it becomes radium C_2, which by loss of a β-particle is converted into an isotope of lead, which, so far as is known, undergoes no further change, and (2) by loss of a β-particle radium C_1 becomes radium C, which, by loss of an α-particle then becomes radium D, also an isotope of lead, but now capable of further radioactive change. These two isotopes then have the same atomic weight, since each was formed from radium C_1 by the loss of one α- and one β-particle, but they have different radioactive properties, showing that these are dependent on the arrangement, as well as on the number, of the charges on the nucleus. The study of the equivalent of lead (*q.v.*) from different sources, uranium, thorium, and non-radioactive minerals, has completely confirmed the existence of isotopes.

The densities of isotopes have been found to be proportional to their atomic weights, so that their atomic volumes are the same. Similarly, the solubilities of compounds of isotopic elements are the same when expressed in gram-molecules per litre, but differ in absolute weights per litre in conformity with the different weights composing the gram-molecule. The spectra of isotopes were at first thought to be identical, but recently [1] slight differences have been reported, indicating that the mass of the nucleus is a factor, even though only a small one, in determining the frequency of vibration of the electrons in the atom.

It is of interest to learn whether isotopes occur among the ordinary, as well as among the radioactive, elements, and this question has been answered in the affirmative by the work of J. J. Thomson [2] and Aston [3] on positive ray analysis. If volatile

[1] Merton, *Proc. Roy. Soc.*, 1920, **96**, [A], 388.

[2] Sir J. J. Thomson, *Positive Ray Analysis.*

[3] *Phil. Mag.*, 1920, **40**, [6], 628; *Journ. Chem. Soc.*, 1921, **119**, 677. See also F. W Aston, *Isotopes*, 1922.

substances are introduced into a Crookes tube of which the cathode is pierced with a small hole, on passing the current positive ions are driven through the perforation in the cathode and may be focussed by means of successive electrostatic and magnetic fields into a sort of "spectrum," the lines of which correspond to a definite ratio of mass to charge. By the action of the discharge in the tube some of the molecules of the gas inside are decomposed and specimens of all the atoms obtainable from the substance as well as molecules are driven as ions through the cathode and their presence is registered by a photographic plate placed at the focus of the "spectrum." Some of the ions will have two or even more charges, giving rise to lines corresponding to the spectra of the second and third order in the case of the ordinary light spectrum, but this rarely introduces any ambiguity, and is sometimes of assistance. In this way, the masses of the various particles present in the tube may be determined with an accuracy of about one part in one thousand. As a result, it has been found that many of the common elements are mixtures of isotopes, so that the atomic weights, as usually determined, are merely a mean value dependent upon the proportions in which the different isotopes happen to be present. Thus the occasional anomalies of the old periodic table, such as the case of the relative positions of argon and potassium, receive a ready explanation.

The most remarkable fact established by this work, however, is that, on the scale O = 16, all the atomic weights are exact whole numbers except that of hydrogen, which is 1·008, thus reviving, in a slightly modified form, Prout's famous hypothesis. The theories this suggests are discussed more fully in the next section.

The separation of isotopes by other methods has also been attempted, any method being hopeful which depends on the mass of the particles alone. Thus Aston has succeeded in partly separating the isotopes of neon by fractional diffusion through pipes of porous clay, and Brönsted and Hevesy, by fractional distillation of mercury at very low pressure, have succeeded in obtaining fractions of different densities, thus indicating a separation of isotopes. It is not, however, to be expected that complete separation can be effected in these ways.

The Structure of the Atom.

42 It is but natural that attempts should have been made to wring from all this new evidence some conception of the structure of the atom, and particularly the relation of the atoms of one element to another throughout the periodic table. This relationship has been emphasised by the natural transformations of one element into another that occur in radioactive changes, and the possibility of anticipating the ambitions of the alchemists of old by effecting these transmutations at will is eagerly anticipated. Several cases of apparent transmutation have been reported, but space forbids more than a reference to the work of Ramsay,[1] of Collie and Patterson,[2] and of Rutherford.[3]

The constitution of the nucleus of the atom is at the same time the most fundamental and the most difficult part of the problem of atomic structure. The starting point for the development of any theory of this is the fact that all atoms, when measured individually and not as a mixture of isotopes, appear to have integral weights on the scale O = 16, except hydrogen; together with the fact that all elements, again excepting hydrogen, have an atomic weight on this scale equal to, or greater than, twice their atomic number. On the electromagnetic theory of mass, this can be explained in the following way. If the helium nucleus is composed of four hydrogen nuclei and two electrons *very closely packed*, the effect of the overlapping of the electric fields can be estimated, on certain not improbable assumptions, as reducing the apparent mass by about 0·8 per cent., thus bringing the atomic weight down from the value 4·032, as obtained by direct addition of the masses of the constituent hydrogen nuclei, to 4·00, as obtained experimentally, whilst the net charge is, of course, 2. The fact that all the other atoms have mass rather greater than twice their atomic number suggests that all other nuclei are constructed, in the main, from these helium nuclei, whilst their integral value indicates that the packing of these among themselves is not sufficiently close to produce any appreciable further reduction of mass. The actual figures obtained for atomic weights also suggest that there must be another condensed nucleus of three hydrogen nuclei with one or two electrons which forms one of the fundamental "bricks" from which other nuclei are built up. The whole question has

[1] *Journ. Chem. Soc.*, 1913, **103**, 264. [2] *Ibid.*, 1913, **103**, 419.
[3] *Proc. Roy. Soc.*, 1920, **97**, [*A*], 374.

been dealt with in a very interesting, if somewhat speculative, way by Harkins and his co-workers.[1]

From the purely chemical point of view, the problem of the arrangement of the electrons surrounding the nucleus is perhaps of even greater importance, since we have seen, from the study of isotopes, that it is on this that the chemical properties depend. An important attempt at the solution of this problem was brought forward by Langmuir [2] as a development of G. N. Lewis's theory of valency already described. Adopting this theory, Langmuir started from the conception that the inert gases, since they show no tendency to combine, must have outer spheres possessing their full complement of electrons and therefore being configurationally quite stable. The atomic numbers of the inert gases are helium, 2; neon, 10; argon, 18; krypton, 36; xenon, 54; and niton, 86, which, as Rydberg pointed out, can be represented by taking an increasing number of the terms of the series $N = 2(1 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2)$, where N is the atomic number. Langmuir suggested that the physical significance of this was that the niton atom was composed of a nucleus with a net positive charge of 86; an inner sphere of radius which we can call unity, with two electrons on the surface; a second sphere of radius just less than two, with eight electrons on its surface; a third sphere of radius just over two, also having eight electrons on its surface; similarly, fourth and fifth spheres of radius just less than and just over three, each having eighteen electrons on its surface, and an outer sphere of radius four, bearing on its surface thirty-two electrons. Since the surfaces of spheres are in the ratio of the squares of their radii, it will be seen that, if the electrons are fixed, each occupies an equal area, no matter on what sphere it may be. All other atoms are supposed to be constructed on the same model, except that those of lower atomic number have not enough electrons, but their structure is arrived at by filling up the spheres one by one, starting with the innermost, until all the available electrons have been placed. In this way, all inner shells will be completed, but the outer shell may be deficient of its full complement. Thus sulphur would consist of a nucleus, of net charge 16; an inner shell containing two electrons; a second shell containing eight electrons, and a third with only six where there are places for eight. Taken over the whole series of elements, the structures thus arrived at account to a considerable extent for the magnetic

[1] *J. Amer. Chem. Soc.*, 1915, **37**, 1367. [2] *Ibid.*, 1919, **41**, 868.

properties shown by the elements. The elements between helium and argon compare strictly with the scheme put forward by Lewis in the way this theoretical structure explains their valency relations, and for elements of higher atomic number the introduction of further hypotheses and conceptions of configurations of pseudo-stability, for details of which the original paper should be consulted, furnish a suitable explanation in this respect.

A drawback to all such conceptions of the atom is that no such arrangement can be stable on the ordinarily accepted laws of electrostatic attraction and repulsion. However, by an ingenious modification of these, Sir J. J. Thomson [1] has overcome this difficulty and in a later paper [2] has developed a theory of atomic structure and chemical combination similar to that of Langmuir, but more in conformity with the point of view and laws of physics.

The problem was previously attacked by Bohr [3] from another direction in an attempt to explain the Balmer series in the lines of the hydrogen spectrum. Bohr supposed that the hydrogen atom was composed of a nucleus around which an electron revolved as a planet does around its sun, the electrostatic attraction between the two being balanced by the centrifugal force, but he too was compelled to modify the classical laws of electrodynamics by assuming that there is a series of orbits in which the electron could rotate without radiating energy. He postulates that energy is radiated only when the electron passes from one of these orbits to another and then introduces Planck's [4] concept of energy quanta and assumes that when such a change of orbits does occur the frequency of the radiated energy is such that one quantum only is emitted. On these lines, the Balmer series can be accounted for and the mathematical development of the theory leads to the expression of an empirical constant, which Rydberg discovered as fundamental in all known spectroscopic series, in terms of known physical constants which can be determined by means quite unconnected with spectroscopy. The agreement between the value thus determined and that arrived at empirically from spectroscopic measurements is extremely satisfactory, being within one-tenth of one per cent.,

[1] *Phil. Mag.*, 1919, **37**, [6], 419.
[2] *Ibid.*, 1921, **41**, [6], 510
[3] *Ibid*, 1913, **26**, [6], 1, 476, 857.
[4] See Lewis, *A System of Physical Chemistry*, vol. iii., "The Quantum Theory."

which is about the limit of the accuracy of the determinations of the physical constants involved, so that there must be a considerable amount of truth behind the mathematical expressions derived, though it may be that they are capable of a somewhat different interpretation. The theory also accounts excellently for the variation of the number of lines of the Balmer series which are visible with the specific volume of the gas, but there are many lines in the hydrogen spectrum for which it does not account, and the attempt to extend the theory to elements of higher atomic number has not been so successful.

CRYSTALLINE FORM OF METALS.

43 All metals, as well as their alloys, can be obtained in the crystalline state, and those occurring as minerals in the native condition are often found crystallised; this is the case with gold, silver, copper, platinum, iridium, palladium, gold-amalgam, and silver-amalgam. In general, the form which they assume is one belonging to the regular system, such as the octahedron or the cube, or a combination of these forms. Some few, such as zinc, antimony, and bismuth, crystallise in the hexagonal system and the two latter metals, which closely resemble arsenic, are found, as this is, crystallised in rhombohedra. On the other hand, a few metals, such as tin and potassium, crystallise in the tetragonal system.

To obtain metals in the crystalline state several processes can be adopted. Crystals of metals which fuse readily can be obtained by solidification after fusion. Bismuth, antimony, lead, and tin may thus be crystallised, and, in a similar way, sodium and potassium; in the latter cases air must of course be excluded. Metals which are easily volatilised, such as zinc, cadmium, and potassium, may be obtained in crystals by condensation from the gaseous state, whilst other metals, such as silver, thallium, and lead, can be readily crystallised by the electrolysis of solutions of their compounds. The metals separate out in lustrous crystalline plates, and the exhibition of this phenomenon on the screen forms one of the most striking and beautiful of lecture-room experiments. The crystallisation of metals is well illustrated also by the formation of the lead-tree when a piece of zinc is immersed in a solution of lead acetate.

Some metals can be obtained in more than one crystalline form, for example, tin. Above 161° the stable form is rhombic with a specific gravity of 6·5; between 161° and 18° the stable form is tetragonal with a specific gravity of 7·2; below 18° the stable form is amorphous, known as grey tin, which has a specific gravity of 5·8.

The fracture of metals is an important characteristic intimately connected with the crystalline form, and in many instances it is of importance as giving a knowledge of the purity, or otherwise, of the metal. The following varieties of fracture are generally recognised :—

(1) Crystalline fracture; as in antimony, bismuth, zinc, spiegel-iron, etc.

(2) Granular fracture; as in grey forge pig-iron.

(3) Fibrous fracture; as in bar and wrought iron when partly broken by bending.

(4) Silky fracture; as in a piece of tough copper.

(5) Columnar fracture; as observed in the grain tin of commerce.

(6) Conchoidal fracture; noticed in the cases of native arsenic and certain brittle alloys, such as that composed of one part of copper to two of zinc (Percy).

COLLOIDAL SOLUTIONS OF METALS.

44 When dilute solutions of many metallic salts are treated with reducing agents, the metal which is produced is not precipitated in the solid form, but remains dissolved in the colloidal state (Vol. I., p. 929). In this way Faraday, as early as 1857, by reducing solutions of gold chloride with phosphorus, succeeded in preparing red-coloured solutions of gold, which could be preserved for many years without depositing any of the metal. Such solutions can be freed from the other products of the reduction and from the excess of reducing agent by dialysis, and then form coloured liquids, which are often stable for a long period, and exhibit in a very characteristic manner the properties of colloidal solutions. They can be boiled as a rule without any metal separating out, and can in some cases, such as that of gold reduced by quinol, be evaporated to dryness, leaving a residue which is soluble in water and retains its

solubility even when preserved for a considerable time in the dry state. The metal will not diffuse through a colloid membrane, and in many respects these solutions present an extremely close analogy with the solutions of the organic colloids, substances which usually possess a very high molecular weight.

Investigation with the ultramicroscope shows that the colloidal solution of a metal consists of extremely minute particles of the metal in a state of suspension. These are in constant motion ("Brownian motion"), the rate of movement increasing as the size of the particles diminishes.[1] With the aid of the ultramicroscope, and by other methods also, the average size of the particles in colloidal solutions of platinum, gold, and silver has been shown to be 2×10^{-5} to 6×10^{-5} mm. The colloidal particles are found to be electrically charged, the sign of the charge depending upon the nature of the metal and on the method of preparation. By the passage of an electric current the metal is deposited in the insoluble form at the appropriate electrode. This precipitation (coagulation) is also brought about by the addition, often in very small amounts, of soluble electrolytes to the solution.

The reducing agents which have been found most suitable for the production of colloidal metals are phosphorus, hypophosphorous acid, ferrous sulphate, hydroxylamine hydrochloride, hydrazine hydrate, formaldehyde, quinol, pyrogallol, and other similar substances.[2]

Another extremely interesting method of preparing colloidal solutions of the metals consists in setting up an electric arc between two poles of the metal under water or very dilute alkali.[3] In these circumstances pulverisation of the cathode occurs, and the finely divided metal thus produced remains in colloidal solution in the water. In this way, for example, almost opaque dark-coloured solutions, containing a maximum of 0·015 per cent. of platinum, and bluish-violet solutions of gold of similar concentration, as well as solutions of silver, iridium, and cadmium, can readily be prepared. A number of other metals, including mercury, copper, iron, nickel, and zinc, can be brought

[1] See Zsigmondy's *Colloids and the Ultramicroscope.*

[2] For details, see Svedberg's *Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe* (Theodor Steinkopff; Dresden, 1909); Wo. Ostwald's *Handbook of Colloid Chemistry* (Churchill); Hatschek, *Introduction to the Physics and Chemistry of Colloids* (Churchill).

[3] Bredig, *Zeit. Elektrochem.*, 1898, **4**, 514; *Zeit. angew. Chem.*, 1898, 954; *Anorganische Fermente* (Englemann, Leipzig, 1901).

into colloidal solution by a slight modification of this method, which consists in employing a thin layer of the metal, deposited on the surface of another metal, as the cathode. By using organic solvents the alkali metals can also be obtained in the colloidal state by this method.

The solutions of platinum obtained in this way promote the combination of hydrogen and oxygen at ordinary temperatures, and decompose hydrogen peroxide in the same way as does platinum black. In its behaviour towards hydrogen peroxide colloidal platinum is strikingly similar to certain organic enzymes, and has accordingly been described by Bredig as "an inorganic ferment."

The stability of solutions of these metallic colloids is much increased by the presence of other colloids such as gelatin. Advantage has been taken of this property, in some cases, by preparing the colloidal metal in the presence of, or even by the reducing action of, an organic colloid. Thus, Carey Lea has described a number of colloidal forms of silver produced in the presence of dextrin and similar substances, whilst Paal has prepared several metals in a remarkably stable colloidal form in presence of certain products of the decomposition of egg-albumin by alkalis. The colloidal forms of certain refractory metals, such as osmium and tungsten, have been employed in the manufacture of filaments for electric lamps.

Colloidal solutions may be regarded as intermediate between solutions of crystalloids or true solutions, in which the particles of solute are of molecular size, and coarse suspensions. But it is not easy to differentiate sharply between the three states which merge into one another gradually. It is found, however, that, when the size of the solute particles comes within the range of approximately $0{\cdot}1\mu$ to $1\mu\mu$, those properties which are looked upon as characteristic of the colloidal state are most markedly developed. For a complete account of these properties text-books dealing with the subject of colloids should be consulted.

The specific properties of the different colloidal metals will be found under the heading of the metals concerned.

ALLOYS AND AMALGAMS.

45 Especially characteristic of the metals as a class are the bodies which different metals form with one another, and to

which the name of alloy is given (derived through the French from the Latin *alligare*, to bind to). Amongst chemical compounds in general, those are found to be most stable, and to show the greatest amount of chemical individuality, the constituents of which are the most diverse. In the case of the alloys, however, the essential properties of the metals are uniformly reproduced. Thus, they all possess metallic lustre and they conduct heat and electricity well, even when they assume distinct crystalline forms and contain their constituents in the proportion of their combining weights. Hence alloys are distinguished from the compounds which the metals form with such elements as oxygen, sulphur, and chlorine, in which the general properties of the metals have undergone a complete change. So great indeed is the resemblance between the alloys and the metals proper that in all ages, in common parlance, they have been confused under the same name. The early Greek alchemists classed electrum, an alloy of gold and silver, amongst the metals, giving to it the sign of Jupiter, and even nowadays the word metal is commonly employed to designate an alloy.

The union of metals to form alloys may be brought about in several different ways, of which only four will be mentioned.

(1) By fusing together the constituent metals.
(2) By strong compression of the finely powdered metals.
(3) By electro-deposition.
(4) By the simultaneous reduction of the constituent metals.

The first method is by far the most important of the four, as almost all alloys are produced in this way on the large scale. The second method has not received any, and the third only a limited technical application, whilst the fourth is the primitive method by which brass and other alloys were first produced, and which has certain applications at the present time. These may therefore be shortly discussed before passing on to the consideration of the first and chief method.

Compression.—The union of powdered metals to form alloys when strongly compressed was first observed by Spring,[1] who subjected the mixed powders to pressures up to forty tons per square inch in a steel cylinder, and in this manner obtained alloys identical with those obtained by fusion. It might be

[1] *Bull. Acad. roy. Belg.*, 1878, **45**, No. 6; 1880, **49**, No. 5; *Ber.*, 1882, **15**, 395.

supposed that the union is effected by the heat evolved during the compression causing the metals to melt; but Spring has shown that this is not the case, since, if the whole of the work done in the compression were converted into heat, this would still be insufficient to effect the fusion of the mass.

Electro-deposition.—Just as copper can be deposited from solutions of its salts by electrolysis, so it is sometimes possible to deposit two metals simultaneously from a mixture of their salts, so that they form an alloy. Thus by electrolysing under suitable conditions a solution containing certain zinc and copper salts, brass is obtained.

Simultaneous Reduction of Metals.—By this method brass was made long before the metal zinc was known in the free state, and, more recently, "calamine brass" has been made by the reduction of calamine in the presence of copper. At the present time this method is used in the production of alloys by the treatment of metallic waste and slags; in the manufacture of ferro-manganese and spiegeleisen in the blast furnace; in that of ferro-chrome, ferro-aluminium, etc., in the electric furnace; and in the manufacture of certain alloys by the Goldschmidt or "thermit" process.

Preparation of Alloys by Fusion.—The method of making alloys by fusion varies according to the nature of the metals to be alloyed. If none of the constituent metals is very volatile, they may be mixed and fused together, but if one of the constituents be a volatile metal, such as zinc, the other constituent or constituents are melted, raised to a sufficiently high temperature to cause the zinc to melt and mix easily, the zinc is then added and the whole stirred. The metals are generally covered with a layer of carbon to prevent oxidation during the process.

When metals are melted together they do not always form a homogeneous product, and a metallic alloy is defined as a mixture of metals which, after melting, does not separate into two layers. When such a separation does occur, each layer becomes a distinct alloy. For example, when lead and zinc are melted together and allowed to cool slowly, they separate into two distinct layers, the bottom one being an alloy of lead and zinc, containing 1·3 per cent. of zinc, and the top one an alloy of zinc and lead containing 1·57 per cent. of lead.

THE STUDY AND EXAMINATION OF ALLOYS.

46 The most important modern methods of research on this subject may be summarised as follows :—

1. Chemical methods. Analysis and separation of the constituents.
2. Thermal methods. Determinations of melting points, and critical changes.
3. Microscopical methods. Examination of crystalline and internal structure.
4. Mechanical methods. Determination of elasticity, tenacity, ductility, etc.
5. Electrical methods. Determination of resistance and E.M.F.
6. Magnetic methods. Examination of the various changes in magnetic properties during heating and cooling.

Illustrations will be given of only two of these methods, viz., the Thermal and the Microscopical.

Examination of Alloys by the Thermal Method.—The melting point of an alloy is usually lower than those of the metals which compose it. This is well seen in the case of ordinary plumbers' solder, consisting of tin and lead, which melts more easily than either of the constituent metals. This fact was known so long ago as the time of Pliny, for he states that tin cannot be soldered without lead, nor lead without tin, and that lead tubes are soldered with a mixture of one part of tin and two parts of lead, a mixture which is used at the present day. Homberg, in 1669, recommended an alloy of equal parts of tin, lead, and bismuth for sealing up anatomical preparations; and in 1772 [1] Valentine Rose the elder discovered the well-known fusible metal which bears his name. This consists of one part of tin, one part of lead, and two parts of bismuth. It melts at 94°, the lowest melting point among the constituents being that of tin, viz., 232°. Another alloy, consisting of eight parts of lead, fifteen of bismuth, four of tin, and three of cadmium, softens at a temperature of 60° and is perfectly liquid at 65°, the melting points of its constituents being tin 232°, bismuth 270°, cadmium 321°, and lead 327°.[2]

[1] *Stralsund Magazine*, 1772, 2.

[2] Lipowitz, *Dingl. Poly. Journ.*, 1860, **158**, 376.

For the experimental investigation of the relation between the freezing point and the composition of the alloy formed by two or more metals, a pyrometer, such as the thermo-couple pyrometer or the electric-resistance pyrometer, is required. The rate of cooling of a quantity of the alloy is then determined and plotted in a curve, any breaks in which indicate points of solidification or other critical changes. A complete series of alloys, such as those of lead and tin, is generally studied together and the points so obtained on the "cooling-curves" are employed for the construction of a second curve which shows the variation in the freezing point with change of composition and forms the freezing point of the series.

Thermal Classification of Binary Alloys.[1]—From the general form of the freezing point curves, binary alloys may be divided into groups as follows :—

Group 1. The curve consists of two branches, starting from the melting points of the pure metals and meeting at a point corresponding to the eutectic alloy. A eutectic alloy is that alloy of any series, or range of series, which has the lowest melting point, and corresponds to the cryohydrate formed by cooling a solution of a salt in water (Vol. I., p. 310). In some series of alloys more than one eutectic is found, but in such a case, each of them corresponds to a different set of constituents. The melting point of a eutectic mixture is lower than that of either constituent.

This type of curve obtains when the metals form neither definite compounds nor isomorphous mixtures, and is illustrated in Fig. 3. This represents the freezing point curve of the lead-tin series, the lines AX and BX corresponding to the separation of lead and tin respectively, and X being the point of solidification of the eutectic alloy. The horizontal line XCD represents the range of the series in which eutectic mixtures will be found, it having been observed that very dilute solutions of tin in lead solidify completely before the eutectic temperature is reached.

As long as the amount of lead present is above 31 per cent., metallic lead separates out first when the liquid alloy is cooled; if the amount of lead is below this, metallic tin separates out. The alloy containing 31 per cent. lead and 69 per cent. tin is the

[1] *Alloys*, H. le Chatelier, *Metallographist*, vol. i., 1898, p. 94. See also *Metallography*, by C. H. Desch (Longmans & Co., 1910).

eutectic alloy, and solidifies at 180°, in which point the curves representing the separation of lead and tin intersect.[1]

The most important members of this group are the alloys of:

Pb and Sn; Zn and Sn; Pb and Sb; Bi and Sn;
Pb and Ag; Zn and Cd; Cu and Ag; Cu and Bi.

Group 2. The curve consists of three branches, two of them starting from the melting points of the pure metals, the third exhibiting a maximum, and intersecting the others in two points corresponding to two eutectics. This obtains when the two metals form a definite compound; in such cases the curve may be divided into two portions, each comparable to Group 1.

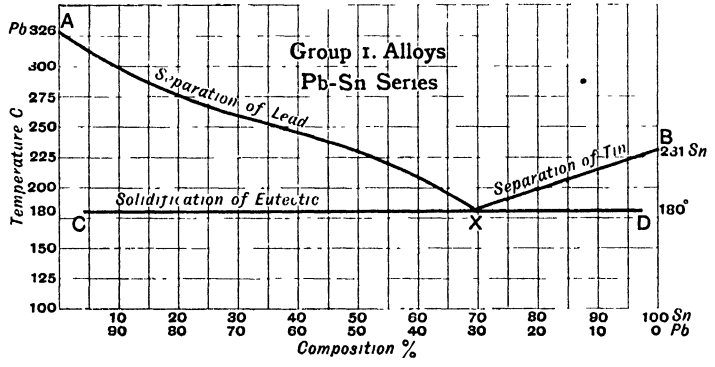


FIG. 3.

In Fig. 4, which illustrates this type of curve for the series Cu and Sb, AX represents the separation of copper, XB the separation of the compound $SbCu_3$, and EXF the range of the corresponding eutectic, which consists of a mixture of Cu and $SbCu_3$. The point B represents the melting point of the alloy containing 38·5 per cent. of antimony, which is a white compound having the formula $SbCu_3$. Beyond this point the curve departs from the simple type, and between B and C a mixture of $SbCu_3$ and $SbCu_2$ separates out, C representing the melting point of this second compound, which is purple in colour. The lines CY and DY correspond to the separation of the compound $SbCu_2$ and metallic antimony respectively, Y being the melting point of the second eutectic, which consists

[1] See also Rosenhain and Tucker, *Phil. Trans.*, [*A*], 1908, **209**, 89.

of a mixture of antimony and $SbCu_2$, and has a range represented by the horizontal line GYH. To this group belong also the alloys of Mg and Pb; Ni and Sn.

Group 3. The curve of fusibility is continuous and unites the melting points of the two metals. This occurs when the metals form isomorphous mixtures. To this group belong the alloys

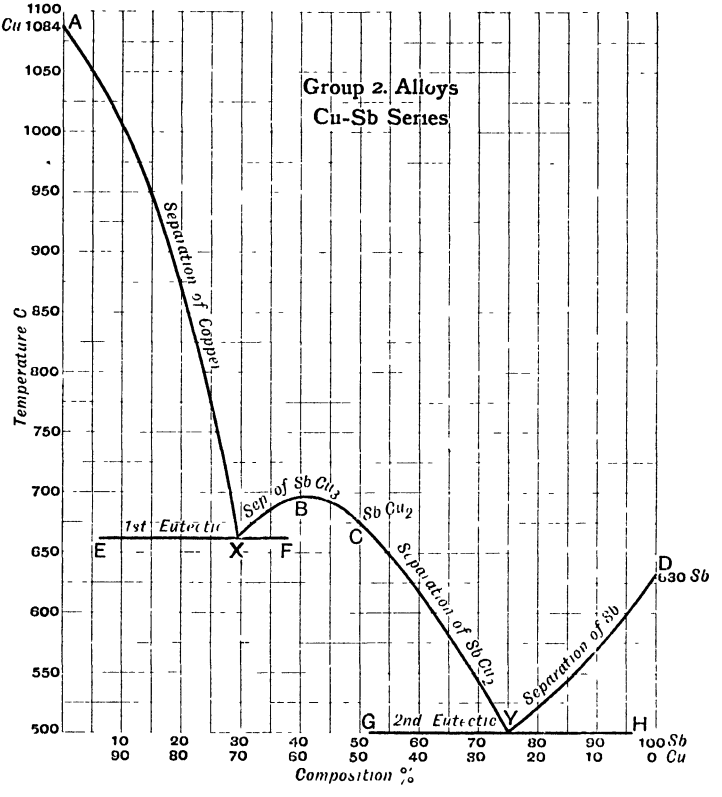


FIG. 4.

of Bi and Sb; Ag and Au; Ni and Co; Cu and Ni; Au and Cu.

Group 4. The curve consists of two branches, starting from the melting points of the metals as in Group 1, but on one branch there is a point at which a change of direction occurs, indicating the formation of a definite compound.

Fig. 5 illustrates this type of curve for the silver-antimony series. The line AB corresponds to the separation of solid solutions of the compound Ag_3Sb in Ag, and the point B represents

the formation of this compound; the lines BD and CD represent the separation of Ag_3Sb and antimony respectively. D is the eutectic point, and the line EDF indicates the range of the eutectic, which consists in this case of a mixture of Ag_3Sb and antimony. To this group belong also the alloys Sn and Ag; Al and Ag; Sb and Sn.

Group 5. Alloys with abnormal curves of fusibility, such as those of Cu and Sn, Cu and Zn, Sb and Sn, Zn and Ag, Al and Au.

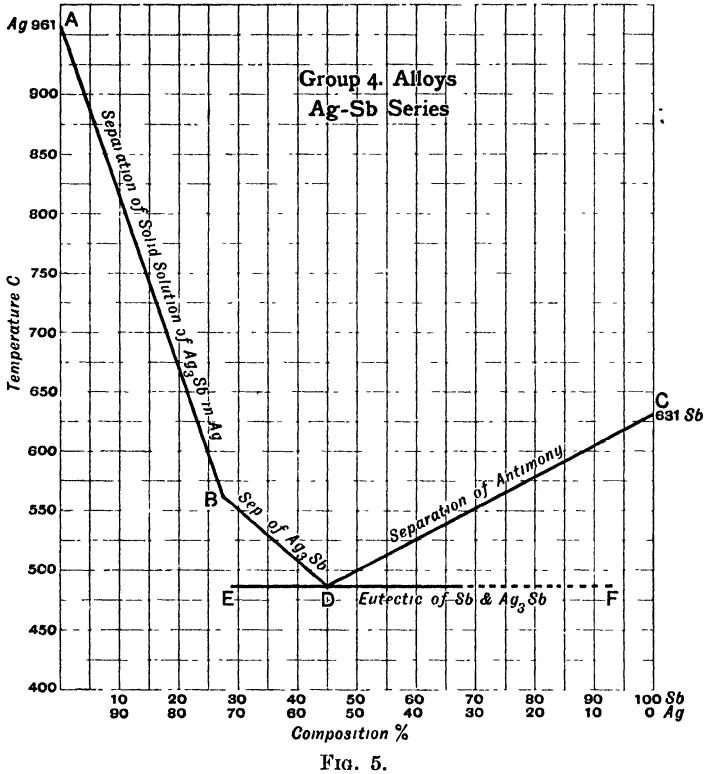


FIG. 5.

47 *The Examination of Alloys by the Microscope.*[1]—By examining a suitably prepared specimen by reflected light evidence may be obtained on the following points :—

Crystalline state of the metal or alloy.
Constitution of the alloy.
Presence of foreign bodies.
Presence of flaws, blow-holes, or cracks.
Presence of eutectics.

[1] See also *Alloys*, by E. F. Law (C. Griffin & Co.).

Preparation of Specimens.—In order to carry out this examination successfully, much care is necessary in the preparation of the specimen. A small piece is cut by means of a hack-saw, and smoothed with files; after this the specimen is rough-polished on emery cloth, and then finished on a series of graded emery papers, such as the French papers marked 0, 00, 000, and 0000.

When the specimen is free from scratches, the surface is treated by some agent which will attack the separate constituents differently as a preliminary to microscopic examination. For this purpose simple attack by some reagent, such as nitric,

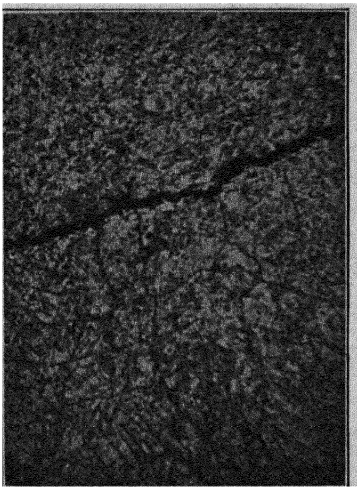


FIG. 6.

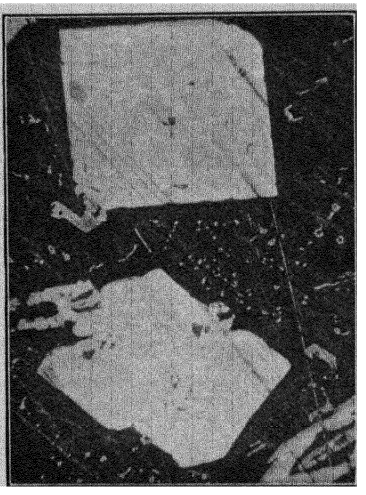


FIG. 7.

sulphuric, or hydrochloric acid, iodine, potassium cyanide, or ammonia, may be used. By this means one constituent may be dissolved more quickly than another, or may be coloured differently, or the joints between adjacent crystals may simply be eaten away. Heat-tinting is another method used, and consists in gently heating the polished surface, whereby the more oxidisable constituents become coloured by oxide tints.

The evidence obtained in this way as to the structure of the alloy is of great value, and is illustrated by the following typical examples :—

Fig. 6 represents the appearance (under a magnification of 100 diameters) of a case-hardened piece of steel which has been quenched, and the specimen polished and then etched

with picric acid. The wide black mark running across is a crack which developed during quenching; above this is seen the structure of saturated steel, containing 0·9 per cent. of carbon. This is known as martensite, and if slowly cooled from a red heat would have formed the eutectoid pearlite (p. 93). Below the crack is seen the structure of supersaturated steel; the black lines consist of carbide of iron, Fe_3C, contained in the ground-mass of martensite.

Fig. 7 is a photomicrograph (magnification 100 diameters) of a Sn-Sb-Cu alloy, containing Sn 83 per cent., Sb 11 per cent., Cu 6 per cent. The large white cubes are crystals of the compound SnSb, the smaller crystals consist of $SbCu_3$, and the dark ground-mass consists of tin containing a small quantity of antimony in solution.

The Constitution of Metallic Alloys.

48 As a result of the numerous researches carried out by the methods indicated above, it is concluded that the possible *constituents* of solid metallic alloys are very varied, the most important being the following [1]:

1. Free metals in the pure state.
2. A solid solution of one metal in another.
3. A solid solution of a definite chemical compound in an excess of metal.
4. Eutectic mixtures.
5. Definite chemical compounds of metals with metals.
6. Definite chemical compounds of metals with certain non-metals.
7. Allotropic modifications of metals.

1. *Free metals in the pure state.*—These are metals which separate from solution, or crystallise in the pure state. They are found in alloys as *crystallites* (*i.e.*, indefinitely crystalline, or incipient forms of crystallisation of the metals), or as perfectly formed crystals, which are produced only when the metal in question is incapable of holding in solid solution one of the other constituents of the alloy. An example of this is afforded by the Pb-Ag alloys containing about 1 per cent. of silver.

[1] "Metallic Alloys," J. E. Stead, Cleveland Institution of Engineers, 1900 (*Metallographist*, 1902, **5**, 110).

2. *Solid solution of one metal in another.*—A solid solution is defined as a homogeneous mixture of two or more substances in the solid state, and solid solutions of one metal in another, when crystalline, are solid isomorphous mixtures or mixed crystals.

Many metals which mix with each other in the liquid state do not remain in solution when solidification occurs; the solids thus formed are called solidified or congealed solutions. It is very important to distinguish between these and the true solid solutions.

Solid solutions crystallise in a form identical with, or very closely approximating to, that of the constituent which predominates. Examples of this are found in the Au-Ag and Ni-Co series.

3. *Solid solution of a definite chemical compound in an excess of metal.*—In many alloys definite chemical compounds are formed, and in some cases these compounds are dissolved in the metal which is in excess, forming a solid solution. Examples of this are found in the Cu-Sn, and Au-Al series.

In the same manner, some non-metallic elements combine with a portion of one of the metals, forming a compound which is dissolved, under suitable conditions, in the excess of metal. Examples are afforded by the behaviour of carbon and phosphorus in iron.

4. *Eutectic mixtures.*—The composition of eutectic mixtures is constant, and, within certain limits, independent of the original proportions of the constituent metals; the composition is not generally in simple atomic proportions, although it sometimes approximates very closely to these. This is the case with the well-known Levol's alloy of the composition Cu 28·1 to Ag 71·9, a relation which practically corresponds with the formula Cu_2Ag_3: and this accounts for the fact that this alloy has been mistaken for a definite chemical compound.

A eutectic consists of a conglomerate of distinct particles of the components, mechanically mixed. These components may be two or more metals which do not chemically unite, one metal and a definite chemical compound, two or more chemical compounds, one free metal and a solid solution, one compound and a solid solution, or two solid solutions.

The pearlite formed in solid steel, when it cools slowly from above 700° to 600°, is a solid solution of carbon in iron above 700°, but splits up into two constituents on cooling, and

is known as a *eutectoid*, to distinguish it from an ordinary eutectic.

5. *Definite chemical compounds of metals with metals.*—Many metals unite chemically in atomic proportions forming compounds which are quite homogeneous, and are recognised by having certain characteristics different from those of the component metals, the colour, hardness, crystalline form, etc., being often quite distinct. Sometimes, on bringing the metals together in the molten form, great heat is evolved, an almost certain sign of chemical action. Thus aluminium and copper combine to form a golden-yellow compound, Cu_3Al, harder, stronger, and tougher than either metal, and also than the compounds $CuAl_2$ and CuAl.

6. *Definite chemical compounds of metals with non-metals.*—In many cases metals combine with non-metals to form definite chemical compounds, which are of considerable importance in commercial alloys. Undoubtedly the most important of these compounds is the carbide of iron, Fe_3C, the amount and condition of which determine most of the valuable properties of steel.

Iron combines also with phosphorus to form phosphides; zinc with arsenic and phosphorus to form white compounds; and copper with phosphorus to form a pale yellow compound.

7. *Allotropic modifications of metals.*—The addition of very small quantities of another element frequently brings about a great change in the properties of a metal, although the quantity of the former added is too small to allow of the supposition that a true compound is formed. Thus, for example, the conductivity of copper is very greatly affected by the presence of extremely small percentages of foreign metals such as tin, and the hardness and tenacity of metals are also greatly altered by small quantities of other elements. Matthiessen was, therefore, led to the conclusion that when a metal is alloyed with small quantities of another, the former frequently undergoes a molecular change, and is converted into an allotropic modification showing very different properties.

It is by no means easy to determine whether an allotropic change has taken place, and there is still much to be learned about the effect of dissolving one metal in another, and about the grouping of atoms in solid solutions.

48 *Segregation or Liquation in Alloys.*—During the solidification

of alloys, perfect diffusion does not take place, and heterogeneous solid masses are therefore formed. Thus carbon segregates in a steel ingot, and the upper part of the axis of the ingot contains more carbon than the other portions. This is due mainly to the following causes: (1) the bottom of the ingot in contact with the cold mould is cooled more quickly than the top: (2) during cooling, the hotter portions rise and the colder portions sink: (3) the protion containing the most carbon is the last to solidify.

Another cause of segregation in alloys is the difference in the specific gravities of the different constituents; for example, in an alloy of tin and antimony, the compound SnSb, which crystallises in cubes, has a lower specific gravity than the bulk of the alloy, and when this is allowed to cool slowly, the top of the ingot is found to be full of these cubes, and the bottom comparatively free from them. Rapid cooling through the freezing range and slow cooling afterwards tend to lessen the amount of segregation.

Diffusion of metals.—Roberts-Austen has shown that metals diffuse into other metals just in the same manner as a salt in water. Thus a ball of gold immersed in a bath of molten lead at 550° diffused into the latter at a rate more than three times as great as that of sodium chloride into water at 18°; similar results have been obtained with gold in molten bismuth and tin, silver in lead and tin, etc. Moreover, diffusion takes place even between solid metals, metallic gold contained in a cylinder of solid lead slowly diffusing into the latter even at the ordinary temperature,[1] the rate of diffusion increasing with the temperature.[2]

Physical Properties of Alloys.

50 Certain of the physical properties of the metal are always preserved in the alloy. Thus, the specific heat and the coefficient of expansion of the alloy approximate to the mean of those of its component metals, except in the case of an alloy which undergoes molecular changes during cooling. In the case of other properties such as hardness, elasticity, tensile strength, etc., a variation takes place. Thus wires of either silver, copper, tin, or zinc in the pure state are lengthened by loads which would have scarcely any effect on similar wires of their alloys, such as gun-metal and brass. Again,

[1] *Proc. Roy. Soc.*, 1900, **67**, 101. [2] *Nature*, 1896, **54**, 55.

whilst the specific gravity of certain of the alloys is the mean of that of their constituent metals, that of others is either greater or less than the mean specific gravity of the constituents. All industrial alloys, with the exception of amalgams, are solid at the ordinary temperature. Many of the alloys of sodium and potassium are liquid at and below 18°.

Conductivity of alloys.—The electrical conductivity of alloys varies with their composition, and a distinct relationship exists between the freezing point curves of the alloys and their conductivity. For example, when a series of alloys is *eutectiferous* throughout, that is, when the eutectic range extends from one end of the series to the other (see line CXD, Fig. 3, p. 78) the conductivity is the mean of that of the constituents, as in the Sn-Zn and Sn-Pb series.[1] In nearly all other cases the conductivity is less than the mean, and when the results are plotted in curves different types are found to exist, each type corresponding to a different group of alloys having similar freezing point curves.

The conductivity of the alloys, like that of the pure metals, decreases with rise of temperature, and *vice versa*. The increase at low temperatures is, however, not so great as with the metals.

The solubility of alloys in acids differs frequently from that of the metals forming them. If an alloy of platinum and silver is boiled with nitric acid, it is completely dissolved, whereas platinum when unalloyed is quite insoluble in this acid. On the other hand, silver by itself readily dissolves in nitric acid, but it does not do so when it is alloyed with much gold, the whole of the silver being soluble only when its quantity is at least double that of the gold. It was formerly believed that in order to separate the whole of the silver not more than one quarter of the alloy must consist of gold, whence the term *quartation*, which is still used for the separation of these metals.

Many alloys are largely employed in the arts and manufactures, as they possess properties which are wanting in the single metals. Thus, pure gold and silver are too soft to be minted, but the addition of a small proportion of copper gives them the necessary hardness. Pure copper is so soft and tenacious that it is not suitable for use in the lathe. The addition of half its weight of zinc produces the alloy brass, which is hard, and yet is sufficiently tough to be readily

[1] Kurnakow and Puschin, *Zeit. anorg. Chem.*, 1902, **30**, 109.

turned. Gun-metal is a very tenacious and hard alloy, containing nine parts of copper to one part of tin. A still harder alloy is bell-metal, consisting of two parts of tin to eight parts of copper. The more tin such an alloy contains, the lighter is its colour. Speculum metal, containing one part of tin to two parts of copper, possesses a white colour, is capable of receiving a very high polish, and is, therefore, used for the specula of telescopes. Type-metal contains various proportions of lead and antimony, generally strengthened by the addition of tin. A very good metal is composed of two parts of lead, one part of antimony, and one part of tin. This alloy is hard, easily fusible, not brittle, and it expands at the moment of solidification—properties which make it most suitable for high-class work.

AMALGAMS.

51 Amalgams are bodies composed of compounds or mixtures of metals with mercury and, although really belonging to the class of alloys, are usually distinguished by this term. The name is first found in the writings of Thomas Aquinas; and Libavius explains the meaning of the word as follows:—"Amalgama corruptum vocabulum esse ex Graeco *μάλαγμα* non dubitant." It is perhaps more probable that the word is derived from, or through, the Arabic, as the form *algamala* also occurs in the writings of the alchemists.

The ancients were acquainted with the fact that mercury can combine with the metals, and they employed this property for the extraction of gold from its ores; Vitruvius even gives a method for extracting by means of mercury the gold from vestments which have been embroidered with gold thread. The Latin Geber speaks more distinctly respecting the compounds of the metals with mercury, for we find in his work, *Summa perfectionis magisterii*, the following words, "Mercurius adhæret tribus mineralibus de facili, Saturno (lead) scilicet, Jovi (tin) et Soli (gold). Lunæ (silver) autem magis difficulter. Veneri (copper) difficilius quam Lunæ. Marti (iron) autem nullo modo, nisi per artificium. Est enim amicabilis et metallis placabilis. Solvuntur Jupiter et Saturnus, Luna et Venus ab eo." Thus it is clear that Geber knew that, with the exception of iron, mercury combines directly with all the metals. The problem of the preparation of iron amalgam was one to which

the alchemists paid great attention, as, according to Geber, it was no easy matter. Libavius gives the first hints towards the solution of this problem, as he says that the common metals require to be purified by corrosive action before they can be made to unite with mercury.

Amalgams are usually obtained by the direct union of the metal with mercury. In this case a fall of temperature is not unfrequently noticed, as when tin is dissolved in mercury. Sometimes, on the other hand, heat is evolved, as when the alkali metals are amalgamated. The metals platinum, iron, aluminium, chromium, manganese, nickel, and cobalt will not unite directly with mercury. Amalgams are produced also by the addition of mercury to a solution of a metallic salt; thus, if mercury be added to a solution of silver nitrate, the amalgam separates out in splendid crystals—the *Arbor Dianæ* of the ancients. Another mode of obtaining an amalgam is to place the metal in a solution of mercuric nitrate, or together with mercury and a dilute acid; and lastly, amalgams are formed by the action of a weak electric current upon a solution of a salt into which a globule of mercury has been poured, the negative pole dipping into the globule.

The amalgams correspond in their chemical relationships to alloys, consisting generally of a mixture of one or more amalgams of definite composition with an excess of mercury. The amalgams containing a large quantity of mercury are often liquid, while those which contain less are frequently found to crystallise. On squeezing the excess of mercury through chamois leather, there is obtained from liquid silver amalgam a residue of fairly uniform composition containing about 30 per cent. of silver. On similarly treating a liquid gold amalgam, a residue is obtained which contains 33 per cent. of gold. When heated above the boiling point of mercury, a number of the amalgams retain a certain proportion of mercury. Thus silver amalgam, when heated to 450°, leaves a residue which still contains 12 per cent. of mercury; and a gold amalgam treated in the same way leaves a residue containing 10 per cent. of mercury.[1] Similar results are obtained with copper, sodium, and potassium, but the metals lead, tin, cadmium, and bismuth do not retain mercury at a temperature of 450°.

On examining the various series of amalgams by the method of thermal analysis, the existence of many definite compounds

[1] De Souza, *Ber.*, 1875, **8**, 1616; 1876, **9**, 1050.

has been established; thus, in the sodium amalgams,[1] the following compounds are known:

$$Hg_4Na,\ Hg_2Na,\ HgNa,\ Hg_2Na_3,\ Hg_2Na_5,\ \text{and}\ HgNa_3.$$

In a similar manner with potassium,[2] HgK, Hg_2K, and Hg_9K; and with silver, Ag_3Hg_4.

Regarded as compounds, such amalgams are very unstable, for Joule[3] has shown that they can be decomposed by subjecting them to a very high pressure.[4]

Many amalgams are used in the arts. Tin amalgam is employed in the silvering of mirrors, gold and silver amalgams in the processes of gilding and silvering in the dry way; zinc and tin amalgams for coating the rubbers of electrical machines, copper and palladium amalgam, and an amalgam of varying proportions of silver, copper, and tin, sometimes with gold and platinum, for stopping teeth.

CONSTITUTION OF SALTS, ACIDS, AND BASES.

52 The word salt even at the present day is commonly applied to sea-salt or sodium chloride, and there can be little doubt that originally the term was given to the same substance, the Greek form of the word (ἅλς) in the feminine being used for the sea itself, whereas in the masculine it denoted the solid residue left when sea-water is evaporated. The growth of the application of the word salt from a special to a generic term appears to have had its origin in the fact that just as common salt is obtained by the evaporation of sea-water, so other kinds of salt can be obtained by the evaporation of other liquids. When, for instance, wood-ashes are boiled with water, the clear solution yields on evaporation a white soluble residue to which the name of salt was applied. This extension of the term was, however, not accompanied by any knowledge of the chemical differences between these various soluble substances. Even up to the end of the eighteenth century this wide application of the word salt may be said to have been prevalent.

Amongst the alchemistic writings of the earliest times the

[1] Schuller, *Zeit. anorg. Chem.*, 1904, **40**, 385.
[2] Janecke, *Zeit. physikal. Chem*, 1907, **53**, 245.
[3] *Mem. Manch. Phil. Soc.*, 1865 (3), **2**, 115.
[4] See also Dudley, *Proc. Amer. Assoc.*, 1890, 145.

words salpetræ, salnitri, salmarinum, salarmoniacum, salvegetabile and the like, occur; these bodies are all soluble in water, and may be obtained again from solution by evaporation. The ideas connected with these salts were vague and indefinite. But a new meaning was afterwards given to the word salt, the term being applied to the solid bodies obtained by the combustion or ignition of substances. This view was upheld by Paracelsus, and was generally, though not universally, adopted by chemists. Thus we find in the seventeenth century that salt was considered to be one of the hypothetical essential constituents of all bodies, every substance being made up of salt, sulphur, and mercury (see Historical Introduction, Vol. I., p. 7). The view that salt is an essential constituent of all bodies was strongly opposed by Boyle, who paid much attention to the investigation of salts, and to whom we owe much of our knowledge of the special nature of the different salts. He did not, however, define exactly to what class of bodies the term salt ought to be applied. This was specially accomplished by Boerhaave, who, in his *Elementa Chemiæ*, published in 1732, describes the special characteristics of salts to be their solubility, fusibility, volatility, and taste, alkalis and acids being, according to this definition, also considered as salts. These were divided into salia alcalina, salia acida, salia salsa, salia media, salia neutra, and salia composita. Under the last named was understood a class of salts obtained by the union of an acid with an alkali or metallic calx. The chief characteristics of the salts still remained their solubility and peculiar taste. It was soon seen that such a definition led to contradictions, for baryta, nitric acid, and sulphuric acid would thus be salts as well as nitrate of barium, whilst sulphate of barium, which is insoluble, and, therefore, possesses no taste, would not be a salt. Hence the necessity became obvious of separating alkalis and acids from the true salts, or salia media as they were called, and the word salt was then taken to mean such substances as are obtained when an acid and a base are brought together, or when an alkali or metallic calx is neutralised by an acid.

Although acids and alkalis were included among the salts, chemists had long recognised that these substances were characterised by special properties. The only acid known to the ancients was vinegar or acetic acid. Hence the name of this substance and the notion of acidity were represented by closely-related words (ὄξος, *acetum*, vinegar; ὀξύς, *acidus*, acid). The

effervescence produced when vinegar is added to the carbonate of an alkali was observed in early times: thus we read in Proverbs xxv. 20, "As he that taketh away a garment in cold weather, and as vinegar upon nitre, so is he that singeth songs to a heavy heart." Nitre in this case stands for natron or native carbonate of soda. It was also well known that vinegar acted as a solvent upon many substances, as in the celebrated story of Cleopatra dissolving pearls. The Arabians were acquainted with many other acids. The Latin Geber termed nitric acid *aqua dissolitiva*, and he gave the same name to the liquid obtained by strongly heating alum in a retort, which was probably dilute sulphuric acid. This shows that the special characteristic of an acid, according to the older alchemists, was its power of dissolving substances which are insoluble in water.

Other properties common to the whole class of acids were not observed until a much later date. In 1668 Tachenius noticed that all acids are capable of combining with alkalis, and he therefore considered silica to be an acid. Boyle[1] points out that the substances known as acids have the following properties. They are bodies which (1) act as solvents, but act with varying power on different bodies; (2) precipitate sulphur and other bodies from their solutions in alkalis; (3) turn blue vegetable colouring matter red, whilst alkalis bring the blue colour back again; (4) can combine with alkalis, when the characteristic properties of each body disappear and a neutral salt is formed. The properties just enumerated were henceforward regarded as the special characteristics of acids, and accordingly F. Hofmann, in 1723, asserted that the *spiritus mineralis*, which exists in many mineral springs, and which we term carbonic acid, belongs to the class of acids since it turns blue litmus solution red. Thirty years later Black confirmed this by showing that this same substance possesses the power of destroying the caustic nature of the alkalis, giving rise to a distinct class of salts.

53 Such alkaline substances as lime, the potashes obtained by the combustion of plants or by heating cream of tartar, and natron, or native carbonate of soda, were well known to the Greeks, Hebrews, and Romans, whilst the spirit of urine became known to the alchemists of the thirteenth century. These substances, however, were not generally looked upon as possessing

[1] *Reflections upon the Hypothesis of Alcali and Acidum*, **4**, 284, and elsewhere.

the common property of alkalinity until the time of the iatrochemists, who ascribed the various diseases of the body to changes in the relative proportions of acid and alkali in the various organs and fluids, and indeed sought to explain all chemical phenomena as action between acids and alkalis. Some of the special characteristics of alkalis which were recognised about this time have already been mentioned in discussing the properties of the acids, and to these was added the power of effervescing with acids. The caustic alkalis which did not effervesce with acids were supposed to be more complex than the mild alkalis. Thus lime was supposed to acquire its caustic properties by taking up igneous particles from the fire in which the limestone was burned; when it was added to a mild alkali, these particles passed into the latter and rendered it caustic. This belief endured until Black in 1755 discovered the true nature of the phenomenon. The alkalis known at about the middle of the eighteenth century were the volatile alkali, and the two fixed alkalis, distinguished as the mineral alkali (soda), and the vegetable alkali (potash).

54 In the new system of chemistry founded by Lavoisier after the overthrow of the phlogistic theory (*see* Vol. I., pp. 25–32), the three classes of substances, acids, bases, and salts were for the first time clearly separated. The acids, distinguished by the properties already discussed, comprised the compounds of certain elements (the acidifiable bases) with oxygen, whilst the alkalis, earths, and metallic oxides possessed the common property of being able to combine with acids to form the third class of substances, the salts, in which the properties of alkalinity and acidity were alike wanting. The discovery of the compound nature of the alkalis by Davy (1807) justified Lavoisier's classification, inasmuch as these substances were thereby proved to be metallic oxides.

The view that all acids contain oxygen—a view to which this element owes its name—was soon adopted generally. On the other hand, it was pointed out by Berthollet that prussic acid and sulphuretted hydrogen, which do not contain oxygen, acted in many respects as acid bodies. Lavoisier's views, however, carried the day, it being assumed that the substances just mentioned really contained oxygen. The next step in the progress of our knowledge on this subject was Davy's investigations on chlorine and hydrochloric acid (1808–1810), which proved the existence of a powerful acid not containing oxygen.

Gay-Lussac's discovery of hydriodic acid, and the proof that prussic acid likewise contains no oxygen (1815), soon supplied further evidence of the same kind. Acids were henceforth divided into two classes, the *oxy-acids* and the *hydracids*, whilst the salts derived from them were known as *amphid* salts (ἀμφί, both, since the acid radicle and the base both contained oxygen), and *haloid* salts (ἅλς, sea-salt, εἶδος, like) respectively. The sulphides and selenides were afterwards included among the amphid salts because of the analogy of sulphur and selenium with oxygen. These elements were for this reason termed amphids, whilst the elements of the chlorine group, which combine directly with metals to form haloid salts, were termed haloids. The oxyacids were the substances which we now term the acid-forming oxides, whilst those bodies which we now term the oxygenated acids were considered to be the hydrates of these oxy-acids.

The dualistic view that salts are formed either by the union of an acid with a metallic oxide, sulphide, or selenide, or by the direct union of a metal with a haloid element, received its most complete expression in the electrochemical theory of Berzelius.

The fundamental principle of this system was laid down by its author in the statement that "in every chemical combination there is a neutralisation of opposite electricities, and that this neutralisation produces heat in the same manner as it is produced by the discharge of a Leyden jar, without being in this latter case accompanied by an act of chemical combination." The application of this principle led to the view that "every compound substance, whatever the number of its constituent principles, may be divided into two parts, one of which is electrically positive towards the other. For example, sulphate of soda is not compounded of sodium, oxygen, and sulphur, but of sulphuric acid and soda, each of which can again be divided into two elements, one positive, the other negative. In the same way alum cannot be regarded as directly compounded of its simple principles; it must rather be considered as the product of the reaction of sulphate of alumina, the negative element, on sulphate of potash, the positive element." [1] In accordance with this theory Berzelius wrote the formula for sodium sulphate $NaO + SO_3$, or in his contracted formulæ $\dot{N}a\dddot{S}$.

[1] Berzelius, *Traité de Chimie*.

The amphid salts were thus looked upon as compounds of the second order, formed by the union of two oxides, each of which was a compound of the first order, formed from its elements. The haloid salts, on the other hand, such as KCl, were compounds of the first order.

55 At this time no distinction was made between what are now known as mono-, di-, and tri-basic acids. Thus nitrate of potash was supposed to be formed in a precisely similar manner to the sulphate, and the formulæ of these two salts were accordingly written by Berzelius, $KO.N_2O_5$, and $KO.SO_3$, the atomic weight which was then adopted for potassium being twice that now in use. When two salts of the same acid and base were known, such as the sulphate and bisulphate of potash, it was supposed that the second salt was formed by the combination of the first with the second molecule of the acid, and was therefore written $KO.SO_3 + H_2O.SO_3$, or $KO.2SO_3$, the water being sometimes omitted.

The researches on the phosphates carried out by Graham in 1833 showed that this theory must be modified, since, if tri-sodium phosphate contained only one atom of base, the formula of phosphoric acid would become $P_{\frac{3}{4}}O_{\frac{5}{4}}$, which was incompatible with the atomic weights of phosphorus and oxygen, as determined independently. Graham showed that the formation of the ortho-phosphates might be readily explained by supposing that phosphoric acid was capable of combining with three atoms of base, and that this base might be either water or a metallic oxide. He therefore formulated orthophosphoric acid and its sodium salts as follows (the modern equivalents of his formulæ being employed):

Orthophosphoric acid . .	$P_2O_5 + 3H_2O$.
Acid sodium phosphate . .	$P_2O_5 + 2H_2O + Na_2O$.
Ordinary sodium phosphate .	$P_2O_5 + H_2O + 2Na_2O$.
Trisodium phosphate . .	$P_2O_5 + 3Na_2O$.

The water in the first, second, and third of these salts is essential to the composition of the salt, since when it is removed new salts are formed (Vol. I., p. 662).

In 1838 Liebig published his important investigation on the constitution of the organic acids, in which he showed that many of these resembled phosphoric acid in their relations to bases. He further proposed that all acids which formed mixed

salts containing two different, non-isomorphous bases, should be considered as belonging to the same class as phosphoric acid. In this memoir, moreover, he discussed the question whether the salts and oxyacids are compounds of a metallic oxide or water with an acid-oxide, or whether all salts and acids may be represented as combinations of metals or hydrogen with some other element or group of elements. This view had been originally suggested by Davy, and independently by Dulong (in 1816), but had not been generally accepted. The difference in constitution between the oxy-acids and the hydracids necessitated a different explanation for reactions which are in fact similar. Thus, for instance, it was assumed that when hydrochloric acid acted upon zinc the metal simply replaced the hydrogen of the acid:

$$Zn + 2HCl = H_2 + ZnCl_2.$$

In the action, however, of sulphuric acid upon zinc it was necessary to assume that the presence of the acid enabled the zinc to decompose the water (predisposing affinity) in order that an oxide might be formed with which the acid could unite; the reaction was, accordingly, represented as taking place in two stages:

$$(1)\ Zn + H_2O = H_2 + ZnO$$
$$(2)\ SO_3 + ZnO = SO_3,ZnO.$$

Similarly, when hydrochloric acid reacts with lime, water is formed, whilst, when the same base combines with sulphuric acid, no water is produced:

$$(1)\ 2HCl + CaO = H_2O + CaCl_2.$$
$$(2)\ SO_3 + CaO = SO_3,CaO.$$

Liebig pointed out that the new view does away with these inconsistencies and also with the distinction between hydracids and oxy-acids, amphid salts and haloid salts; acids are simply hydrogen compounds, the hydrogen in which can be replaced by metals, so giving rise to salts. In Liebig's opinion this view is less applicable to inorganic than to organic compounds. The analogous constitution of acids and salts was, however, not generally admitted until certain facts became known which were favourable to this theory.

56 If aqueous hydrochloric acid is decomposed by an electric current between platinum electrodes, chlorine is evolved at the

positive and hydrogen at the negative pole respectively. If dilute sulphuric acid is treated in a similar way, a simple decomposition of water apparently takes place, for at the positive pole we obtain only oxygen and at the negative pure hydrogen. The same phenomenon is observed in the electrolytic decomposition of a solution of sodium sulphate, but, in addition, sulphuric acid is produced at the positive pole, and soda at the negative pole. Hence it was argued that in this case, the current decomposed both the water into its elements, and the salt into its immediate components. If a solution of sulphate of copper is subjected to the same treatment, oxygen is evolved and sulphuric acid is produced at the positive pole, whilst at the negative pole metallic copper separates out; this was explained by the supposition that the copper oxide which ought to be deposited is reduced to the condition of metal by the nascent hydrogen.

These phenomena were specially examined by Daniell.[1] It appeared to him important to determine the relation between the quantities of oxygen and hydrogen, on the one hand, and of the acid and the alkali on the other, formed in the electrolysis of a salt of an alkali. As the result of a large number of careful experiments, he found that these several substances are produced in the proportion of their equivalents, and that this is true not only with sodium sulphate, but also with other salts of the alkalis. Daniell recorded also the remarkable fact that the same current which apparently is capable of producing these two decompositions is capable of liberating exactly the same quantities of hydrogen and of oxygen from dilute sulphuric acid. In the latter case, the current is apparently able to effect only half the work which it can do in the electrolysis of an aqueous saline solution, because in the latter case not only the salt but, as it seems, the water also, undergoes decomposition. This is, however, clearly impossible, and the phenomena observed can be readily explained by assuming that in the decomposition both of aqueous sulphuric acid, and of the solution of a sulphate, either hydrogen or a metal is liberated at the negative pole, whilst at the positive pole the group SO_4 is set free. But this group cannot exist in the free condition, and decomposes at once into oxygen and sulphur trioxide, the latter dissolving instantly to form sulphuric acid. When a salt of an alkali is electrolysed, the metal which is liberated instantly decomposes the water with evolution

[1] *Introduction to Chemical Philosophy*, second edition (1843), p. 533.

of hydrogen. According to this view, the electrolytic decomposition of the oxysalts is exactly analogous to that of the chlorides, and hence they must be similarly constituted. Daniell proposed a new nomenclature for the oxysalts:

H_2SO_4	Hydrogen oxysulfion,
Na_2SO_4	Sodium oxysulfion,
HNO_3	Hydrogen oxynitrion, etc.,

which, however, has never been generally adopted.

The further development of chemical theory has completely confirmed the view that acids and salts are strictly analogous, salts being derived from acids by the replacement of hydrogen by a metal. This analogy has received expression in the nomenclature employed by many chemists for these substances, according to which the acids are termed hydrogen salts. Thus, just as nitre is called potassium nitrate, nitric acid is called hydrogen nitrate, sulphuric acid hydrogen sulphate, etc. In 1851 Williamson pointed out that the basic oxides and hydroxides, the oxygen acids and their salts, might all be considered as derived from one or more molecules of water, by the partial or complete replacement of the hydrogen by other elements or groups. When the hydrogen of water is replaced by a metal, a basic oxide or hydroxide is produced, so that caustic potash and oxide of potassium have the formulæ $\overset{K}{H}O$ and $\overset{K}{K}O$. When, on the other hand, the hydrogen is partially replaced by chlorine, or a group of atoms such as NO_2, ClO_3, SO_2, &c., acids are formed, viz.:—$\overset{NO_2}{H}O$, $\overset{(ClO_3)}{H}O$, $\overset{SO_2}{H_2}O_2$, etc., the hydrogen of which can be replaced by metals to form salts.[1]

57 If we ask ourselves the question, What is the cause of the acid character of bodies? we may say that acids must contain hydrogen together with certain elements or groups of elements which are termed negative elements or groups, inasmuch as these separate out at the positive pole in the process of electrolysis. A compound may, however, contain these negative elements or groups of elements, and also hydrogen, and yet not belong to the class of acids. Hence it appears that the atoms or groups of atoms must be combined with hydrogen according to a particular plan in order that the compound may assume the character of an acid. Sir Humphry Davy,[2] in 1816, pointed out perfectly

[1] *Journ. Chem. Soc.*, 1852, **4**, 350. [2] *Journ. Sci. and Arts, Roy Inst*, 1816.

correctly that it is impossible to assert that a particular body is an acid-forming or an alkali-forming principle, and that such a definition would be nothing more than to re-introduce *qualitates occultas* into science. The chemical properties of a body, said Davy, are determined by "the corpuscular arrangement" of the constituent particles.

Amongst the different acids, the hydrogen compounds of the elements of the chlorine group possess the simplest constitution. They contain one atom of hydrogen combined with one atom of a powerful negative element. In the oxygen acids the hydrogen which can be replaced by metals is always found to be combined with oxygen in the form of the radical hydroxyl, OH; this is proved by the fact that these acids can as a rule be obtained by the action of water on the corresponding chlorides:

$$SO_2\begin{matrix}Cl\\Cl\end{matrix} + 2H_2O = SO_2\begin{matrix}OH\\OH\end{matrix} + 2HCl.$$

The ease with which the hydrogen of such a hydroxyl group can be replaced by a metal depends upon the nature of the group with which it is combined. This is well illustrated by many organic compounds, which assist us more than any other class in the solution of the problem as to what determines the acid nature of a compound. From a study of the organic acids it appears that when the OH group is combined with the group CO, the compound containing these groups is an acid, whilst when the OH group is united with the groups CH_2 or CH_3 the compound is not an acid. Thus formic and acetic acids are monobasic acids, malonic and oxalic are dibasic acids:

H	CH_3	CO.OH	$CH_2\begin{matrix}CO.OH\\CO.OH\end{matrix}$
CO.OH	CO.OH	CO.OH	
Formic acid.	Acetic acid.	Oxalic acid.	Malonic acid.

whilst alcohol, $CH_3.CH_2.OH$, is not an acid; hydroxy-acetic acid, which contains two OH groups, is nevertheless monobasic, and tartaric acid, which contains four OH groups, is only dibasic:

CH_3	$CH_2.OH$	CH(OH).CO.OH
$CH_2.OH$	CO.OH	CH(OH).CO.OH
Alcohol.	Hydroxy-acetic acid.	Tartaric acid.

The group SO_2 exerts a similar influence, so that such a substance as $C_6H_5.SO_2.OH$ is also found to be an acid.

Although it is characteristic of all acids that they contain hydrogen which can be replaced by metals, some substances which fulfil this condition are not acids. Thus compounds of such different properties as ammonia, NH_3, water, H_2O, and alcohol, C_2H_5OH, all yield metallic derivatives, NH_2Na, NaOH, and C_2H_5ONa, when they are directly acted on by metallic sodium; whilst marsh gas, CH_4, and benzene, C_6H_6, can by indirect means be converted into organo-metallic derivatives such as $(CH_3)_2Zn$ and $(C_6H_5)_2Hg$. It is therefore usual to define acids as compounds which contain hydrogen capable of being replaced by a metal when the latter is presented to them in the form of a hydroxide. It is, however, impossible to draw a hard and fast line between substances which are, and those which are not acids, since, especially among the organic compounds, the two classes pass imperceptibly into one another.

Constitution of Salts, Acids, and Bases in Dilute Solution.

58 As already explained (Vol. I., pp. 122—126), the behaviour of acids, bases, and salts in dilute solution has led to the conclusion that these substances are dissociated into equal quantities of positively charged ions, or kations, and negatively charged ions, or anions, the extent of dissociation increasing in all cases with the dilution of the solution. Acid properties are found to be peculiar to substances which yield hydrogen as a kation, whilst the anion OH is characteristic of basic substances. Weak acids and bases, such as acetic acid, boric acid, ammonia, &c., are found to be only very slightly dissociated, whilst strong acids and bases, such as hydrochloric and nitric acids, caustic soda, and caustic potash, are very largely dissociated even in moderately strong solution. The percentage of dissociated molecules in solutions which contain 1 gram equivalent per litre of the various substances, is about 80 for the strongest acids and bases, and 0—10 for weak acids and bases. Salts which yield a univalent kation and a univalent anion are dissociated, at the afore-mentioned concentration, to the extent of 60—70 per cent., even when the acid and base from which the salt is derived are both weak.

The action of acids, bases, and salts on the colouring matters known as indicators, such as litmus, phenolphthalein, etc.,

receives a very interesting explanation in the light of this theory. The substances which are used as indicators are themselves either weak acids, or weak bases, or salts derived from them. Thus blue litmus solution contains the sodium salt of a very weak acid, the ions being the colourless kation $\overset{+}{\text{Na}}$, and a complex anion which gives the liquid its blue colour. When an acid is added to the solution these complex anions are brought into the presence of free hydrogen ions, with which they immediately unite to form molecules of the weak acid of litmus. This is much less dissociated than its sodium salt, and causes the liquid to appear red, the change of colour being due to the fact that the molecule of the undissociated acid has a different colour from that of the anion.

It follows from the above that an acid indicator will be sensitive only to acids which are much more strongly dissociated than itself, since only such acids will bring about the practically complete removal of the anions of the litmus acid by combination with hydrogen ions. Hence it is that the various indicators differ in their sensibility towards acids, and that some weak acids such as boric acid do not show an acid reaction towards litmus. In the same way, methyl-orange is not affected by carbonic acid or by sulphuretted hydrogen; properties of which advantage is taken in various methods of volumetric analysis. Similar considerations hold with regard to the reactions of basic substances. Thus, when caustic soda is added to a solution of red litmus, the few free hydrogen ions of the litmus acid unite with the $\overset{-}{\text{OH}}$ anions of the caustic soda, forming water. Equilibrium being thus disturbed, fresh molecules of the acid undergo dissociation; the hydrogen ions thus liberated unite with the $\overset{-}{\text{OH}}$ anions, and this process goes on until practically the whole of the molecules of the acid have been dissociated; the corresponding number of molecules of water are formed, and the solution finally contains kations of $\overset{+}{\text{Na}}$, the $\overset{-}{\text{OH}}$ anions from the excess of caustic soda, and the anions of the litmus acid, which render the liquid blue.[1]

Molecules capable of yielding more than two ions appear to be only very partially dissociated even at fairly low concentrations. Thus, for example, sulphuric acid, which is capable of

[1] For this and other theories of indicators, see Thiel, *Ahrens' Sammlung*, 1911, **16**, 307.; also Prideaux, *The Theory of Indication*.

yielding the three ions $\overset{+}{H}$, $\overset{+}{H}$, $\overset{--}{SO_4}$, is found in dilute solutions to be mainly dissociated into the two ions $\overset{+}{H}$, and $\overset{-}{HSO_4}$, whilst only a comparatively small proportion of the $\overset{-}{HSO_4}$ ions are further dissociated into $\overset{+}{H}$ and $\overset{--}{SO_4}$. The second stage of the dissociation does not become very prominent until concentrations of the order of one-tenth or one-hundredth of a gram equivalent per litre are reached.

Some salts in which no replaceable hydrogen is present do not give a neutral reaction when dissolved in water, whilst others containing replaceable hydrogen are not acid to indicators. Thus salts formed from a strong acid and a weak base, such as ferric chloride, chromic chloride, aluminium sulphate, etc., usually have an acid reaction, whilst, on the other hand, salts formed from a weak acid and a strong base have an alkaline reaction, as is seen in the case of sodium carbonate, sodium borate, sodium nitrite, sodium aluminate, sodium silicate, etc. Moreover, disodium hydrogen phosphate, Na_2HPO_4, sodium bicarbonate, $NaHCO_3$, and similar acid salts are neutral, or even alkaline, to indicators. It seems probable that in such cases the salt is partially decomposed or hydrolysed by the solvent water, which, as shown by its electrical conductivity, contains a certain number of free hydrogen and hydroxyl ions, although this number must be a very small one (Vol. I., p. 300). Taking the example of a salt of a weak monobasic acid, such as nitrous acid, with a strong base, such as caustic soda, we have the following relations. When sodium nitrite is dissolved in water the following reaction probably occurs between a few of the ions of the salt and the free ions $\overset{+}{H}$ and $\overset{-}{OH}$, to which reference has just been made, molecules of the weak, slightly dissociated acid, HNO_2, being formed:

$$\overset{+}{Na} + \overset{-}{NO_2} + \overset{+}{H} + \overset{-}{OH} = \overset{+}{Na} + \overset{-}{OH} + HNO_2.$$

As a result of this action there remains an excess of hydroxyl ions, and the solution has therefore an alkaline reaction. Similar conditions prevail in solutions of many salts of weak acids, for example, those of potassium cyanide, which always smell of hydrogen cyanide. When, on the other hand, the salt has been formed from a strong acid and a weak base, the hydrogen ions are present in excess, and the solution has an acid

reaction. Some salts which have been formed from a weak acid and a weak base are completely decomposed in dilute solution. This is especially characteristic of the salts of the weak organic bases.[1]

METALLIC OXIDES, HYDROXIDES, AND SALTS.

59 All the metals combine with oxygen. Some, such as those of the alkalis and alkaline earths, unite with oxygen so readily that they have to be preserved out of contact with air. Other metals withstand the action of oxygen at the ordinary temperature, but combine with it when heated. When such metals are easily volatile, as is the case with magnesium and zinc, they burn with a bright flame in the air or in oxygen. If they do not volatilise readily, *e.g.*, tin and lead, the metals gradually undergo oxidation without production of light. A few metals, such as gold and platinum, cannot be made to unite directly with oxygen, even at the highest temperatures, but their oxides can be prepared by indirect means. Chlorine attacks all metals, and if the chlorides of those metals which are not directly oxidisable are decomposed by an alkali, their oxides or hydroxides are formed: thus—

$$2AuCl + 2KOH = Au_2O + 2KCl + H_2O.$$

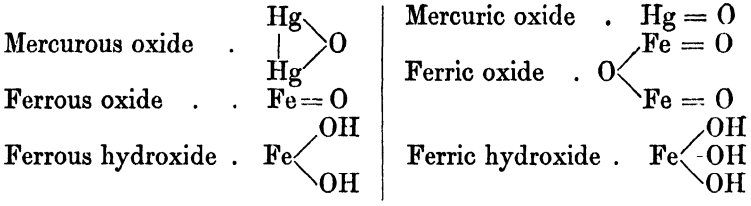
Representatives of each of the three classes—basic oxides, peroxides, and acid-forming oxides—into which the oxides in general may be roughly divided (Vol. I., p. 260), are found among the oxides of the metals.

(a) *Basic Oxides.*—The term basic oxide is applied only to such oxides as react with acids to form the corresponding salt and water, and hence all these oxides are formulated as derived from water by the replacement of hydrogen by a metal, or a radical containing a metal united with oxygen. Thus in uranium oxide, UO_3, which yields salts such as $UO_2(NO_3)_2$, the hydrogen of water is replaced by the radical UO_2, which is present also in the salts. When only a part of the hydrogen is replaced by a metal or radical, the resulting compound is termed a hydroxide, *e.g.*, $Ca\begin{smallmatrix}OH\\OH\end{smallmatrix}$. The hydroxides were formerly

[1] See Ostwald, *The Scientific Foundations of Analytical Chemistry.* Translated by McGowan (Macmillan, 1900). See also Lewis, *A System of Physical Chemistry* (Longmans), for a fuller account of hydrolysis.

called hydrates, as they were supposed to be compounds of the oxides with water.

Many of the metals form several basic oxides and corresponding series of salts, in which they have a different equivalent, as shown in the following list:



It must be remembered that only the empirical formula of most of the oxides and hydroxides is known, and that therefore no conclusion as to the valency of the metal can be drawn from these formulæ. Thus ferrous oxide may, for all we know, have the formula Fe_2O_2, and the constitution O = Fe—Fe = O.

The basic oxides are, as a rule, obtained by the direct oxidation of the metal, or by one of the following methods:

(1) The decomposition by heat of a salt derived from the metal and an acid the anhydride of which is volatile, or yields volatile decomposition products:

$$PbCO_3 = PbO + CO_2.$$
$$ZnSO_4 = ZnO + SO_3.$$
$$4Al(NO_3)_3 = 2Al_2O_3 + 12NO_2 + 3O_2.$$

(2) The decomposition of the hydroxide by heat:

$$2Cr(OH)_3 = Cr_2O_3 + 3H_2O.$$

The basic hydroxides are usually prepared as follows:

(1) By the reaction of a soluble hydroxide on a salt of the metal:

$$2NaHO + ZnSO_4 = Na_2SO_4 + Zn(OH)_2.$$

The oxide itself is, however, sometimes formed in this reaction instead of the hydroxide:

$$2NaOH + 2AgNO_3 = 2NaNO_3 + Ag_2O + H_2O.$$

(2) By the direct combination of the oxide with water:

$$CaO + H_2O = Ca(OH)_2.$$

The hydroxides of the alkali metals are the most soluble. They are termed *alkalis*, and are distinguished by their caustic

taste. The hydroxides of the metals of the alkaline earths are less soluble. Most of the other hydroxides and basic oxides are almost insoluble in water. Exceptions to this are thallous hydroxide, which is very soluble in water, and the oxides of lead, silver, and magnesium, which dissolve very slightly.

(b) *Acid-forming Oxides.*—The hydroxides corresponding with these oxides are the acids, but only comparatively few of these are known in the free state among the derivatives of the metals. Like the basic oxides, they are formulated as derived from water by the complete or partial replacement of the hydrogen by a metal or radical. They are usually obtained by the addition of a stronger acid to a salt derived from the acid-forming oxide in question:

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + 2CrO_3 + H_2O.$$

It is a general rule that the acid-forming oxides of a metal contain more oxygen than the basic oxides of the same metal. Thus Bi_2O_3 is a basic oxide, while Bi_2O_5 is a weak acid-forming oxide; again, VO is a basic oxide, whilst V_2O_5 yields a strong acid which forms stable salts.

(c) *Peroxides.*—The term peroxide is applied generally to oxides which are neither basic nor acid-forming, but contain more oxygen than the basic oxides of the same metal. Many of these peroxides appear to be derived from hydrogen peroxide in the same way as the basic and acid-forming oxides are derived from water. Thus, when they are treated with an acid they yield a salt and hydrogen peroxide:

$$Ba\begin{matrix}O\\|\\O\end{matrix} + 2HCl = BaCl_2 + H.O.O.H,$$

while some of them may be prepared by double decomposition between a salt of the metal and hydrogen peroxide. In some cases such oxides are to be considered as having a mixed constitution, part of their oxygen being derived from water and part from hydrogen peroxide.

Peroxides which are not true derivatives of hydrogen peroxide, on the other hand, act in the presence of acids simply as oxidising agents. Thus, when they are treated with hydrochloric acid, chlorine is evolved, and the salt corresponding to a lower basic oxide is formed:

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2.$$

It is, however, impossible to employ this reaction as the basis of a rigid classification of the peroxides, since the behaviour of the various oxides towards hydrochloric acid has not been sufficiently investigated.

This action of hydrochloric acid on the higher oxides of the metals is frequently employed for the determination of the composition of these oxides, and for their analytical estimation (Bunsen). The chlorine evolved from a known weight of the oxide is passed into a solution of potassium iodide, and the iodine liberated is estimated by means of a standard solution of sodium thiosulphate. Many oxides which are not peroxides undergo the same reaction, a salt corresponding with a lower oxide being formed :

$$2CrO_3 + 12HCl = 6H_2O + 2CrCl_3 + 3Cl_2.$$

60 In addition to the classes of oxides which have already been discussed, many metals also yield *sub-oxides*, containing less oxygen than the lowest oxide of the metal which is capable of yielding salts, *e.g.*, Cu_4O, Pb_2O, &c. The constitution of these oxides is not at present understood. Many metals, moreover, form *intermediate oxides*, to which no corresponding salts are known. Such oxides are intermediate in composition between two of the other oxides of the metal, and generally yield a mixture of products when treated with acids. Thus magnetic oxide of iron, Fe_3O_4, which is intermediate between ferrous and ferric oxides, FeO and Fe_2O_3, yields a mixture of ferrous and ferric chlorides when it is dissolved in hydrochloric acid :

$$Fe_3O_4 + 8HCl = FeCl_2 + 2FeCl_3 + 4H_2O.$$

Red lead, Pb_3O_4, on the other hand, which is intermediate between the monoxide and the peroxide of lead, PbO and PbO_2, is converted into lead nitrate and lead peroxide when it is treated with dilute nitric acid :

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O.$$

61 It will be seen from the foregoing that the classification of the oxides is based mainly on the behaviour of these compounds with regard to the formation of salts. Since an oxide may exhibit varying behaviour in this respect when it is placed under different conditions, it follows that the same oxide may be found as a member of more than one class. Many oxides,

for example, act as basic oxides towards strong acids, but as acid-forming oxides towards strong bases, and on this ground are described as "amphoteric." Thus aluminium hydroxide is dissolved by sulphuric acid with formation of aluminium sulphate:

$$2Al(OH)_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 6H_2O,$$

and also by caustic soda with formation of sodium aluminate,

$$Al(OH)_3 + NaOH = Al(OH)_2ONa + H_2O.$$

Again, when black oxide of manganese, MnO_2, is warmed with hydrochloric acid, chlorine is evolved and manganous chloride is formed, so that the oxide behaves as a peroxide:

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

At a lower temperature, however, an unstable salt is formed which is known only in solution, so that in this case the oxide acts as a basic one:

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O.$$

The same oxide combines also with strongly basic oxides such as lime, CaO, to form unstable manganites, such as $CaO.MnO_2$, in which it plays the part of an acid-forming oxide.

62 Salts may be divided into several groups.

(1) *Normal salts* are those in which the whole of the replaceable hydrogen of an acid is completely replaced by a metal. These were formerly called *neutral salts*, or *salia media*, because it was noticed that when an alkali was added in the right proportion to a powerful acid the resulting salt possessed neither an alkaline nor an acid reaction. This, however, is not the case with every normal salt (see p. 111).

Polybasic acids can form salts containing two or more different metals: as, for instance, potassium sodium carbonate, $CO\begin{cases}OK\\ONa\end{cases}$. Polyacid bases, on the other hand, may give rise to salts which contain two acid radicals: *e.g.*, $Sr\begin{cases}ONO_2\\OC_2H_3O\end{cases}$, a compound which is at the same time a nitrate and an acetate; as another and more complex example the mineral vanadinite may be cited, $VO\begin{cases}O\\O\\OCaCl\end{cases}\!\!\begin{matrix}\\\}Ca\\\\\end{matrix}$, which is a cal-

cium salt of tribasic vanadic acid, and at the same time a chloride.

The salts formed by the union of an acid-forming oxide with a normal salt, or by the removal of water from an acid salt, are sometimes called acid salts, but are really normal salts derived from complex acids, which, however, often do not exist in the free state. Sodium pyrophosphate, for instance, which is obtained by heating ordinary sodium phosphate to redness,

$$\begin{matrix} PO\{(ONa)_2 \\ PO\{OH \end{matrix} = \begin{matrix} PO\{(ONa)_2 \\ \quad O \\ PO\{(ONa)_2 \end{matrix} + H_2O,$$

is the normal salt of pyrophosphoric acid, $H_4P_2O_7$, which can be prepared in the free state, and also yields an acid salt, $Na_2H_2P_2O_7$. The acids corresponding with potassium dichromate, $K_2Cr_2O_7$, borax, $Na_2B_4O_7$, etc., on the other hand, are not known. Further examples of this class of substances are potassium disulphate or pyrosulphate, obtained by heating potassium hydrogen sulphate,

$$\begin{matrix} SO_2\{OK \\ SO_2\{OH \end{matrix} = \begin{matrix} SO_2\{OK \\ \quad O \\ SO_2\{OK \end{matrix} + H_2O,$$

sodium metabisulphite, $Na_2S_2O_5$, and many complex phosphates, borates, and silicates (Vol. I., pp. 671, 736, 930).

(2) *Acid salts* are formed when only a portion of the replaceable hydrogen contained in a polybasic acid is substituted by a metal. The acid salts often possess an acid reaction, as is the case with acid potassium sulphate, $SO_2\{^{OK}_{OH}$, but, as we have seen, this reaction is dependent on the nature of the acid and the base (see p. 111).

(3) *Basic salts* stand in the same relation to the basic hydroxides as the acid salts to the acids. They may be regarded as formed from the basic hydroxides by the reaction of only a part of their hydroxyl groups with the hydrogen of an acid, *e.g.*, $Zn\{^{OH}_{Cl}$.

Some of these salts do not contain a hydroxyl group, and

these may be considered as the normal salts of complex basic radicals. Thus, basic bismuth chloride (bismuth oxychloride), BiOCl, may be looked upon as the chloride of BiO(OH), derived by loss of water from bismuth hydroxide, $Bi(OH)_3$, just as meta-phosphoric acid from ortho-phosphoric acid.

Basic salts are sometimes formed by the combination of a normal salt with a hydroxide. Thus, if a solution of lead nitrate is boiled with lead hydroxide, a basic lead nitrate is formed;

$$Pb\begin{cases}ONO_2\\ONO_2\end{cases} + Pb\begin{cases}OH\\OH\end{cases} = 2Pb\begin{cases}OH\\ONO_2\end{cases}.$$

Basic zinc chloride, $Zn\begin{cases}Cl\\OH\end{cases}$, may be obtained in the same way.

Basic bismuth nitrate, on the other hand, is obtained by the action of water on the normal salt:

$$Bi\begin{cases}ONO_2\\ONO_2\\ONO_2\end{cases} + 2H_2O = Bi\begin{cases}OH\\OH\\ONO_2\end{cases} + 2NO_2OH.$$

Amongst other basic salts may be mentioned:

Malachite. $CO\begin{cases}OCuOH\\OCuOH\end{cases}$

Blue Carbonate of Copper. $CO\begin{cases}OCuOH\\O\end{cases}Cu \quad CO\begin{cases}O\\OCuOH\end{cases}$

White Lead. $CO\begin{cases}OPbOH\\O\end{cases}Pb \quad CO\begin{cases}O\\OPbOH.\end{cases}$

Basic Mercuric Sulphate. $SO_2\begin{cases}OHgO\\OHgO\end{cases}Hg.$

(4) *Complex and Double Salts.* When two salts are dissolved in water and the solution evaporated, it frequently happens that the crystals which are formed contain the two salts combined in definite molecular proportions, often along with water of crystallisation. Thus, when potassium sulphate, K_2SO_4, and aluminium sulphate, $Al_2(SO_4)_3,18H_2O$, are treated in this way, crystals of potash alum, $K_2SO_4,Al_2(SO_4)_3,24H_2O$, are obtained; whilst potassium chloride, KCl, and platinic chloride, $PtCl_4$, yield the compound K_2PtCl_6, potassium platinichloride. A distinction is usually made between complex salts such as potass-

ium platinichloride, and double salts such as potash alum (Ostwald). Members of the former class yield, even in dilute solution, a complex ion, which differs from the ions of either of the component salts, whereas true double salts yield the same ions as the single salts from which they have been formed. Thus the salt K_2PtCl_6 yields the complex anion $\overline{PtCl}_6$, whilst alum yields the same ions as potassium sulphate and aluminium sulphate. This distinction, however, is not absolute, since most double salts yield a certain proportion of complex ions, at all events in concentrated solution.

Complex salts are best regarded as the salts of complex acids or bases, and their chemical behaviour, as has already been pointed out (Vol. I., p. 126), is often quite different from that of their constituent salts.

Double salts. Although very many double salts have been prepared, very little is known as to the constitution of compounds of this class. Their aqueous solutions as a rule exhibit the properties which would be expected of a mixture of the solutions of the component salts, although there is evidence in some cases of the existence in solution of an unstable complex. The relation of the solid salts to water is of great importance, and is discussed later (p. 127).

Among the double salts are found many series of isomorphous salts: a typical example is furnished by the double sulphates $R'_2SO_4,R''SO_4,6H_2O$, in which R′ represents the alkali metals K, Rb, and Cs, together with NH_4 and Tl′, whilst R″ represents the divalent metals such as Mg, Zn, Cd, Mn″, Fe″, Ni, and Co.

Solubility of Salts.

63 A very important property of salts is the manner in which they behave when treated with water. Strictly speaking, all salts are soluble to some extent in these circumstances, but in many cases the amount dissolved is so minute that for most purposes it may be neglected, and it is usual to classify salts roughly as soluble, sparingly soluble, and insoluble, in water.

The extent of the variation in the solubility of different salts is illustrated by the following table, the figures in which represent the weight, in grams of anhydrous salt, dissolved by 100 grams of water at 15–18° C. The formula gives in each case

the composition of the solid which is in equilibrium with the saturated solution at the same temperature.

Potassium carbonate, $K_2CO_3\,2H_2O$	110·5
Calcium chloride, $CaCl_2,6H_2O$	66
Sodium chloride, NaCl . .	35·9
Potassium nitrate, KNO_3 .	26
Potassium sulphate, K_2SO_4	10·3
Potassium perchlorate, $KClO_4$	1·5
Calcium sulphate, $CaSO_4,2H_2O$.	0·20
Strontium sulphate, $SrSO_4$	0·011
Lead sulphate, $PbSO_4$.	0·0041
Barium sulphate, $BaSO_4$	0·00026
Silver chloride, AgCl	0·00014
Silver bromide, AgBr	0·00001
Silver iodide, AgI . .	0·0000002

The solubility of a given salt has a definite value at each temperature. In a few instances, such as calcium hydroxide, and the calcium salts of certain organic acids, the solubility diminishes with rising temperature, but the great majority of salts exhibit an increase of solubility as the temperature rises. In some cases, such as that of potassium chloride, the solubility increases proportionally to the rise of temperature, *i.e.*, the solubility curve is a straight line, but, as a general rule, the curve becomes steeper as the temperature rises. Instances of this will be found in Fig. 8, where a number of solubility-temperature curves are reproduced, the abscissæ representing temperatures, and the ordinates the weights of salt dissolved by 100 grams of water.

The variation of solubility with temperature may be conveniently represented also by interpolation formulæ, the constants in which are deduced from direct experiment. Thus, if S represents solubility at the temperature $t°$ C., we have for potassium nitrate:

$$S = 13{\cdot}32 + 0{\cdot}5738t + 0{\cdot}01717t^2 + 0{\cdot}000003598t^3.$$

The process of dissolution of a salt in water is generally accompanied by absorption of heat, but there are many cases in which heat is evolved. The heat of solution, for instance, of a hydrated salt is generally negative, whereas that of the corresponding anhydrous salt is positive. Salts which do not form hydrates have, as a rule, a negative heat of solution.

The first action of water on a salt, or, speaking generally, of a solvent on any crystalline substance, is to liberate those molecules with which it is in contact, and to allow them to distribute themselves equally throughout the liquid; this process

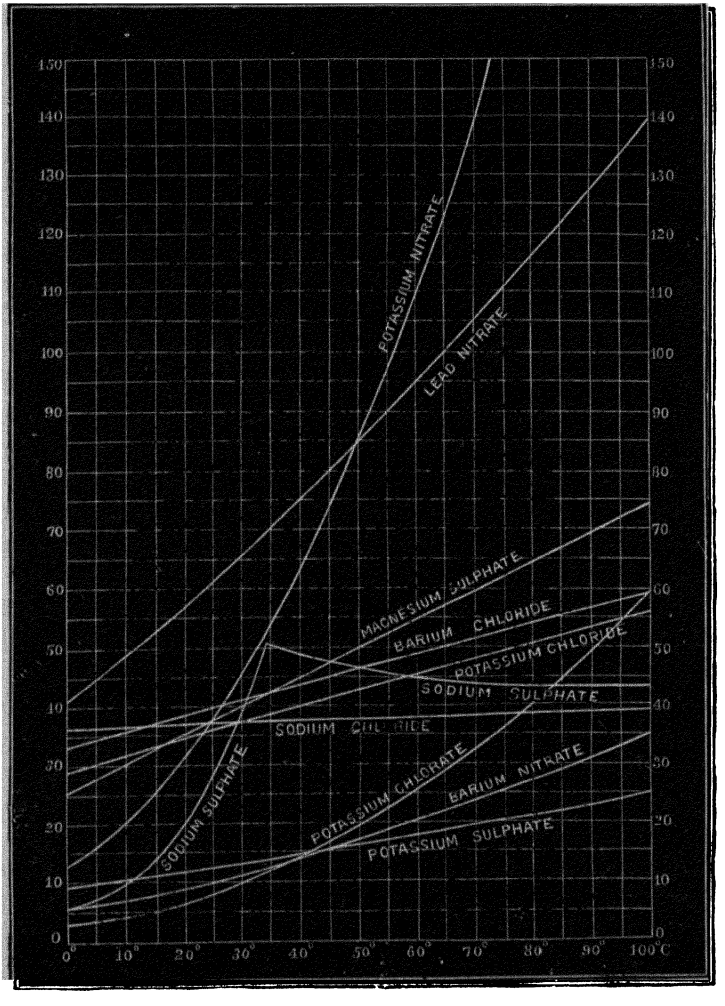


FIG. 8.

continues, provided an excess of the salt is present, until no more of the latter is dissolved, a condition of equilibrium being thus established between the solution and the salt. The condition of equilibrium is expressed by the solubility, which, as already shown, varies according to the nature of the salt

and the temperature. Hence the solubility at a given temperature depends upon the exact nature of the solid present, and when a salt crystallises in two different forms the solubility may be different in the two cases. Thus it is that the solubility of an anhydrous salt is different from that of each of its hydrates, as, for example, in the case of calcium sulphate, which is much more soluble as the hemihydrate than when combined with two molecules of water to form gypsum.

The fact that the solubility depends on the exact nature of the solid in equilibrium with the saturated solution has also supplied the explanation of certain cases of abnormal solubility, of which sodium sulphate is a typical example. As will be seen from the diagram, Fig. 9, the solubility of this salt rises rapidly from 0° to 32·5°, but decreases from that point onwards, and is considerably less at 100°. It was formerly supposed that up to 32·5° the liquid contained the hydrate $Na_2SO_4,10H_2O$ in solution, and that above this temperature the latter underwent dissociation, the solution then containing the anhydrous salt. There is, however, no evidence of any sudden change in the properties of the solution, such as its vapour pressure or viscosity, at any point, and it has been shown that the above behaviour is really due, not to any change in the constitution of the liquid, but to a change in the solid substance with which the saturated solution is in equilibrium. Up to 32·5° the solid salt present is $Na_2SO_4,10H_2O$, and below that temperature the curve represents the solubility of this hydrate in water; at 32·5° the crystals of the hydrate are dissociated into water and anhydrous salt, and above that temperature the curve represents the diminishing solubility of the latter with rise of temperature; the curve, therefore, is a combination of two separate solubility curves which meet at 32·5°. When a solution which has been saturated at 32·5° is warmed, the anhydrous salt is deposited, whilst when it is cooled the hydrate $Na_2SO_4,10H_2O$ separates out.

64 The temperature 32·5°, at which the change from $Na_2SO_4,10H_2O$ to Na_2SO_4 occurs, is called the *transition temperature* for this pair of substances, and, like the melting point of a solid, is a perfectly definite temperature, depending only on the pressure. Above 32·5°, the decahydrate is unstable, below it, the anhydrous salt and water form an unstable system and unite to form the decahydrate. Such transition temperatures are very definite points, and on this ground may be

employed in the standardisation of thermometers.[1] Like the melting point, moreover, the transition temperature is a point at which absorption of heat, change of volume, and change of vapour pressure occur, and it can be determined experimentally by observations of any of these effects.

The break in the solubility curve occurring at a transition temperature is generally much less marked than in the case of sodium sulphate. When each of the hydrates which are in equilibrium at the transition temperature becomes more soluble with rising temperature, the slopes of the solubility curves for the two compounds may not be very different. Instances of this are found in connection with the hydrates of copper nitrate and lithium nitrate.

65 The examination of the relations of a salt to water in the manner exemplified above by the case of sodium sulphate is of great importance for the study of the various hydrates formed by the salt. In the investigation of the conditions of equilibrium in various systems of solids, liquids, and gases, of which the foregoing is a special case, each of the chemical substances present is called a *component* of the system, and each uniform solid, liquid, or gas present is termed a *phase*. The state of equilibrium of any such system is fully defined when the three variable factors of temperature, pressure, and concentration are known. These are not, however, always independent of each other, since in many systems when one of them is fixed the other two must also have fixed and invariable values. When hydrated sodium sulphate is in equilibrium with water, for example, only one of these factors can be independently varied, since a change in one of them brings with it a corresponding change in the others, and a new condition of equilibrium. Thus a change of temperature necessitates a change in the concentration and vapour pressure of the saturated solution. Such a system, in which it is necessary to fix only one of the three variable factors in order to have a fully defined state of equilibrium, is said to have one degree of freedom, and other systems exist which have two, three, or no degrees of freedom.

It has been found that the number of degrees of freedom depends entirely on the number of components and phases which are present, and the general law expressing the relation between these was established by Willard Gibbs in 1874, and is

[1] See Richards and others, *Zeit. physikal. Chem.*, 1898, **26**, 690; **28**, 313; 1903, **43**, 465; 1906, **56**, 348; 1907, **61**, 313.

known as the *phase rule*. This states that, in any system which is in equilibrium, the number of degrees of freedom may be calculated by adding two to the number of components and subtracting the number of phases. Considering the case of the solubility of sodium sulphate in water, the components of the system are sodium sulphate and water. Below 32·5°, there are three phases, solid hydrated sodium sulphate, $Na_2SO_4,10H_2O$, liquid solution, and water vapour, and this system, as already mentioned, has one degree of freedom. At the transition temperature, when the solid decahydrate and the anhydrous salt co-exist in contact with the saturated solution, there are four phases, viz., the two solid phases just mentioned, together with the liquid solution and the water vapour. At this temperature, therefore, the system has no degree of freedom, and any change in one of the variable factors, for example, the temperature, will lead to the disappearance of one of the phases. Above 32·5°, there are again only three phases present, viz., solid anhydrous sodium sulphate, its saturated solution, and water vapour, and the system has as before one degree of freedom. The application of the phase rule to the study of equilibria cannot be further pursued here, and reference must be made to works on physical chemistry in which it is fully treated [1]

66 The change of the decahydrate into the anhydrous salt does not invariably occur as soon as the transition temperature is passed, but may be delayed until a somewhat higher temperature is attained, provided that the anhydrous salt is absent; but if some of this is then introduced, the change commences at once, and proceeds until the whole of the decahydrate has been converted into the anhydrous salt. In a case like this the system is said to be *metastable*, *i.e.*, the system is in itself stable and no spontaneous change occurs, but as soon as a particular new phase is introduced the system at once becomes unstable and undergoes change with the production of this new phase. When, on the other hand, a system undergoes spontaneous change it is said to be *labile* or *unstable*.[2] A system can often exist in metastable equilibrium through a considerable range of temperature, and in fact some hydrates have been prepared which are known only in the metastable condition.

[1] Bancroft, *The Phase Rule* (Leipzig and Ithaca, 1897); Findlay, *The Phase Rule* (Longmans, 1918); Roozeboom, *Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre* (Vieweg, Braunschweig, 1901).

[2] Ostwald, *Zeit. physikal. Chem.*, 1897, **22**, 302.

Sodium sulphate affords instances of all these phenomena. The solubility curve of the anhydrous salt (Fig. 9, curve *B*) has been traced below the transition point to 18°, and that of the decahydrate (curve *A*) above it to 34°. The dotted portions of the curves represent the solubility at temperatures beyond the transition point, in regions in which the systems are therefore in metastable equilibrium. These dotted curves are continuous with the curves obtained for the stable systems, and this circumstance shows clearly that the abnormality of the solubility curve of sodium sulphate is due to the fact that it is made up of portions of the two curves *A* and *B*, representing

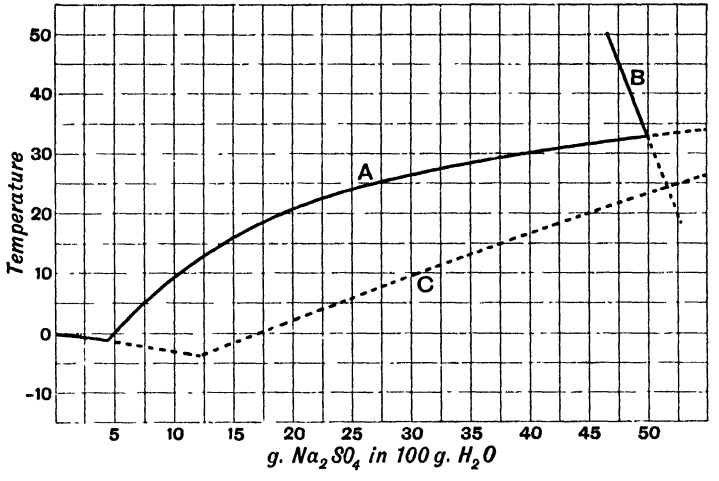


FIG. 9.

the solubilities of the two distinct substances $Na_2SO_4.10H_2O$ and Na_2SO_4. A third hydrate, $Na_2SO_4,7H_2O$, has also been prepared by allowing a solution of sodium sulphate to crystallise at 17°, and its solubility is shown by the curve *C*, which cuts the curve *B* at 24·2°. This substance is more soluble than the decahydrate throughout the whole course of the curve, and hence if a crystal of the decahydrate were introduced at any temperature into a solution saturated with the heptahydrate, Na_2SO, $10H_2O$ would crystallise out until the solution had the composition represented by the point on the curve *A* corresponding with the temperature at which the addition had been made. In other words, the heptahydrate is metastable throughout with respect to the decahydrate. This case is a typical one, for it

is the rule that the solubility of a metastable hydrate is greater than that of the hydrate which is stable at the same temperature.

67 Somewhat different conditions prevail when the hydrated salt melts completely at a definite temperature, forming a single liquid phase of the same composition as the hydrate. In this case the hydrate behaves like an individual compound, and its melting point is accordingly lowered by the addition of any

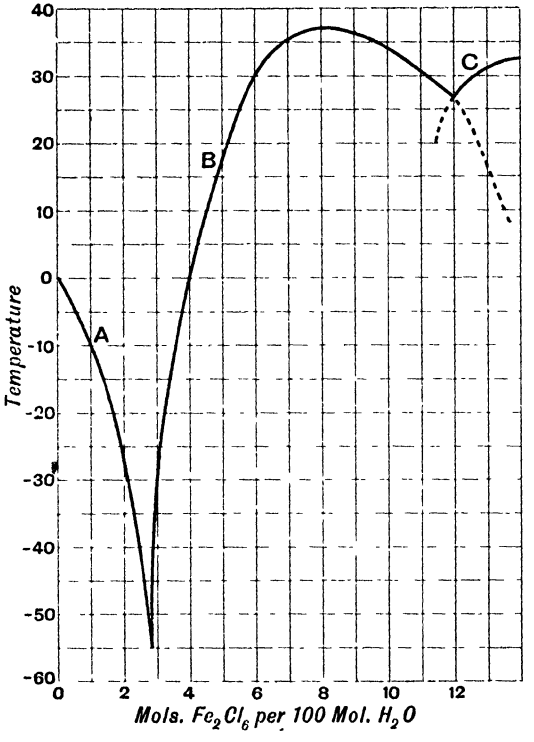


FIG. 10.

other soluble substance. It follows from this that the addition of either water or the anhydrous salt lowers the temperature at which the solid hydrate separates out, so that the melting point of the hydrate represents a point of maximum solubility. This is well shown in the case of ferric chloride,[1] Fe_2Cl_6, which forms hydrates with 12, 7, 5, and 4 molecules of water, each of which exhibits this behaviour. The complete equilibrium curve for the hydrate with $12H_2O$ and its saturated solution is shown in

[1] Roozeboom, *Zeit. physikal. Chem.*, 1892, **10**, 477. The formula Fe_2Cl_6 is chosen to obtain simple formulæ for the hydrates.

Fig. 10, in which the solubility is expressed in molecules of Fe_2Cl_6 per hundred molecules of water. Curve *A*, extending from 0° to −55°, represents the temperatures of separation of ice from solutions of increasing concentration; the lowest temperature at which the hydrate with $12H_2O$ is formed is −55°, and the solubility rapidly rises (curve *B*) until 37° is reached, at which temperature the hydrate melts. From this point, the temperature of equilibrium between the hydrate and the solution falls with increase of concentration, and this reflexed portion of the curve has been traced back as far as 8°. Below 27·4°, the equilibrium becomes metastable, since at this point the curve intersects the solubility curve (*C*) of the hydrate $Fe_2Cl_6,7H_2O$. Similar behaviour is shown also by the other hydrates of ferric chloride, by the hexahydrate of calcium chloride, and by many other analogous substances.

It is instructive to compare the solubility–temperature curves for salts which form well-defined hydrates with the freezing-point curves of binary alloys (see p. 89). The results obtained in both cases are to be interpreted in a similar manner.

68 *Double Salts.*—The conditions of formation and stability of double salts, and their behaviour towards solvents, form a subject of great importance, the development of which is due mainly to van't Hoff and Roozeboom. Only their main conclusions can be mentioned here. The formation of a double salt from two salts dissolved in water depends in the first place on the temperature of the system. In some cases the double salt can exist only below a certain temperature ($2KCl,CuCl_2,2H_2O$), in others it is formed only above a certain temperature ($Na_2SO_4,MgSO_4,4H_2O$), but in each case there is a transition temperature at which the double salt and its component single salts can exist together in the solid state in equilibrium with a saturated solution.

When equivalent amounts of hydrated sodium sulphate, $Na_2SO_4,10H_2O$, and hydrated magnesium sulphate, $MgSO_4,7H_2O$, are treated with a small quantity of water at 15°, a solution is obtained which is saturated with both substances and is in equilibrium with the solid salts. A 22°, which is the transition point for a mixture of these salts and astracanite, $Na_2SO_4,MgSO_4,4H_2O$, a certain amount of this soluble salt is formed, and there is then equilibrium between the double salt, the two single salts, and the saturated solution. As the temperature rises above 22°, the single salts gradually dissolve and

the less soluble astracanite separates out, and if the molecular solubility of the two single salts were equal, the whole of the solid would thus be converted at once into the double salt. Owing, however, to the greater solubility of magnesium sulphate, some sodium sulphate is at first left undissolved, whilst the solution contains more molecules of magnesium sulphate than of sodium sulphate. Thus at 23°, the solution contains about 1·4 mols. of magnesium sulphate to each molecule of sodium sulphate, whilst the solid present is a mixture of sodium sulphate with astracanite. This inequality finally disappears at 27°, and at this temperature solid astracanite alone is left in contact with a saturated solution containing the sulphates of sodium and magnesium in the same proportion as the solid salt. The range of temperature between 22° and 25° is termed the *transition interval*, and it is only at temperatures beyond the transition interval that a double salt is not decomposed by water. Below 22°, then, astracanite, when brought into contact with water is completely decomposed into its constituent single salts; at 22°, it exists in equilibrium with both of them; from 22° to 25°, it is decomposed with separation of sodium sulphate, and above 25° it is not decomposed by water at all.

Potassium cupric chloride, $2KCl,CuCl_2,2H_2O$, in contrast with astracanite, is stable in contact with its saturated solution at ordinary temperatures, but decomposes at 92°, the transition point, into potassium chloride and a new soluble salt, $KCl,CuCl_2$. Carnallite, $KCl,MgCl_2,6H_2O$, is completely decomposed by water at 167·8° into the chlorides of magnesium and potassium, and is partially decomposed at all temperatures below this with separation of potassium chloride, so that a pure saturated solution of carnallite in water cannot be prepared. Potash alum, on the other hand, is stable in presence of its solution at all temperatures up to 92·5°.

When the salts present are capable of undergoing chemical change, such as double decomposition, and when more than two single salts are present, the conditions of equilibrium become much more involved. Many extremely complicated cases have been examined by van't Hoff in a series of researches on the formation of the Stassfurt minerals, for an account of which the original papers must be consulted.[1]

[1] van't Hoff, *Bildung und Spaltung von Doppelsalzen. Zur Bildung der ozeanischen Salzablagerungen* (Braunschweig, 1905). See also E. F. Armstrong, *British Assoc. Reports*, 1901, 262; Findlay, *The Phase Rule*.

69 Metallic salts are, as a rule, insoluble or very sparingly soluble in organic liquids. Some liquids, however, such as alcohol, acetic acid, ether, acetone, pyridine, benzonitrile, etc., dissolve certain salts with some freedom. Thus calcium chloride, calcium nitrate, potassium iodide, and many others are soluble in alcohol, whilst mercuric chloride and zinc chloride are soluble both in alcohol and ether, and the solubility of cadmium bromide in a mixture of these two solvents has been made use of in the wet process of photography. Salts which are insoluble in alcohol are precipitated in the form of minute crystals when alcohol is added to their aqueous solutions, and this substance is therefore often used in quantitative analysis, having been first proposed for this purpose by Bergman in 1778.

70 *Supersaturated Solutions.*—When a solution of a salt free from any undissolved crystals is allowed to cool quietly in closed vessels, it is frequently observed that no crystals separate out, although the quantity of salt contained in the liquid is greater than that which can exist in solution at that temperature in contact with the solid salt. Such solutions are termed *supersaturated.* If, however, a crystal of the salt is added, a rapid crystallisation occurs, and the clear solution is then found to contain the normal amount of dissolved salt. Sodium acetate shows the phenomenon of supersaturation in a striking manner. For this purpose the crystallised salt is gently warmed in a flask with one quarter of its weight of water until all is dissolved; the liquid, if not perfectly free from suspended matter, is then filtered into a flask, the neck of which is then closed with a plug of cotton-wool. If the smallest crystal of sodium acetate is thrown into the liquid when cold, crystallisation at once commences round the small particle, and in a few seconds the whole has assumed the solid form, the change being accompanied by a considerable rise of temperature.

When a hot saturated solution of a salt is allowed to cool in the absence of the solid salt, the supersaturated solution which is produced is at first metastable (p. 124), and during this period crystallisation can be brought about only by the introduction of a crystal of the solid salt, or of one isomorphous with it. As soon as a certain temperature is reached, however, the solution becomes unstable or labile, and crystallisation then occurs spontaneously, its first appearance being much aided by stirring and friction. At each temperature, therefore, the solution remains metastable only up to a certain definite limit

of concentration, beyond which it becomes labile.[1] A curve of "supersolubility" can thus be constructed for each salt, and it is found that such a curve is, as a rule, approximately parallel to the solubility curve. The exact temperature at which the change from the metastable to the labile state occurs is best determined by observing the sudden change in the refractive index of the well-stirred solution which accompanies the separation of crystals. Thus a solution of sodium nitrate containing 48·8 per cent. of the salt becomes labile at 20°; spontaneous crystallisation then occurs, and the concentration of the solution falls to that of a saturated solution at this temperature, which contains 45·8 per cent. of the salt. A solution of the same salt containing 51·2 per cent. of salt becomes labile at 30°.

The indifference of a supersaturated solution to crystals of non-isomorphous salts can readily be shown experimentally. A supersaturated solution of sodium acetate, prepared as described above, is poured gently on to the surface of a supersaturated solution of sodium thiosulphate, made by simply melting the crystals of the hydrated salt in a long test-tube. If, after cooling, a crystal of sodium thiosulphate is dropped into the tube, it falls through the lighter solution of sodium acetate without inducing crystallisation, but causes the immediate formation of crystals as soon as it comes into the heavier solution of sodium thiosulphate. A supersaturated solution of magnesium sulphate may be made to crystallise by adding either magnesium sulphate itself, or any one of the isomorphous sulphates of iron, zinc, nickel, etc., whilst sodium sulphate, sodium chloride, etc., have no action upon it. Supersaturated solutions of sodium sulphate crystallise very readily when exposed to the air, and it has been shown that this is due to the presence of minute crystals of this salt in the atmosphere.

The amount of a solid salt required to induce crystallisation in a metastable solution is extremely small, amounting to about one ten-millionth of a milligram (10^{-10} gram) in the case of sodium chlorate.[2] Whether this minimum amount varies with the degree of supersaturation of the solution has not yet been ascertained.

[1] Miers and Isaac, *Journ. Chem. Soc.*, 1906, **89**, 413. See also Hartley, Jones, and Hutchinson, *ibid.*, 1908, **93**, 825; Jones, *ibid.*, 1908, **93**, 1739; 1909, **95**, 1672; Jones and Shah, *ibid.*, 1913, **103**, 1043.

[2] Ostwald, *Zeit. physikal. Chem.*, 1897, **22**, 289.

Fusibility and Volatility of Salts.

71 Most of the metallic salts melt at temperatures beyond the range of the ordinary mercurial thermometer, but many melting points have been determined with accuracy by means of resistance or thermo-electric pyrometers. As already mentioned (p. 65), Carnelley has shown that, in the case of the salts which the metals form with the same acid, the melting point is a periodic function of the atomic weight of the metal contained in the salt, just as is the case with the metals themselves.

The boiling point has been determined only in the case of a few halides, but the comparative volatility of certain salts was approximately ascertained by Bunsen [1] by the following method. A small bead of each salt weighing one centigram is placed in the zone of fusion of a Bunsen flame having a temperature of about 1300°, and the time ascertained which the bead takes to volatilise. The following numbers give the relative volatility for certain salts, that of sodium chloride being taken as the standard :

	NaCl	KCl	KBr	KI	K_2SO_4	K_2CO_3
Seconds.	84·2	63·4	41·0	29·8	665·2	272·0
Volatility.	1·000	1·288	2·055	2·828	0·127	0·310

It has been shown by Bailey [2] that certain salts are slightly volatile when their aqueous solutions are evaporated, even when all precautions are taken to prevent their being carried over mechanically. This phenomenon has been more closely examined in the case of the chlorides of the alkali metals, and it has been shown that the volatility increases with the molecular weight of the chloride and the concentration of the solution.

Generic Properties of Salts.

72 The generic properties of the metallic salts have in most cases been already given in Vol. I., under the respective acids. The most important points, however, are shortly recapitulated here.

Fluorides.—In their general properties the fluorides closely resemble the chlorides, but are, as a rule, much less soluble in water. Potassium, ammonium, silver, and stannous fluoride dissolve readily, the sodium and lithium salts less easily, those of the alkaline earth metals very sparingly, whilst the remainder

[1] *Phil. Mag.*, 1866, [4], **32**, 85. [2] *Journ. Chem. Soc.*, 1894, **65**, 445.

are almost insoluble. The alkali fluorides unite with hydrogen fluoride, and with the fluorides of the more electronegative elements, to form double fluorides, which usually crystallise well. Thus we have :

Potassium hydrofluoride, $KF,HF = KHF_2$
Potassium borofluoride, $KF,BF_3 = KBF_4$
Potassium silicofluoride, $2KF,SiF_4 = K_2SiF_6$
Potassium tantalofluoride, $2KF,TaF_5 = K_2TaF_7$.

Chlorides.—The greater number of the chlorides are solids, but a few, such as stannic chloride, $SnCl_4$, titanic chloride, $TiCl_4$, and antimony pentachloride, $SbCl_5$, are liquids, and these, as well as mercuric chloride, $HgCl_2$, and antimony trichloride, $SbCl_3$, may be readily volatilised. The majority melt at a fairly high temperature, and can be volatilised only at a red heat or higher temperature. A few, such as gold chloride, $AuCl_3$, and platinum chloride, $PtCl_4$, decompose into their elements when strongly heated. With the following exceptions, they dissolve readily in water : aurous chloride, AuCl, silver chloride, AgCl, mercurous chloride, Hg_2Cl_2, cuprous chloride, Cu_2Cl_2, platinous chloride, $PtCl_2$, palladious chloride, $PdCl_2$, thallous chloride, TlCl, and lead chloride, $PbCl_2$; the last two dissolve to a slight extent in cold, and readily in hot water.

In some cases the chlorides are chemically acted on by water, giving rise to basic compounds; thus, the trichlorides of bismuth and antimony yield insoluble oxychlorides :

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

Others, such as titanium chloride, are completely decomposed into hydrochloric acid and a hydroxide of the metal.

Many double chlorides are also known, similar to the double fluorides, but the tendency to the formation of the former is not so strong. The most characteristic are the *platinichlorides*, such as potassium and ammonium platinichlorides, K_2PtCl_6 and $(NH_4)_2PtCl_6$, which may be regarded as salts of the acid H_2PtCl_6.

Bromides and *Iodides* closely resemble the corresponding chlorides.

Cyanides.—These salts are classed with the halides, which they closely resemble in properties. The cyanides of the alkali and alkaline-earth metals and mercury are soluble in water; the

remainder are insoluble, but dissolve in a solution of potassium cyanide, forming double cyanides.

Some of these double cyanides are properly described as complex salts, no longer giving the reactions of the characteristic metal (other than potassium) which is present. Thus, potassium ferrocyanide and ferricyanide in neutral or acid solution do not give the reactions which are typical of ordinary ferrous and ferric salts. According to the electrolytic dissociation theory, the iron in the ferro- and ferri-cyanides is part of a complex negative ion, the reactions of which are quite different from those of the positive iron ion.

The complex formation is less stable in the case of potassium silver cyanide, $KAg(CN)_2$, obtained by the action of potassium cyanide on silver cyanide. In aqueous solution this substance appears to be dissociated mainly into the ions $\overset{+}{K}$ and $\overline{Ag(CN)_2}$, for when the solution is electrolysed the silver migrates towards the anode as part of the negative ion. A solution of potassium silver cyanide gives only a few of the ordinary reactions of silver salts: that it does so at all is probably due to the presence of a small quantity of $\overset{+}{Ag}$ ion, arising from the slight dissociation of the $\overline{Ag(CN)_2}$, ion.

Differences in the stability of double cyanides are utilised in the qualitative separation of copper and cadmium on the one hand, and of nickel and cobalt on the other.

Hypochlorites.—The salts of hypochlorous acid are almost unknown in the free state, as they are generally obtained together with chlorides by the action of chlorine on cold solutions of the hydroxides of the metals, and cannot be isolated from the solution.

Chlorates.—The chlorates are all soluble in water, that of potassium being one of the least soluble, and they all decompose on heating, giving off oxygen and leaving the chloride.

Perchlorates.—These salts are also, without exception, soluble in water, the least soluble being the potassium salt; like the salts of the other oxy-acids of chlorine, they are completely decomposed by heat into oxygen and the chloride of the metal.

Iodates and Periodates.—Several series of both iodates and periodates are known, which have already been described (Vol. I., p. 370).

Sulphides.—The compounds of the metals with sulphur correspond in general with the oxides, although there are cases in

which no sulphide is known corresponding to a particular oxide, and *vice versa*. The sulphides and hydrosulphides of the alkali metals and the hydrosulphides of metals of the alkaline earths are soluble in water; the solutions when allowed to remain in contact with free sulphur are converted into polysulphides, and are oxidised by the oxygen of the air to sulphites, thiosulphates, and sulphates. The remaining sulphides are almost all insoluble in water, some of them being dissolved by dilute acids with evolution of sulphuretted hydrogen, whilst others undergo no change under these conditions. The different solubilities of the sulphides in water and acids are utilised in the qualitative and quantitative separation of the metals.

The sulphides of the more electro-negative metals dissolve in solutions of the alkaline sulphides, forming sulpho-salts, just as the corresponding oxides unite together to form oxy-salts. Thus potassium oxide combines with arsenic oxide to form potassium arsenate, and potassium sulphide combines with arsenic sulphide to form potassium thioarsenate:

$$3H_2O + As_2O_5 = 2K_3AsO_4$$
$$3K_2S + As_2S_5 = 2K_3AsS_4.$$

Subjoined is a list of some of the analogous oxy-salts and sulpho-salts which have been prepared, in the formulæ of which M represents an atom of a monad metal.

Oxy-salts.	Sulpho-salts.
Carbonates, M_2CO_3	Thiocarbonates, M_2CS_3
Pyrophosphates, $M_4P_2O_7$	Pyrothiophosphates, $M_2P_2S_7$
Metarsenates, $MAsO_3$,	Metathioarsenates, $MAsS_3$
Orthoarsenates, M_3AsO_4	Orthothioarsenates, M_3AsS_4
Metastannates, M_2SnO_3	Metathiostannates, M_2SnS_3
Orthostannates, M_4SnO_4	Orthothiostannates, M_2SnS_4.

Similar salts are also known containing selenium and tellurium in place of sulphur.

Sulphites.—Sulphurous acid, being a dibasic acid, forms two series of salts, viz., normal and acid sulphites, such as Na_2SO_3 and $NaHSO_3$. Those of the alkali metals are soluble in water, but the remainder are for the most part sparingly soluble or insoluble, although they dissolve in a solution of sulphurous acid. They are fairly stable in the dry state, but gradually oxidise in presence of moisture, forming sulphates.

In addition to these, a series of sulphites known as the

metabisulphites or *disulphites* has been prepared, the constitution of which is probably represented by the general formula: $M—SO_2—O—SO_2—M$.

Sulphates.—With the exception of those of barium, strontium, and lead, which are almost insoluble in water, and those of calcium, silver, and mercury, which are sparingly soluble, all the sulphates dissolve readily; on evaporation, the solutions yield well-developed crystals, usually containing water of crystallisation. The metals of the alkalis form normal and acid sulphates, the metals of the alkaline earths and magnesium yield only normal sulphates, whilst many other metals form soluble normal salts, as well as more or less insoluble basic sulphates. Many sulphates possess the property of forming crystallisable double salts. This is especially the case with the sulphates of the isomorphous metals of the magnesium group, which yield compounds with the sulphates of the alkali metals having the general formula $M^{II}SO_4,M^{I}_2SO_4,6H_2O$, for instance, schönite, $MgSO_4,K_2SO_4,6H_2O$.

Another important group of the double sulphates is that of the *alums*, which have the general formula $M^{III}_2(SO_4)_3,M^{I}_2SO_4,24H_2O$; for example:

$Al_2(SO_4)_3,K_2SO_4,24H_2O$,	$Fe_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$,
$Cr_2(SO_4)_3,K_2SO_4,24H_2O$,	$Al_2(SO_4)_3,Na_2SO_4,24H_2O$,
$Al_2(SO_4)_3,Ag_2SO_4,24H_2O$,	$In_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$.

Nitrides.—Many of the metals such as magnesium, calcium, vanadium, titanium, and lithium, unite with nitrogen when strongly heated in the gas, forming stable nitrides, but in other cases these compounds can be obtained only indirectly by the action of ammonia on the heated oxides or chlorides. They are usually dull brown or black powders, the composition of which has in many cases not been accurately determined, and a number of them are undoubtedly mixtures.

The salts of azoimide (Vol. I., p. 521) form a special class of nitrides which contain the group $.N\begin{matrix}N\\ \|\\ N\end{matrix}$; these are all extremely explosive substances.

Nitrites.—These salts are for the most part soluble in water, and are decomposed when strongly heated into oxides of nitrogen and the oxide of the metal. Dilute mineral acids decompose nitrites, yielding nitric oxide.

Nitrates.—With the exception of one or two basic nitrates, such as that of bismuth, all the nitrates dissolve in water, and usually crystallise well. They melt at low temperatures, and on further heating those of the alkali and alkaline earth metals are converted, first into nitrites with evolution of oxygen, and then into oxides of nitrogen and the oxide of the metal; with the nitrates of the other metals the intermediate formation of nitrite is not usually observed, and in cases where the oxide is unstable at high temperatures the metal itself remains as the final product. Owing to the ease with which they lose oxygen, the nitrates are often used as oxidising agents.

Phosphides.—Most of the metals combine with phosphorus to form phosphides. Some of these, for example, the phosphides of iron and zinc, are crystalline, but a large number have been obtained only as difficultly fusible masses, which have not as yet been closely examined, and are probably far from pure. Those of the alkali and alkaline earth metals are decomposed by water with formation of hydrogen phosphides.

Hypophosphites, Phosphites, Phosphates, Arsenites, and Arsenates.—For the relations between the different modifications of the corresponding acids, and the general properties of their salts, see Vol. I., pp. 651–674, 699–707.

Carbides.—Most of the metals combine with carbon when either they or the oxides are heated together with carbon to a very high temperature in an electric furnace. Those of the alkali and alkaline-earth metals are decomposed by water with formation of the hydroxide and evolution of acetylene, whilst that of aluminium yields methane in place of acetylene. Many of the other carbides crystallise well. The most important are those of iron; they are always present in commercial iron and exert an immense influence on its properties.

Carbonates.—Most of the metals form salts with carbonic acid, the monovalent alkali metals yielding normal and acid salts of the general formulæ M_2CO_3 and $MHCO_3$; a few metals, such as aluminium, do not appear to form carbonates; others, such as magnesium, bismuth, and copper, yield basic carbonates.

With the exception of the carbonates of the alkali metals and of thallium, all the carbonates are insoluble in water, but many of them dissolve in water containing carbonic acid, probably owing to the formation of an unstable acid carbonate. They are decomposed by heat with evolution of carbon dioxide and formation of the oxide of the metal, unless this is itself

decomposed at the temperature employed. The temperature at which the decomposition takes place varies considerably: thus, the carbonates of the alkali metals are only slightly decomposed at a bright red heat, whilst those of the alkaline earth metals are completely decomposed at this temperature, if the carbon dioxide is removed as it is formed; the other carbonates decompose for the most part at a lower temperature.

Borates and Silicates.—These salts have already been discussed (Vol. I., pp. 736–738; 930-933.)

CHEMICAL CHANGE AND THE LAW OF MASS ACTION.

73 *Reversible or Balanced Reactions.*—The older chemists thought that substances combined with one another only when they possessed a common principle, and hence they gave the name of "affinity" (*affinis*, related) to the particular property in virtue of which substances unite. It was afterwards seen that substances which have nothing in common nevertheless react with one another chemically, and this was ascribed to a mutual attraction between the particles of the substances (Newton). It was thought, moreover, that this attraction was elective in its character, so that when the particles of three substances were all brought together, those two would combine between which there was the strongest attraction, to the exclusion of the third. Thus, if a substance A, capable of uniting with C, were presented to a compound BC, made up of two substances united together, no change would occur if the attraction of C for B were stronger than that of C for A; whilst, if the opposite were the case, C would unite with A, and leave B in the free state. This view was supported especially by Geoffroy (1718) and Bergman (1775), who drew up tables of affinity or attraction, showing the order of strength of the affinities of the various bases, metals, etc., for the acids and other substances with which they were capable of combining. The true state of affairs was, however, first recognised by Berthollet, who demonstrated by a series of experiments that the course of a reaction does not depend solely on the affinities of the substances concerned, but also on the relative quantities of them which are present. Thus, according to the view held by Berthollet, it follows that "in opposing the body A to the combination BC, the combination AC can never

take place; but that the body C will be divided between the bodies A and B proportionally to the affinity and the quantity of each." [1] These views were afterwards developed by Berthollet in his celebrated *Essai de Statique Chimique.*

The further progress of investigation in this department of chemistry [2] has confirmed the opinions expressed by Berthollet. When careful experiments are made it is frequently found that a reaction does not proceed until one or other of the substances concerned has entirely disappeared, but that a certain fraction of the original substances remains unaltered. In those cases where a complete reaction appears to occur, equilibrium is reached only when an exceedingly small proportion of the substances originally concerned is left unchanged.

Thus, when calcium carbonate is heated in a closed vessel it evolves carbon dioxide until a certain pressure of this gas is reached, after which no further change in composition occurs until the conditions are in some way altered. If the temperature is raised, more carbon dioxide is evolved, until another definite pressure, higher than the previous one, is attained, after which the system again undergoes no further change so long as the circumstances remain unaltered. It is, moreover, found that to every temperature there is a corresponding equilibrium pressure of carbon dioxide, which is perfectly definite and constant. The increase of the equilibrium pressure with rising temperature is shown by the following figures: [3]

Temperature.	Pressure.
547°	27 mm. of mercury.
610	46 „ „
740	255 „ „
810	678 „ „
865	1333 „ „

If, on the other hand, the temperature is kept constant, but the pressure of the carbon dioxide is lowered by pumping out some of the gas, an additional quantity of the calcium carbonate decomposes until the original pressure is again attained. In order to decompose calcium carbonate completely by heat it is

[1] *Researches into the Laws of Chemical Affinity*, p. 6 (English translation, London, 1804).

[2] A fuller account of this subject will be found in Lothar Meyer, *Modern Theories of Chemistry*; Nernst, *Theoretical Chemistry*; Ostwald, *Allgemeine Chemie*, vol. ii.; Mellor, *Chemical Statics and Dynamics* (Longmans, 1904); Lewis, *A System of Physical Chemistry.*

[3] Le Chatelier, *Compt. rend.*, 1886, **102**, 1243.

therefore necessary to keep the pressure of the carbon dioxide as low as possible. This is effected by heating the carbonate in a current of air freed from carbon dioxide, or, more usually, in the open air; in this latter case the pressure of carbon dioxide is negligibly small, and hence in the ordinary form of the experiment, *e.g.*, the "burning" of limestone, the decomposition is practically complete. The reactions on which Brin's process for the manufacture of oxygen (Vol. I., p. 246) is based furnish another illustration of the extent to which the decomposition of a compound may be influenced by the pressure of one of the products of decomposition.

Many reactions, then, are not complete, but proceed only until a certain definite state of equilibrium is set up. This state of equilibrium is quite analogous to what occurs in many physical phenomena. Thus, when water or any liquid evaporates in a confined space, the evaporation proceeds only until the vapour of the liquid exerts a certain definite pressure on the surface of the liquid; this equilibrium pressure is constant for any particular temperature, and increases rapidly as the temperature rises. When the condition of equilibrium has been attained, the relative amounts of vapour and liquid are unaltered so long as the other conditions remain the same. The maintenance of this state of equilibrium depends upon the fact that the evaporation of the liquid is proceeding at exactly the same rate as the condensation of the vapour, so that the actual proportion of vapour to liquid remains the same.

Precisely the same considerations hold with regard to chemical equilibrium. Thus, recurring to the example of calcium carbonate, when equilibrium is set up at any particular temperature, the calcium carbonate is being decomposed into lime and carbon dioxide at exactly the same rate as these two compounds are combining to form calcium carbonate.

All simple chemical equilibria may be similarly regarded as resolvable into two reactions proceeding in opposite senses and at equal rates, so that the actual proportions of the substances present undergo no change. Chemical changes of this kind, which can proceed in either sense according to the circumstances of the experiment and which finally reach a definite position of equilibrium are known as *reversible* or *balanced reactions*, and are often indicated symbolically by a special sign placed between the two parts of the equation:

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

As already suggested, it is probable that all chemical changes really belong to the class of reversible reactions, although in a great many cases the position of equilibrium lies very much at one extreme, and the reversibility cannot be realised in practice.

74 *Velocity of Reaction.*—We have conceived the equilibrium reached in a reversible reaction as a dynamic one, depending on the equal and opposite effects of two opposing reactions; it is therefore of great importance to ascertain what conditions determine the velocity of a reaction. The attainment of equilibrium takes time, although in many cases the reaction proceeds so rapidly that this time cannot be measured; thus, when hydrochloric acid is added to caustic soda solution, when silver nitrate is added to solution of sodium chloride, and in many similar instances, the reaction appears to be complete as soon as the substances have been brought into contact, and no measurement of the rate of the reaction is possible. When, however, the reaction proceeds slowly, such measurements can be made, and it is thus possible to ascertain the influence of various factors on the velocity of the change.

The most important result of the experiments which have been made on this subject is the generalisation known as the *law of mass action*, which states that the velocity of any reaction is directly proportional to the concentrations (or active masses) of the substances concerned. This law follows from the investigations of Wilhelmy (1850), Harcourt and Esson (1866), Guldberg and Waage (1867), van't Hoff, and others.[1]

The law may be definitely formulated in the following way. Let us suppose that we are dealing with the reversible reaction $A + B \rightleftarrows C + D$, and that the concentrations of the four substances involved are, at the moment, p, q, p', and q' respectively. If v is the velocity of the forward reaction, *i.e.*, the rate at which A and B unite to form C and D, then, according to the law of mass action, $v = k.pq$, where k is the so-called velocity coefficient, and has a definite value for a given reaction at a constant temperature. Similarly, if v' is the velocity of the back reaction, *i.e.*, the rate at which C and D are uniting to form A and B, we have $v' = k'.p'q'$, k' al eing a velocity coefficient. The velocity of the resultant re. n, which alone can be measured by experiment, will then be $v - v' = k.pq - k'.p'q'$. If the reaction is one in which the position of equilibrium

[1] For a fuller account of the Law of Mass Action, see Lewis; *A System of Physical Chemistry.*

lies at the right hand extreme, *i.e.*, if the change proceeds until either A or B has practically disappeared, then the back reaction may be neglected, and the velocity of the reaction as a whole is given by the formula : $v = k.pq$.

The experiments of Harcourt and Esson [1] may be cited as an instance of the results obtained in studying the applicability of the law of mass action. They were carried out by allowing potassium permanganate to act on oxalic acid dissolved in water in presence of manganese sulphate, which is necessary to the reaction, and sulphuric acid. The amounts of the various substances present could all be varied, and the reaction was very thoroughly investigated. The amount of unaltered potassium permanganate present in the solution at any moment was determined by adding an excess of potassium iodide solution and estimating the iodine liberated.

The simplest case of this reaction occurs when the oxalic acid is in large excess, as in these circumstances the change of concentration of this substance may be neglected. It is then found that under these conditions the rate at which the potassium permanganate is disappearing at any moment is proportional to the amount still left unreduced. This may be expressed more simply by saying that the same fraction of the permanganate still present in the solution is reduced in each successive equal interval of time. In the following table the experimental figures obtained with a mixture of the molecular composition $2KMnO_4 + 14MnSO_4 + 108C_2H_2O_4$ are compared with those calculated on the assumption that the law of mass action holds for this particular change; as will be seen, the agreement is excellent :

Time.	Amount of Permanganate left in the solution.	
	Observed.	Calculated.
2	94·8	94·8
5	87·9	87·6
11	74·9	74·7
27	49·3	48·9
35	39·1	39·6
47	28·3	28·8
68	17·0	16·5

In reactions in which the concentrations of two substances are

[1] *Phil. Trans.*, 1866, **156**, 193.

both altering at the same time, such as the saponification of ethyl acetate by caustic soda,

$$C_2H_3O_2 \cdot C_2H_5 + NaOH = C_2H_5 \cdot OH + NaC_2H_3O_2,$$

the matter is more complicated, since the rate of the reaction at any moment is now proportional to the product of the active masses of the two substances at that moment. Here again, however, the observed numbers agree well with those obtained by calculation from the law of mass action. In many cases, especially when solutions of weak acids or bases are concerned, the active mass is not that of the total substance present, only that portion of the substance which is electrolytically dissociated taking an active part in the change. Thus, when an equivalent amount of ammonia, which is dissociated to a much smaller extent than caustic soda, is substituted for the latter in the above reaction, the rate of saponification becomes much slower, and is still further diminished by the addition of any substance, such as an ammonium salt, which lessens the dissociation of the ammonia.

Rise of temperature has a very marked effect on the rate of chemical change, and, on the average, the velocity of reaction is trebled for a rise of 10°. The very high value of the temperature coefficient of reaction velocity makes it intelligible that substances which, at certain temperatures, react rapidly and reach a position of equilibrium, have yet no apparent action on each other at much lower temperatures. Thus, a mixture of hydrogen and oxgyen, which cannot be in true equilibrium, can be kept for any length of time at the ordinary temperature without an appreciable quantity of water being produced.

The accurate investigation of reaction velocities has been of great service in the study of catalytic action. The value of the velocity coefficient obtained for a catalytically accelerated reaction is a measure of the efficiency of the catalytic agent. Thus, by comparing the values obtained for the velocity coefficient in different experiments, one can ascertain how the efficiency of a catalytic agent is affected by the conditions under which it works, and how the efficiency of one catalytic agent compares with that of another under the same conditions.[1]

75 *Chemical Equilibrium.*[2]—The velocity with which a revers-

[1] For a short account of the study of catalysis on these lines, see the article on "Chemical Affinity," in Thorpe's *Dictionary of Applied Chemistry*; also Rideal, *Catalysis in Theory and Practice.*

[2] For a more detailed account, see Lewis, *loc. cit.*

ible reaction approaches its point of equilibrium is, as already shown (p. 140), given by the formula :—

$$v - v' = k.pq - k'.p'q'.$$

When equilibrium is reached, $v - v' = 0$, and therefore, $k.pq = k'.p'q'$, or $\frac{k}{k'} = \frac{p'q'}{pq}$, where p, q, p', q', are now the concentions of A, B, C, and D respectively at the point of equilibrium. The ratio $\frac{k}{k'} = \mathrm{K}$ is known as the *equilibrium constant*, and can be determined experimentally by ascertaining the amounts of the various substances which are actually present when equilibrium is established.

Thus, when alcohol is mixed with acetid acid, the following reaction occurs :

$$\mathrm{C_2H_5.OH + C_2H_4O_2 \rightleftharpoons C_2H_5O.C_2H_3O + H_2O.}$$

If known quantities of acid and alcohol are taken, the amount of change which has occurred during any period can readily be measured by titrating the acid still present, and subtracting the amount thus found from that originally taken. The quantities of alcohol, ethyl acetate, and water present can then all be calculated from this number by means of the equation representing the reaction. If equivalent amounts of acid and alcohol are taken, it is found when equilibrium is established, a process which requires several days at the ordinary temperature, that $\frac{2}{3}$ of the alcohol and acetic acid have undergone the reaction, whilst $\frac{1}{3}$ of each is left unaltered. Exactly the same state of equilibrium is reached if equivalent amounts of ethyl acetate and water are allowed to react. In this condition, therefore, $pq = \frac{1}{3} \times \frac{1}{3} = \frac{1}{9}$, whilst $p'q' = \frac{2}{3} \times \frac{2}{3} = \frac{4}{9}$, so that

$$\mathrm{K} = \frac{p'q'}{pq} = 4.$$

When the value of the equilibrium constant has once been determined, it is possible to calculate the composition of the equilibrium mixture when the reacting substances are taken in other than equivalent proportions. Thus, if a molecules of alcohol and b molecules of acetic acid are taken in the above instance, and if x is the number of molecules of ester present in the equilibrium mixture, then

$$p = a - x,\ q = b - x,\ p' = q' = x.$$

By substituting these values in the equation given above, the value of x can be obtained. The numbers calculated in this way agree well with those obtained by experiment.

It is found experimentally, in harmony with the formula for the equilibrium constant, that if a large excess of alcohol is taken, practically the whole of the acetic acid is converted into ethyl acetate, whilst if a large excess of acid is taken almost the whole of the alcohol undergoes the reaction. These facts have an important bearing upon the reactions used in analytical processes. In these cases it is essential that equilibrium be not established until practically the whole of the substance which is being estimated has undergone the particular reaction. In the processes of gravimetric analysis the substance which is being analysed, or some one of its elements, is converted into a sparingly soluble compound. In this way the product which is precipitated is continually withdrawn from the solution, the equilibrium is thereby disturbed, and fresh quantities of the substance are formed and precipitated, the reaction thus proceeding until it is practically complete. This effect is further aided in most cases by the use of an excess of the reagent, which, as we have just seen, tends to increase the extent to which the other substance undergoes the reaction. In the processes of volumetric analysis it is also necessary to choose reactions for which the equilibrium constant is very high, and which, moreover, proceed rapidly. Thus, the reaction between equivalent quantities of caustic soda and hydrochloric acid can be utilised for estimating the amount of the former present, because the reaction proceeds rapidly, and equilibrium is established only when practically the whole of the acid and alkali present have reacted. The completion of the reaction is therefore indicated by the fact that the solution becomes neutral. On the other hand, it is impossible to estimate alcohol by titration with hydrochloric acid, because the constant of equilibrium for this reaction is low (8·44 at 99° [1]), and equilibrium is attained long before the whole of the alcohol has been converted into ethyl chloride, and therefore before the solution has become neutral, so that it is impossible to ascertain by the aid of an indicator when an equivalent of the acid has been added.

Many cases of chemical equilibrium have been experimentally studied on the lines indicated above. Special mention may be made of the investigation of the following reactions, some of

[1] Cain, *Zeit. physikal. Chem.*, 1893, **12**, 751.

which are of technical importance:—$CO_2 + H_2 \rightleftharpoons CO + H_2O$[1] $2SO_2 + O_2 \rightleftharpoons 2SO_3$[2]; $4HCl + O_2 \rightleftharpoons 2Cl_2 + 2H_2O$[3]; $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$[4].

The study of gaseous dissociations from the point of view of the law of mass action presents many interesting features. When a gas is decomposed by heat into several new molecules, which may either be all of the same kind, as in the case of nitrogen peroxide, N_2O_4, or of different kinds, as in the case of phosphorus pentachloride, and these reunite to form the original gas when the whole is allowed to cool, the gas is said to dissociate when heated. In the case of such a partly dissociated vapour the quantities of the several gases present are proportional to their partial pressures in the mixture. Thus, if p be the pressure due to the undissociated molecules, and p_1 that of each of the two new gases formed, the equation of equilibrium becomes

$$K = \frac{p_1^2}{p}.$$

If now the pressure of one of the products of dissociation is increased by adding some of it to the mixture without altering the volume, it follows that the numerator of this fraction must increase, and that therefore, since K must remain constant, p must also increase. In other words, the dissociation of the gas must be diminished. This result has been experimentally verified in many cases. Thus when phosphorus pentachloride is vaporised, it dissociates partially into phosphorus trichloride and chlorine:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2.$$

When, however, the pressure of either the phosphorus trichloride vapour or the chlorine is increased, the dissociation of the gas is diminished, and the vapour density is increased. The same is true for ammonium chloride; dissociation is diminished in presence of ammonia or hydrogen chloride.

A similar phenomenon occurs in solutions of electrolytes; when two substances having a common ion are present in a solution, neither is electrolytically dissociated to as great an extent as it would be were the other substance absent.

[1] Hahn, *Zeit. physikal. Chem.*, 1903, **44**, 513.

[2] Bodenstein and Pohl, *Zeit. Elektrochem.*, 1905, **11**, 373.

[3] von Falckenstein, *Zeit. physikal. Chem.*, 1907, **49**, 313; 1909, **65**, 371.

[4] Deville, *Compt. rend.*, 1870, **70**, 1105, 1201; **71**, 30; Preuner, *Zeit. physikal. Chem.*, 1904, **47**, 385.

The effect of temperature and pressure on chemical equilibrium has also been carefully studied for many partially dissociated gases. The particular state of equilibrium attained by any system of reacting substances depends on the physical conditions to which the system is subjected, but the extent by which the state of equilibrium is altered by change of temperature and pressure varies very largely according to the nature of the special reaction concerned. It may be taken as a general law that rise of temperature tends to produce such a change in the equilibrium of the system as is attended by an absorption of heat, whilst a lowering of the temperature has an effect in the opposite direction. Thus, when a gas such as nitrogen peroxide, N_2O_4, is heated to a definite temperature it decomposes to a perfectly definite extent into molecules of the simpler gas, NO_2, a change which is accompanied by absorption of heat. If now the temperature is raised, the effect is to increase the dissociation of the gas in harmony with the general law just enunciated. If a reaction proceeds without much evolution or absorption of heat, the effect of change of temperature on the position of equilibrium is correspondingly small: an instance of this is furnished by the reaction between ethyl alcohol and acetic acid.

The effect of a rise of temperature on a chemical reaction is therefore of two kinds. In the first place, it increases the velocity of the reaction, and, in the second place, it alters the final state of equilibrium which is attained. This is well illustrated in the case of hydrogen and iodine, which has been very thoroughly investigated by Lemoine[1] and Bodenstein.[2] When these two elements are heated together at 290°, several weeks are required for the establishment of equilibrium, in which condition 16·37 per cent. of the total hydrogen is present in the free state; at 448°, on the other hand, the state of equilibrium is reached in a few hours, 23·63 per cent. of the total hydrogen being free.

The exact extent to which the position of equilibrium is shifted by altering the temperature is given by the formula:— $\frac{d(\log_e K)}{dT} = -\frac{q}{RT^2}$, where K is the equilibrium constant of the reaction at the absolute temperature T, R is the gas constant, and q is the heat evolved when the reaction goes completely from left to right. The applicability of this formula has been

[1] *Ann. Chim. Phys.*, 1877, [5], **12**, 145.
[2] *Zeit. physikal. Chem.*, 1896, **13**, 56.

tested, for instance, in connection with the equilibrium between sulphur trioxide, sulphur dioxide, and oxygen.[1]

Increase of pressure produces such a change in the position of equilibrium as is attended by a diminution of volume. Thus, when the external pressure on such a gas as nitrogen peroxide is increased, whilst the temperature is maintained constant, the dissociation of the gas is diminished, the combination of the NO_2 molecules being accompanied by a diminution of volume:

$$2NO_2 = N_2O_4.$$

This is shown by the following numbers obtained by E. and L. Natanson [2] at a temperature of 49·7° :—

Pressure.	Vapour density.
26·80 mm.	1·663
93·75	1·788
182·69	1·894
261·37	1·993
497·75	2·144

On the other hand, increase of pressure produces no change in the dissociation equilibrium of hydrogen iodide, the decomposition of this substance being unattended by any change in the number of molecules:

$$2HI \rightleftharpoons H_2 + I_2.$$

[1] Bodenstein and Pohl, *Zeit. Elektrochem*, 1905, **11**, 373.

[2] *Ann. Phys. Chem.*, 1885, **24**, 454; 1886, **27**, 656.

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SPECTRUM ANALYSIS.

76 The following pages contain a short statement of the principles of spectrum analysis, and of the application of these principles to the detection of certain elementary and compound bodies. A complete treatise on spectrum analysis would be out of place; for the subject has not only outgrown the space which can be assigned to it in a work like the present, but much diversity of opinion is still expressed on various important points, and a discussion of these views cannot be attempted here.[1]

Although the spectroscope has been employed for chemical investigations only since the year 1860, it has been the means of effecting some of the most striking discoveries of modern times. By its help the chemist is able to investigate the composition of terrestrial matter with a degree of exactitude previously undreamt of, and the discovery of the following new elementary bodies, as well as of many members of the group of rare earths, indicates the importance of the spectroscope in chemical analysis:

Cæsium and Rubidium, by Kirchhoff and Bunsen.
Thallium, by Crookes.
Indium, by Reich and Richter.
Gallium, by Lecoq de Boisbaudran.
Helium, by Ramsay.

In addition to this, the application of the methods of spectrum analysis to the investigation of the nature of the light emitted by the heavenly bodies has opened out a completely new field of research, and has laid the foundations of a new science, that of *Celestial Chemistry*. Such has been the progress made in this direction that not only are we now assured of the existence of many of our well-known terrestrial metals in the

[1] See Kayser, *Handbuch der Spectroscopie* (Hirzel, Leipzig, 1900–1912); Baly, *Spectroscopy* (Longmans); Watts, *Introduction to the Study of Spectrum Analysis* (Longmans).

atmospheres of the sun and the fixed stars, but we have gained a knowledge of the physical condition of our luminary such as we formerly could not have thought possible, and have even been able to form a definite opinion concerning the physical and chemical constitution of the nebulæ and stars.

Moreover, it appears that the study of the spectrum is capable of leading to most interesting and important conclusions respecting the structure of the molecule, both at ordinary temperatures and at the highest of which we have any knowledge. It seems probable also that spectrum observations will prove of great assistance in our endeavours to ascertain the structure of the atom and to trace the changes involved in its disintegration.[1]

77 The principles upon which spectrum analysis is founded are simple enough. When any solid or liquid bodies are gradually heated they will all be seen to become luminous at some temperature. If the light which these bodies emit, when they begin to glow or become luminous, is examined by means of a prism and suitable optical arrangements, the rays of least refrangibility, viz., the red rays, are seen first, and, as the temperature rises, light of greater refrangibility is gradually emitted, until at last the body gives off blue or violet rays. When this point is reached the substance appears to the naked eye to be white-hot, as all the differently coloured rays, when brought together on the retina, produce the effect which we term white light. It is thus clear that the spectrum of every incandescent solid or liquid is the same, a bright continuous coloured band, the rays of which extend without a break through all the colours of the rainbow from red to violet.

With gases glowing at a high temperature, however, the case is quite different. The light which these bodies emit does not consist of light of all degrees of refrangibility. The spectrum of a glowing gas, instead of being continuous, is more or less broken up. Incandescent gases emit only rays of definite degrees of refrangibility, and their spectra consist, therefore, of bright lines, the position of which undergoes no change when the temperature is raised. Thus the vapour of sodium when incandescent emits a yellow light, and its spectrum consists of a double yellow line having wave-lengths of 5896 and 5890 ten-millionths of a millimetre, and being coincident with the dark lines in the solar spectrum termed by Fraunhofer the D lines. These two bright sodium lines do not alter their position when the temperature

[1] See Sommerfeld, *Atombau und Spektrallinien*, 2nd edition, 1921.

of the vapour is raised; sodium vapour, as soon as it becomes luminous, glows with a yellow light, and by no rise of temperature can it be made white-hot. The peculiar colour of incandescent sodium vapour is best seen by fusing a small bead of sodium chloride on to the end of a fine platinum wire, and placing it in the non-luminous gas-flame. The salt volatilises, and the flame is coloured intensely yellow (Fig. 11).

78 Melville, in 1752, was the first to notice this yellow sodium flame, but he was unacquainted with its cause. In the year 1822, Brewster introduced his monochromatic lamp, the first idea being, however, due to Melville. In this same year John

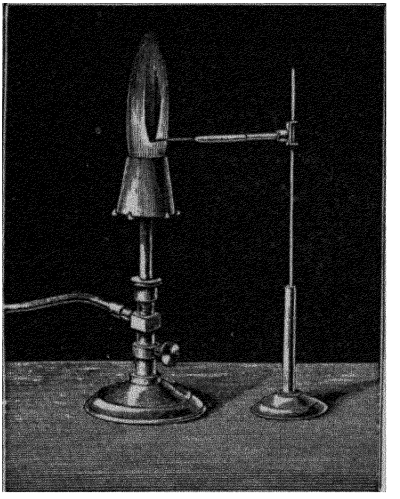


Fig. 11.

Herschel investigated the spectra of many coloured flames, especially those obtained from the chlorides of copper and strontium, as well as from boracic acid, and in 1827 he writes concerning these observations—"the colour thus contributed by different objects to flame affords in many cases a ready and neat way of detecting extremely minute quantities of them." Again, Fox Talbot writes as follows in 1826:—"The red fire of the theatres gave a most beautiful spectrum, with many lines or maxima of light. In the red these lines were more numerous and crowded, with dark spaces between them, besides an exterior ray greatly separated from the rest, and probably due to the nitre in the composition. In the orange was one bright line, one in the yellow, three in the green, and several that were fainter."

The extreme delicacy of the sodium reaction, and the universal distribution of this element, were facts unknown to Talbot, and he consequently attributes the yellow line first to sulphur, and afterwards to the presence of water. He adds, "if this opinion"—as to the cause of the production of the lines—"should prove correct, and applicable to the other definite rays, a glance at the prismatic spectrum of a flame might show it to contain substances which it would otherwise require a laborious chemical analysis to detect." In 1834 Talbot again writes:—"Lithia and strontia are two bodies characterised by the fine red tint which they communicate to the flame. Now it is very difficult to distinguish the lithia-red from the strontia-red by the naked eye, but the prism betrays between them the most marked distinction which can be imagined. The strontia flame exhibits a great number of red rays well separated from each other by dark intervals, not to mention an orange and a very definite bright blue ray. The lithia exhibits one single red ray. Hence I hesitate not to say that optical analysis can distinguish the portions of these two substances from each other with as much certainty as, if not more than, any known method."

In the year 1845 Wm. Allen Miller published the results of experiments on the spectra of coloured flames, together with drawings, but owing to the fact that in these researches a luminous flame was made use of, the representations of the several spectra are wanting in clearness and individuality. Swan was the first to point out that the bright yellow line coincident with Fraunhofer's D, which was seen in every flame, is caused by the presence of sodium salts, and it is to him that we are indebted for the discovery of the extreme delicacy of the sodium reaction, and for the proof of the universal distribution of this element.

The earliest observations of the spectra of the metals which cannot be volatilised at the temperature of the non-luminous gas-flame were made in 1835 by Wheatstone. He allowed electric sparks to pass between poles of different metals, and found that the spectra of the sparks thus obtained were dissimilar. From this he concluded that the electric spark resulted from the volatilisation of the metal of the poles. "These differences," he says, "are so obvious that one metal may easily be distinguished from another by the appearance of its spark; and we here have a mode of discriminating metallic bodies more readily than that of chemical examination, and which may hereafter be employed for useful purposes."

In 1855 Ångström thoroughly investigated the nature of the electric spark, proving the important fact that the spark yields two superimposed spectra; one derived from the metal of the pole, and the other from the gas or air through which the spark passes.

The results obtained by the above-mentioned observers were, however, but little known, and the method was never applied to the solutions of problems in analytical chemistry, until the year 1860, when Bunsen and Kirchhoff began their classical researches. It is to these two philosophers that we must in truth ascribe the discovery of the spectroscopic method, for they were the first to bring to bear upon this subject the sound principles of modern research, and to establish it upon the firm

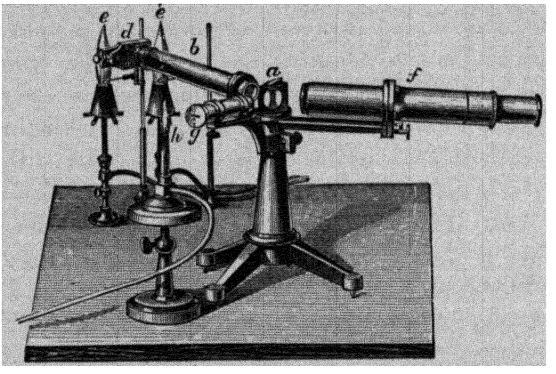


FIG. 12.

foundation of exact experiment.[1] Their labours soon met with reward. A new alkali metal (cæsium) was discovered almost immediately,[2] and the presence of various well-known metals in the solar atmosphere was at the same time ascertained beyond doubt.[3]

79 *Construction and Use of the Spectroscope.*—The construction and arrangement of the spectroscope best suited to ordinary chemical purposes is shown in Fig. 12. This instrument consists of a prism (*a*) fixed upon a firm iron stand, and a tube (*b*) called a collimator, carrying the slit (*d*), seen on an enlarged scale in Fig. 14. Through this slit the rays from the coloured flame which is being examined (*e*) fall upon the prism, being rendered

[1] Kirchhoff and Bunsen, "Chemical Analysis by Spectrum Observations," *Phil. Mag*, [4], 1860, **20**, 89; 1861, **22**, 329, 498.

[2] *Berlin Akad. Ber.*, May 10, 1860; *Chem. News*, 1861, **3**, 132.

[3] *Berlin Akad. Ber.*, Oct. 27, 1859; *Phil. Mag.*, 1860, [4], **19**, 193.

parallel by passing through a lens placed at the other end of the tube. The light, having been refracted by the prism (*a*), is received by the telescope (*f*), and the image is magnified before reaching the eye. The small luminous gas-flame (*h*,

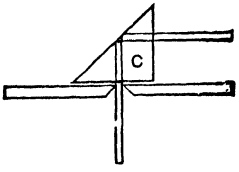


FIG. 13.

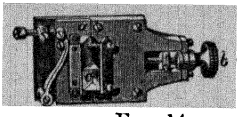


FIG. 14.

Fig. 12) is placed so as to illuminate a fixed scale contained inside the tube (*g*); this is reflected from the surface of the prism (*a*) into the telescope, and serves as a means of determining the position of the lines.

If, as is often the case, it is desired to observe two spectra

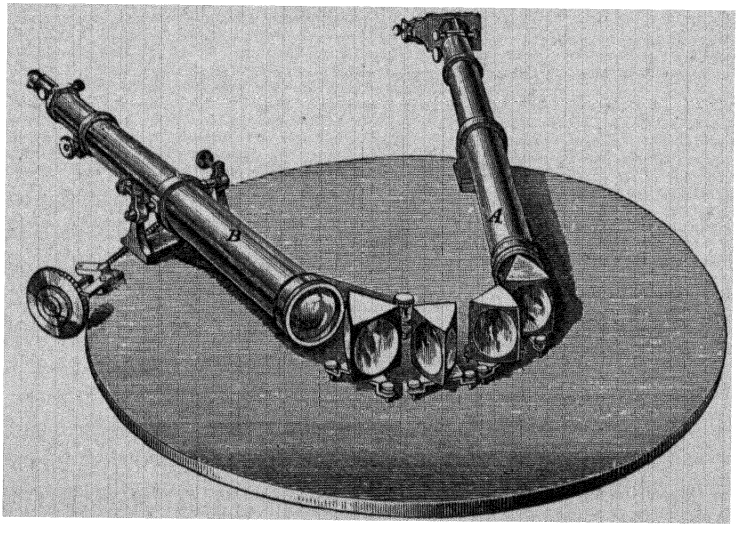


FIG. 15.

simultaneously, so as to compare the position of the lines, this is effected by placing a small prism (*c*, Figs. 13 and 14) over one half of the slit. The rays from a second source of light (*e'*, Fig. 12) may thus be brought into the collimator by internal reflection, so that of the two spectra produced, one occupies the upper half, and the other the lower half of the field of view.

In spectroscopes adapted for more accurate measurements, the

illuminated scale is discarded, and the telescope is made to move along a divided circle, by means of which the angular dispersion of the various lines may be measured.

Greater dispersion and separation of the lines is attained by the use of a series of prisms instead of a single prism (Fig. 15), which is a representation of the form of instrument used by Kirchhoff in his classical researches on the chemical composition of the solar atmosphere. In such instruments the intensity of the light is much weakened, and they can therefore be used with advantage only when the source of light is of considerable intensity.

Greater accuracy in definition and wider dispersion are attained by the substitution of a diffraction grating, either plane or concave, for the prism, and such gratings, which usually contain from 5,000 to 20,000 lines per inch, are always employed for the most accurate work, when the source of light is of sufficient intensity.

METHODS OF PRODUCING EMISSION SPECTRA.

80 In order to obtain the peculiar spectrum of a chemical substance it is necessary to examine the light which the substance emits in a state of glowing gas. The method employed for this purpose differs according as the substance is solid, liquid, or gaseous.

Flame-spectra.—Slightly volatile substances, such as the salts of the metals of the alkalis and alkaline earths, may be placed upon a fine platinum wire, and this is then brought into the non-luminous Bunsen flame. The salts there volatilise, the flame assumes a characteristic colour, and this coloured flame when examined by the spectroscope, exhibits the peculiar spectrum of the given substance. Apparatus specially adapted for the continuous introduction of salts into the Bunsen flame has been described by Beckmann.[1]

Many substances which yield no bright line spectra in the Bunsen flame do so in the oxy-hydrogen flame.

Arc- and Spark-spectra.—When the substance is non-volatile at the temperature of the non-luminous flame, as is the case with most metals, and requires a much higher temperature to convert

[1] *Zeit. physikal. Chem.*, 1907, **57**, 641.

it into gas, either a powerful electric spark or the electric arc must be employed. The arrangement used for obtaining the spectra of metals by means of the electric spark is seen in Fig. 16. It is only necessary to allow a powerful and bright spark to pass between poles made of the metal in question to obtain the characteristic bright-line spectrum of the metal, although it is to be remembered that the bright lines of the gases through which the spark passes (the air lines) will likewise be observed.

Another method of examining spark-spectra with especial regard to the easy chemical detection of the difficultly volatile metals was proposed by Bunsen.[1] The spark passes between

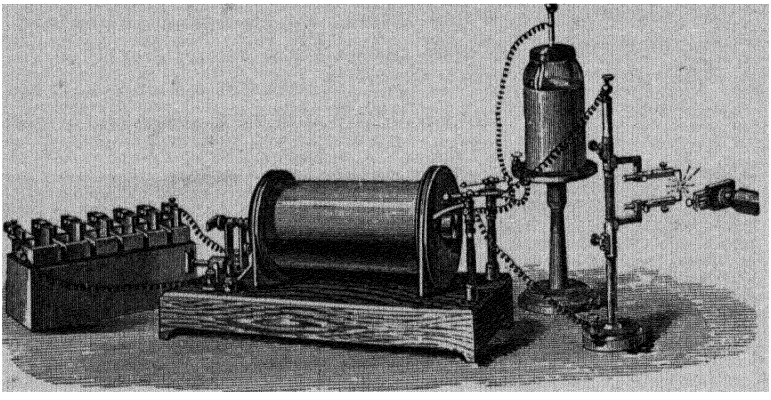


FIG. 16.

two small cones of pure porous carbon, these having been impregnated with a solution of a pure compound of the metal under examination. The advantage of this spark-spectrum method is well shown in the case of the detection of the allied rare metals cerium, lanthanum, praseodymium, and neodymium; yttrium and erbium. The chlorides of these metals do not volatilise at the temperature of the non-luminous flame, but yield well-defined and characteristic spark-spectra by which they can be recognised without difficulty.

Another method which is of special value in observing the spectra given by the soluble salts of the metals has been perfected by Lecoq de Boisbaudran. It consists in connecting the solution of the salt with the negative wire from the induction coil, and then passing the spark from a positive pole of platinum placed just above the surface of the liquid. This method has

[1] *Phil. Mag.*, 1875, [4], **50**, 418, 527.

proved of great value in the examination of the compounds of rare earths.

For arc-spectra the ordinary arc between carbon points is used, the substance to be examined being placed on the positive pole, or packed in a hole bored along the axis of the carbons. In the case of metals, the poles may be made of the metal itself.

If the substance is a gas at the ordinary temperature the gaseous particles can be made to glow, and then to emit the rays which are peculiar to them, by passing an electric discharge through the gas. The colour of the electric spark or discharge will then be found to vary according to the nature of the gas, and a spectroscopic examination of the light then emitted reveals the characteristic spectrum of the gas. The examination of the spectra of gases at low pressures is effected by means of *Geissler's Tubes* (Fig. 17). These contain the gases in a highly rarefied condition, and are furnished with platinum or aluminium wires

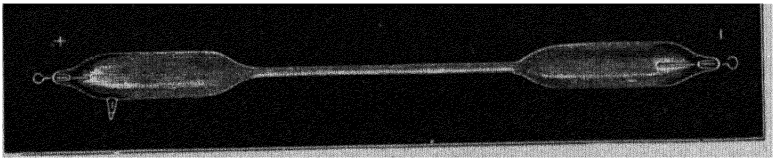


FIG. 17.

fused into the glass. As the rarefied gases offer little resistance to the passage of the electricity, the discharge passes readily through a long narrow tube, producing a brightly luminous column. The vapours of liquids which are easily volatilised can also be examined in this way.

The effect appears to be electrical rather than thermal. Michelson,[1] from a study of the effect of temperature on the breadth of spectral lines, found that the temperature of ordinary discharge through hydrogen in a vacuum tube was probably about 50°. In all cases of arc or spark spectra electrical stresses play an important part and the effects observed cannot be attributed to thermal influence alone.[2]

The spectra of gases at the ordinary pressure, or under increased pressure, can be observed by passing a spark (as described above) between metal poles in an atmosphere of the gas at the required pressure. It must be remembered that in such experiments the lines due to the metallic poles are also seen.

[1] *Astrophys. Journ.*, **3**, 251 (1896).

[2] Lockyer, *Proc. Roy Soc*, **76**, 145 (1905).

Phosphorescence spectra are shown by many substances when they are exposed to the cathode discharge in a highly exhausted glass bulb (Crookes). This method has been much used for the examination and characterisation of the rare earths.

When the invisible portions of the spectrum are to be examined it must be remembered that glass is much less transparent to the infra-red rays than to ordinary light, and is almost opaque to the ultra-violet rays. These last are, however, transmitted by quartz prisms and lenses, and then can be photographed, or rendered visible by means of a screen coated with some phosphorescent substance such as platinocyanide of barium or potassium. The infra-red spectrum is best obtained by means of a metallic diffraction grating.

81 *X-Ray Spectra.*—Another type of spectra, not usually included under the head of spectroscopy, is produced when substances are exposed to the bombardment of a stream of cathode rays. In these circumstances electro-magnetic disturbances are set up essentially similar to those of light, except that the wave-length is very much less and that only one pulse is sent out by the stoppage of each electron. Whilst there is always a certain amount of general radiation of continuously varied wave-length, yet, under certain conditions, rays of definite wave-length, termed *characteristic radiation*, are given off with much greater intensity. These correspond in all respects to the "lines" of definite wave-length produced in the ordinary spectra of glowing gases. Owing, however, to the much shorter wave-length, ordinary prisms and gratings are quite unable to resolve the X radiation. This difficulty was surmounted by Laue in 1912 by using a crystal as a natural diffraction grating and a modification of this method introduced by W. L. Bragg made it possible to measure the wave-length of X-rays almost as easily as with ordinary light (p. 218).

MAPPING AND MEASURING SPECTRA.

82 The following method of mapping spectra as observed with a spectroscope provided with an illuminated scale, was proposed by Bunsen as a convenient mode of recording the position, breadth, and intensity of the lines constituting the various spectra. "For the purpose of facilitating the numerical comparison of the data of various spectrum observations, we give in Fig. 18 graphical representations of the observations which are taken from the guiding lines given in the chromo-

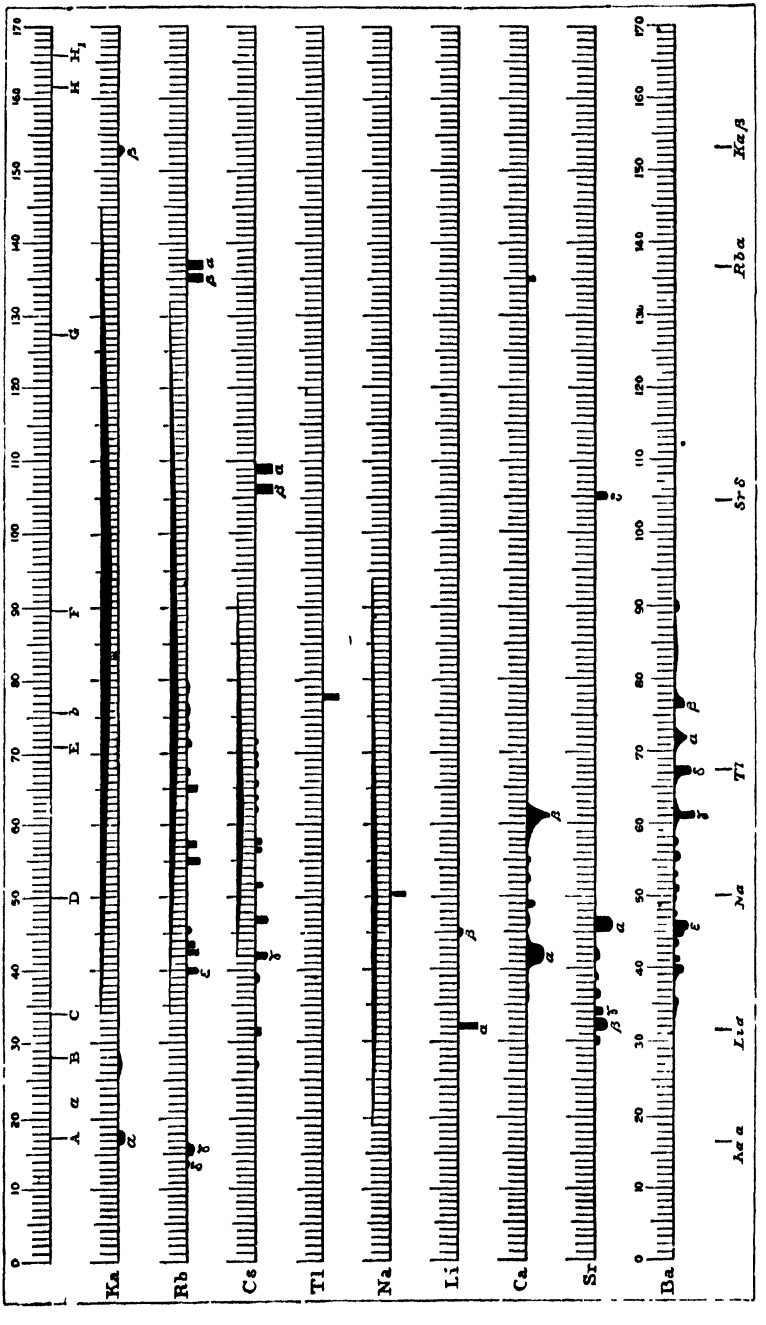


FIG. 18.

lithograph drawings of the spectra published in our former memoirs, and in which the prism was placed at the angle of minimum deviation. The ordinate edges of the small blackened surfaces, referred to the divisions of the scale as abscissæ, represent the intensity of the several lines, with their characteristic gradations of shade. These drawings were made when the slit was so broad, and the flame of such a temperature, that the fine bright line upon the broad Ca α band began to be distinctly visible.

"This breadth of the slit was equal to the fortieth part of the distance between the sodium line and the lithium line α. For the sake of perspicuity, the continuous spectra which some bodies exhibit are specially represented on the upper edge of the scale, to the divisions of which they are referred as abscissæ."

The positions of the lines in a spectrum are now generally recorded in terms of their *wave-lengths*, which are usually expressed in ten-millionths of a millimetre (1×10^{-7} millimetre), a unit of measurement which is known as Ångström's unit (Å.U.), or as a "tenth metre," since it equals 1×10^{-10} metre. Wave-lengths are, however, sometimes expressed in terms of $\mu = 0{\cdot}001$ millimetre, or of $\mu\mu = 0{\cdot}000001$ millimetre. For many purposes it is more convenient to deal with the oscillation frequency of the ray, *i.e.*, the number of waves in a given unit of length, the centimetre being usually chosen. Thus, the less refrangible yellow sodium line has the wave-length 5896·2 Å.U. (589·62 $\mu\mu$; 0·58962 μ), and the oscillation frequency 16960·1.

In order to ascertain the wave-lengths of the various lines observed, it is necessary to draw a curve which represents the dispersion of the particular instrument which is being employed. This is done by selecting a number of lines as standard lines, and plotting the wave-lengths of these as ordinates, and their positions on the scale of the instrument as abscissæ. The curve joining the points thus obtained can then be used for determining the wave-length of a line observed at any position on the scale. Precisely the same process may be carried out with the oscillation frequencies.

Some instruments are provided with illumination scales, divided and numbered so as to permit of the direct determination of the wave-length for any region of the visible spectrum. Such scales are similar to that shown in Fig. 19, and give wave-lengths in $\mu\mu$, in accordance with the determinations of Ångström.

The divisions of the scale enable the observer to read directly to the second significant figure, and to estimate the third. Such scales are sufficiently accurate for ordinary qualitative work, but can be employed only with a prism of the same dispersive power as that for which they have been constructed.

The most accurate method of recording the spectrum given by any substance is to allow the image of the spectrum to fall upon a photographic plate, contained in a holder fitting into a camera which replaces the eye-piece of the telescope. The great advantage of the photographic method is that it is thus possible to determine with great accuracy the positions of a much larger number of lines than can be done by mere observations with the eye, very faint lines being recorded when the time of exposure is increased. This is shown by the fact that in the portion of the spectrum between wave-lengths 3900 and 4100 the

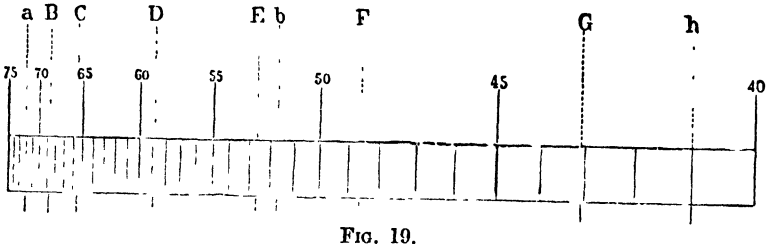


FIG. 19.

number of lines of twelve metals noted by Lockyer is 416, as against 39 lines observed by Thalén. The photographic method can, moreover, be extended to those portions of the spectrum which are invisible to the eye.

If the spectrum of some standard substance is photographed on the same plate as the spectrum to be examined, the unknown wave-lengths of the new lines can readily be determined by interpolation from the known wave-lengths of the lines of the standard substance.

It has been found possible to photograph the spectrum between wave-lengths 20000 Å.U. in the infra-red and 1000 Å.U. in the ultra-violet, but very special methods are required to obtain records beyond the interval 9000–2100. In the infra-red, measurements may be made also by means of the bolometer, an instrument devised by Langley, which detects the heating effect of the rays by the change of resistance produced in a thin metallic wire. By the use of this instrument radiations of wave-length 1,000,000 Å.U. (0·1 mm.) have been detected.

83 *Variations observed in Spectra.*—The nature of the spectrum emitted by a gas depends upon the temperature and pressure to which the gas is subjected. When an electric discharge of low intensity is passed through a highly rarefied gas, in a Geissler tube, the spectrum usually consists of a series of broad bright bands, which are made up of a great number of very fine lines crowded closely together; this is termed a "channelled" spectrum (Plücker). The band spectrum of the discharge in the neighbourhood of the positive pole is, moreover, often different from that near the negative pole. At a higher temperature, produced by a discharge of greater intensity, the spectrum consists of bright lines. Finally, when the pressure is increased, under certain conditions, many gases are found to give continuous spectra.

These variations are well exemplified by the cases of oxygen and nitrogen, the former of which gives no fewer than seven different spectra, among which are included the absorption spectra of both oxygen and ozone.

Argon, krypton, and xenon behave in a somewhat different manner from the foregoing gases, yielding two distinct bright line spectra according as the ordinary discharge or the jar discharge is employed.

Further, it is often found that variation in the pressure of the gas, or the intensity of the discharge produces a variation in the relative intensity of the lines of the spectrum. Thus, in helium at a pressure of 7—8 mm., the yellow lines are the most conspicuous, and the gas glows with a yellow light; whilst at a lower pressure, the most conspicuous line is in the green, and the gas glows with a greenish coloured light.

The cause of these variations is at present unknown. It appears probable, however, that the characteristic spectrum of each element is due to the vibrations of the corpuscles which are present in its atoms (p. 40), rather than to the vibrations of the atom as a whole, so that a change in the spectrum corresponds to some alteration in the mode of vibration of some or all of the corpuscles making up the atom.[1]

[1] See J. J. Thomson, "Some applications of the theory of electric discharge through gases to Spectroscopy," *Nature*, 1906, **73**, 495; compare Stark, *Physikal. Zeit.*, 1908, **9**, 85.

THE SPECTRA OF THE ELEMENTS.

84 If we compare the spectra of the various elements, obtained according to one or other of the above methods, we find that each element yields a characteristic spectrum, consisting of a larger or smaller number of bright lines, and that no two elements have even a single line in common.

These lines do not undergo any alteration in relative position, or in degree of refrangibility, when the temperature is raised. The double sodium line D is always seen at the same position of the spectrum, viz., wave-lengths 5896 and 5890, to whatever temperature the vapour may be raised. The *number* of lines visible in any given spectrum, as well as their relative intensities,

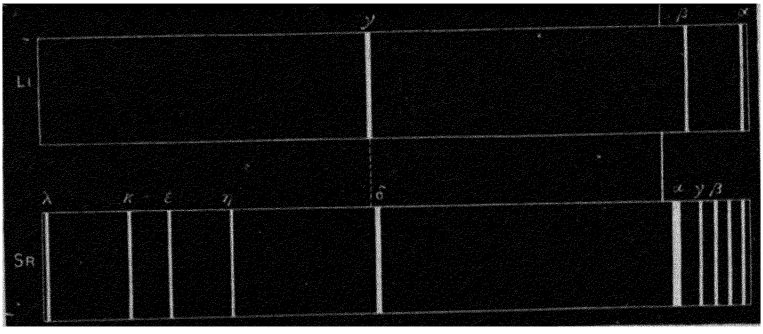


FIG. 20.

may, on the contrary, undergo considerable changes dependent upon the temperature of the glowing gas, the pressure to which it is subjected, and the thickness of the incandescent layer. Thus, for example, the spectrum of lithium, as obtained by placing some salt of the metal in a non-luminous gas-flame, consists of one very bright red line, α, wave-length 6708, and a very faint orange line, β, wave-length 6104 (Fig. 20). If, however, the spectrum of lithium obtained by placing one of its salts in the electric arc, or even in the oxy-hydrogen flame, is examined, a new and splendid blue line (γ), wave-length 4602, makes its appearance, along with several others of less intensity, making in all twenty lines. The same phenomenon is observed in the case of the strontium spectrum (Fig. 20), where no fewer than four new lines (ϵ, η, κ, and λ) make their appearance on raising the temperature of the incandescent vapour of the metal.

A very important feature of the spark spectra of the metals

was first observed by Lockyer, making use of a method in which the image of the electric arc formed by the incandescence of the metal was projected by a lens on the slit of the spectroscope. By this process he was enabled to examine the spectrum of various portions of the arc, and was thus led to the remarkable discovery that in each metallic spectrum certain lines are not only brighter than others, but are also *longer* than the rest. That is, one line of a given metal is seen to stretch across from pole to pole, whilst another line appears only in the neighbourhood of the poles, where the temperature is highest and the density of the incandescent gas may be supposed to be greatest. The longest lines are the ones which exist in the spectrum produced at lower temperatures.

The application of instruments possessing greater powers of resolution to the study of the spectrum has shown that the great majority of the bright lines observed in the spectra of the elements are in reality composed of a number of separate lines differing only very slightly in wave-length, but often varying considerably in intensity. Thus, the red line of hydrogen consists in reality of two lines of unequal brightness, differing in wave-length by only 0·14 Å.U. Again, the green line of thallium is triple, and certain of the lines of mercury are quadruple.

85 Great interest attaches to the question as to whether isotopes possess the same spectra. Various researches with the isotopes of lead failed to distinguish any variation until eventually Aronberg [1] detected a difference, subsequently confirmed by Merton,[2] of 0·0043 Å.U. in the line 4058 Å.U.

The X-ray spectra of elements [3] are of exceptional theoretical importance. Those of the elements of smaller atomic weight than that of silver give in each case X-rays of two definite and not very different wave-lengths. As we proceed from elements of lower to those of higher atomic weight the wave-length decreases and a very simple relationship exists between the frequency (which is the reciprocal of the wave-length) of the characteristic radiation and the atomic number, namely, $\nu = \frac{3}{4}\nu_0(N - n)^2$, where ν is the frequency of the characteristic radiation, ν_0 is Rydberg's universal constant (*v. i*), N is the atomic number of the element, and n a constant nearly equal to unity.

[1] *Astrophys. Journ.*, **47**, 96 (1918).
[2] *Proc. Roy. Soc.*, **96**, [*A*], 388 (1920); **100**, [*A*], 84 (1922).
[3] Moseley, *Phil. Mag.*, 1913, **26**, 1024; 1914, **27**, 703.

These radiations from successive elements form a series usually denoted by the letter K. The elements from zirconium to gold give rise to an additional series, also of two lines in each case, known as the L series. A similar equation to the above, but with a different factor of proportionality, connects the frequency of these to the atomic numbers. This series has a greater wave-length than the former. For example, in the case of silver the K radiation has a wave-length of $0{\cdot}560 \times 10^{-8}$, and the L of $4{\cdot}17 \times 10^{-8}$.

The elements from zirconium to silver have been found to give lines of both series, and probably the other elements also do so, though experimental difficulties have hitherto prevented their observation.

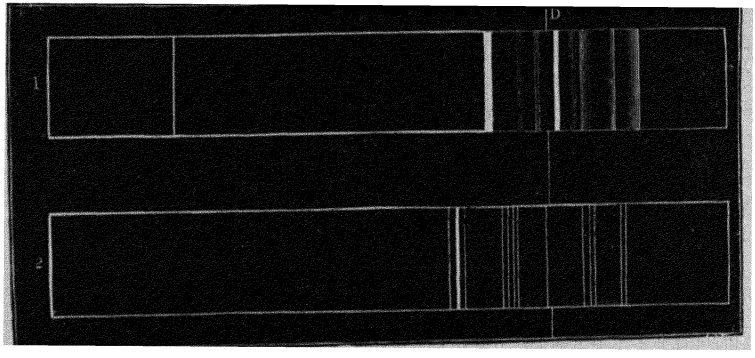


FIG. 21.

The relationship noted above leads directly to a knowledge of the number of elements that can exist between hydrogen and uranium. (See Atomic Numbers, p. 72.)

So far no difference has been found between the X-ray spectra of isotopes.[1]

THE SPECTRA OF COMPOUNDS.

86 It appears probable that every individual compound possesses a characteristic spectrum which consists of broad bands, and not of lines like the spark spectrum of an element. It is, however, impossible in many cases to observe this, because the compound is decomposed before it reaches a sufficiently high temperature to produce a spectrum. Thus, when the compounds

[1] Siegbahn and Stenstrom, *Compt. rend.*, **165**, 428 (1917).

of one of the alkali metals are introduced into a Bunsen flame, the spectrum produced is the same whatever compound is used, and consists of lines which are all found in the spark spectrum of the metal. On the other hand, the different salts of barium, calcium, or strontium yield different spectra, and these, moreover, scarcely contain a single line which occurs in the actual spectrum of the metal. Thus, if a bead of calcium chloride is brought into the flame a reddish tint is observed, caused by the volatilisation of the salt. The spectrum of this coloured flame consists of a series of differently coloured broad bands, the positions of which are indicated in No. 1, Fig. 21, and which are mainly due to the unaltered chloride and the oxide formed from it by calcination. If, now, the same bead is placed between two metallic poles, and a bright electric spark is allowed to strike round the bead, the spark is seen to assume a bright-red tint and when this coloured spark is observed by means of a spectroscope a spectrum of fine bright lines, shown in No. 2, Fig. 21, is seen. In the first instance, the spectrum is that of a calcium compound; in the second, it is that of the metal itself.

RELATIONS BETWEEN SPECTRAL LINES.

87 *The Spectrum of a Given Element.*—It appears from the work of Liveing and Dewar, Hartley, and especially of Balmer, Rydberg, Schuster, and Kayser and Runge,[1] that relations exist between the wave-lengths of the lines in the spectrum of a given element. In the spectra of many elements certain series of lines have been found, the wave-lengths of which can be expressed as functions of a series of whole numbers.

Kayser and Runge employ the formula,

$$\frac{1}{\lambda} = A - Bn^{-2} - Cn^{-4},$$

in which λ is the wave-length, A, B, and C are constants determined from the observations, and n takes the values of successive whole numbers.

Rydberg,[2] on the other hand, proposes the more rational equation,

$$n = n_0 - \frac{109675}{(m + \mu)^2},$$

[1] *Journ. Chem. Soc.*, 1883, **43**, 390; *Phil. Trans.*, 1883, **174**, 187; *Nature*, 1895, **52**, 106; *British Assoc.*, 1888, 1895; *Ann. Physik*, 1894, **52**, 114.

[2] *K. Svenska Vetensk. Akad. Hand.*, 1890, **23**, No. 11.

in which m takes the value of successive whole numbers, n is the oscillation frequency expressed as the number of waves per centimetre, μ is a constant characteristic of the special series, and n_0 is the value of n when m becomes infinite; n_0 is thus the theoretical limit of the series, and is termed the *convergence frequency*. Series of this kind were first discovered in the spectrum of hydrogen by Balmer,[1] but they are best exemplified by the spectra of the alkali metals, all of which appear to be of the same type. Thus, the arc-spectrum of sodium may be regarded as consisting of a large number of pairs of lines, and among these there have been detected three series each consisting of paired lines. The first of these is called the *principal series*, because it contains the most important and conspicuous lines of the spectrum. It consists, in the case of sodium, of numerous pairs of lines, the frequency difference between the members of the pairs becoming smaller as the frequency increases, so that the members of the pairs are closer together in the ultra-violet than in the visible spectrum.

The second is called the *first subordinate series*, or since the lines are diffuse, the *nebulous* series; it consists of a number of pairs, with a constant frequency difference of 17·2 between the members of the pairs. The third is called the *second subordinate series* or the *sharp* series; the lines are sharply defined, and there is a constant frequency difference of 17·2 between the pairs.

The equations given by Rydberg for the less refrangible line of the pairs in these three series are

$$\text{Principal series } n = 41452{\cdot}61 - \frac{109675}{(m + 1{\cdot}116329)^2}.$$

$$\text{Nebulous series } n = 24470{\cdot}13 - \frac{109675}{(m + 0{\cdot}64984)^2}.$$

$$\text{Sharp series } \quad n = 24470{\cdot}13 - \frac{109675}{(m + 0{\cdot}088436)^2}.$$

In the principal series the more refrangible lines of the pairs are given when $\mu = 1{\cdot}117072$; in the other series μ remains constant, but the convergence frequency for the second line of the pair is greater by 17·2.

These formulæ indicate that the two subordinate series have

[1] *Ann. Physik*, 1885, **25**, 80.

the same convergence frequency, and further bring out a relation of great importance between the principal series and the subordinate series, which is known as the Rydberg-Schuster law, having been independently discovered by these two observers. This consists in the fact that the frequency of the first line of the principal series is equal to the difference between the convergence frequencies of the principal and subordinate series. Thus in the case of sodium this difference is 41452·61—24470·13 = 16982·48, and this number is the oscillation frequency of the less refrangible D line (wave-length 5896·16). Other relations also exist which clearly indicate that these three series are closely related to each other and are not represented merely by independent empirical formulæ.[1]

Similar relations are found in the spectra of the other alkali metals. In the spectra of the metals magnesium, calcium, strontium, zinc, cadmium, and mercury, the principal series are wanting, or only very scantily represented, but in all these cases the nebulous and sharp series have been found, each composed of triplets of lines instead of the pairs present in the spectra of the alkali metals. It must be remembered that, as a rule, the spectrum contains also many lines which do not fall into these series.

In other cases, such as tin, lead, arsenic, antimony, bismuth, etc., no series have been discovered, but numerous groups of lines of constant frequency difference have been observed. Attempts have been made to connect the existence of these various relations between the lines of a spectrum with the mode of vibration and form of the atom, but no very definite success has yet been attained.[2]

88 *The Spectra of Allied Elements.*—Relations also undoubtedly exist between the spectra of allied elements, and this is well seen in the case of the alkali metals. The resemblance between these spectra was first noticed by Lecoq de Boisbaudran in 1869, the general effect being a shifting of the lines towards the red as the atomic weight increases. Ramage [3] has carried the matter somewhat further by showing that the oscillation frequencies of

[1] For recent work on spectral series, see Hicks, *Phil. Trans.*, [*A*], 1909, **210**, 57; 1912, [*A*], **212**, 33; 1913, [*A*], **213**, 323; also *Œuvres de Walther Ritz* (Gauthier-Villars; Paris, 1911); *Monthly Notices of the Roy. Astronom. Soc.*, 1914, **74**, 354; Fowler, "The Bakerian Lecture, *Phil. Trans.*, 1914, [*A*], **214**, 225; and "Report on Series in Line Spectra," *Phys. Soc.* Lond., 1922.

[2] See Lindemann, *The Monist*, Jan. 1906, and *Nature*, 1906, **73**, 392.

[3] *Proc. Roy. Soc.*, 1902, **70**, 1303.

the corresponding lines in the series found in the spectra of potassium, rubidium, and cæsium, bear a simple relation to the squares of the atomic weights of the metals. A somewhat similar relation has been brought out by Marshall Watts,[1] who has indicated that the atomic weight of a metal, such as zinc, may be calculated from a comparison between its spectrum and that of an allied metal of known atomic weight, such as cadmium. Such a calculation is based on the fact that the differences between the oscillation frequencies of corresponding lines in the two spectra are in the ratio of the squares of the atomic weights of the metals. Thus taking the following pairs of corresponding lines,

Cadmium.		Zinc.	
30654·4 31905·5	diff. 1251·1,	32500·0 32928·7	diff. 428·7,

we have $$\frac{1251{\cdot}1}{428{\cdot}7} = \frac{(111{\cdot}83)^2}{(65{\cdot}4)^2}.$$

Our knowledge of the whole question of the relations between the separate lines of a spectrum, and between the spectra of different elements, is still in a very rudimentary state, although the question is one of the most interesting in the whole field of chemical and physical inquiry.

APPLICATION OF THE SPECTROSCOPE TO CHEMICAL ANALYSIS.

89 This instrument is especially valuable in ordinary qualitative analysis for the detection of the metals of the alkalis and alkaline earths, and of the more recently discovered metals, thallium, indium, and gallium, inasmuch as the salts of all these metals can be volatilised in the non-luminous gas-flame. The following extract from Bunsen and Kirchhoff's memoir (1860) on this subject gives some idea of the ease and accuracy with which the presence of certain of these metals can be detected, and leads to the conclusion that the sodium salts are universally distributed:

"The following experiment shows that the chemist possesses no reaction which in the slightest degree will bear comparison

[1] *Phil. Mag.*, 1903, **5**, 203. For application of this relationship in calculating the atomic weight of radium, see Runge and Precht, *Phil. Mag.*, 1903, **5**, 476; Watts, *ibid.*, 1909, **18**, 411.

as regards delicacy with this spectrum analytical determination of sodium. In a far corner of our experiment room, the capacity of which was about sixty cubic metres, we burnt a mixture of three milligrams of chlorate of sodium with milk sugar, whilst the non-luminous colourless flame of the lamp was observed through the slit of the telescope. Within a few minutes, the flame, which gradually became pale yellow, gave a distinct sodium line, which, after lasting for ten minutes, entirely disappeared. From the weight of sodium salt burned and the capacity of the room, it is easy to calculate that in one part by weight of air there is suspended less than $\frac{1}{20,000,000,000}$ of a part of soda smoke. As the reaction can be observed with all possible comfort in one second, and as in this time the quantity of air, which is heated to ignition by the flame, is found to be only about 50 cub. cent., or 0·0647 gram of air, containing less than $\frac{1}{20,000,000,000}$ of sodium salt, it follows that the eye is able to detect with the greatest ease quantities of sodium salt less than $\frac{1}{3,000,000}$ of a milligram in weight. With a reaction so delicate, it is easy to understand why a sodium reaction is almost always noticed in ignited atmospheric air. More than two-thirds of the earth's surface is covered with a solution of chloride of sodium, fine particles of which are continually being carried unto the air by the action of the waves. These particles of sea-water, cast thus into the atmosphere, evaporate, leaving almost inconceivably small residues which, floating about, are almost always present in the air, and are rendered evident to our eyes in the sunbeams. These minute particles perhaps serve to supply the smaller organised bodies with the salt which larger animals and plants obtain from the ground. In another point of view, however, the presence of this chloride of sodium is of interest. If, as is scarcely doubtful at the present time, the explanation of the spread of contagious disease is to be sought for in some peculiar contact action, it is possible that the presence of so antiseptic a substance as chloride of sodium, even in almost infinitely small quantities, may not be without influence upon such occurrences in the atmosphere.

" By means of daily and long-continued spectrum observations it would be easy to discover whether the alterations of intensity in the line Naα produced by the sodium in the air have any connection with the appearance and the direction of march of an epidemic disease.

"The unexampled delicacy of the sodium reaction explains also the well-observed fact, that all bodies after a lengthened exposure to the air show the sodium line when brought into a flame, and that it is only possible in a few salts to get rid of the line even after repeated crystallisation from water which has been in contact with platinum only. A thin platinum wire freed from every trace of sodium salt by ignition shows the reaction most visibly on allowing it to stand for a few hours in the air; in the same way the dust which settles from the air in a room shows the bright line Naα. To render this evident it is only necessary to knock a dusty book, for instance, at a distance of some feet from the flame, when a wonderfully bright flash of the yellow band is seen."

Again, to quote from Bunsen's Memoir: "Minerals containing lithium, such as triphylline, triphane, petalite, and lepidolite, require only to be held in the flame in order to obtain the bright line in the most satisfactory manner. In this way the presence of lithium in many felspars can be directly detected as, for instance, in the orthoclase from Baveno. The line is only seen for a few moments, directly after the mineral is brought into the flame. In the same way the mica from Altenburg and Penig was found to contain lithium, whereas micas from Miask, Aschaffenburg, Modum, Bengal, Pennsylvania, etc., were found to be free from this metal. In natural silicates which contain only small traces of lithium this metal is not observed so readily.

"In this way we arrive at the unexpected conclusion that lithium is most widely distributed throughout nature, occurring in almost all bodies. Lithium was easily detected in forty cubic centimetres of water of the Atlantic Ocean, collected in 41° 41′ N. latitude and 39° 14′ W. longitude.

"Ashes of marine plants (kelp) driven by the Gulf Stream on to the Scottish coasts contain evident traces of this metal. All the orthoclase and quartz from the granite of the Odenwald which we have examined contains lithium. A very pure spring water from the granite in Schleierbach, on the west side of the valley of the Neckar, was found to contain lithium, whereas the water from the red sandstone which supplies the Heidelberg laboratory was shown to contain none of this metal. Mineral waters, in a litre of which lithium could hardly be detected according to the ordinary methods of analysis, gave the line Liα even if only a drop of the water on a platinum wire were brought into the flame. All the ashes of plants growing in the

Odenwald on a granite soil, as well as Russian and other potash, contain lithium.

"Even in the ashes of tobacco, in vine leaves, in the wood of the vine and in the grapes, as well as in the ashes of the crops grown on the Rhine plains near Wäghausel, Deidesheim, and Heidelberg, on a non-granite soil, was lithium found. The milk of the animals fed on these crops also contains this widely diffused metal."

90 *Discovery of New Elements.*—The discovery by Bunsen of two new akali metals in the mineral water of Dürkheim[1] was one of the first results of the application of the spectroscope to chemical analysis. Both these new elements are contained in the mineral water in extremely small quantities, so that 44,000 kilos. of the water had to be evaporated in order to obtain 16·5 grams of the mixed chlorides. The first of these new metals yields a spectrum distinguished by two splendid bright blue lines, and hence the name *Cæsium* (*cæsius*, the blue colour of the sky) was given to it. The second new metal is characterised by a spectrum which contains a bright red line, less refrangible than the potassium line Kα, and also a line in the violet. As the red line is the one by which the presence of this metal can be most readily and certainly detected, Bunsen gave to it the name of *Rubidium* (*rubidus*, dark-red).

Since this discovery in 1860, chemists have recognised the presence of both these metals in very varied situations; one of them, rubidium, being comparatively widely distributed, and found in very many mineral waters. Thus, for example, the celebrated water of Bourbonne-les-Bains contains 0·032 gm. of cæsium chloride and 0·010 gm. of rubidium chloride in one litre of water; whilst in the well-known springs of Vichy, Gastein, Nauheim, Karlsbrunn, and many more, either one or both of these new metals have been discovered. Rubidium has been found to be more widely diffused than cæsium, occurring in animate as well as in inanimate nature. It has been found in beetroot, in tobacco, in the ash of the oak (*Quercus pubescens*), in coffee, in tea, and in cocoa.

In their general chemical characters, as in their spectroscopic relations, these two new metals exhibit the closest analogy with potassium. So much so is this the case, that without the aid of the spectroscope, and the differences which the spectra of these three metals present, it was absolutely impossible to

[1] For an analysis of this water, see vol. i., p. 326.

distinguish between them. Chemists had, in fact, experimented upon cæsium but had mistaken it for potassium. (See under Cæsium.)

Soon after the discovery of the new alkali metals by Bunsen, Crookes, in 1861, proved the presence of a new metal in a seleniferous deposit from a sulphuric acid chamber at Tilkerode in the Harz. To this new element he gave the name of *Thallium*, from *thallus*, a young twig, owing to the bright green colour which this substance and its compounds impart to the non-luminous flame. The spectrum of thallium is a simple one, consisting of one bright green line (Tlα), with a wave-length of 5349. Thallium has since been shown to occur frequently in iron pyrites and several other minerals, so that it is a somewhat widely distributed element. It exhibits very remarkable and interesting chemical properties, since in certain respects it closely resembles the metals of the alkalis, whilst in others it more nearly approaches the heavy metal lead. Hence thallium was very appropriately termed by Dumas the ornithorhynchus amongst the metals.

A fourth new metal was discovered in the year 1864, by Reich and Richter, in Freiberg. They gave to this substance the name of *Indium*, owing to the fact that it imparts a dark-blue or indigo tint to the flame and its spectrum consists of two indigo-coloured lines. It has been found, although in small quantities only, in the zinc blendes from Freiberg, Goslar, and a few other places.

In 1875, Lecoq de Boisbaudran found another new metal in zinc blendes from the Pyrenees. To this substance he gave the name of *Gallium*. Its spectrum consists of two violet lines, which are best seen in the arc spectrum. The brightest of these lines has a wave-length of 4172, the second line having a wave-length of 4033.

The application of spectrum analysis to the study of the rare earths has made us acquainted with many new substances, among which may be mentioned scandium, ytterbium, and samarium. Of surpassing interest is Ramsay's discovery of helium (1895) in the gas evolved by the action of sulphuric acid on clèveite, a rare uranate of uranyl, lead, and the rare earths. The gas evolved in this reaction was supposed by certain observers to be nitrogen, but examination showed that its emission spectrum differed entirely from that of nitrogen, and was characterised by a double yellow line of wave-length 5876 which occupies the same place in the spectrum as a double dark line in the solar

spectrum. This solar line had been observed previously, and since it did not coincide with a bright line of any known element, had been ascribed by Lockyer to an element, which he named helium, since it occurred in the sun but not in the earth. Further investigations have shown that the gas in question contains this solar element which is present also in the terrestrial atmosphere (Vol. I., p. 945).

ABSORPTION SPECTRA.

91 In accordance with the important optical law known as the law of exchanges, every incandescent body is capable of absorbing, at the same temperature, exactly those kinds of rays which it emits. Hence a glowing body which yields a continuous

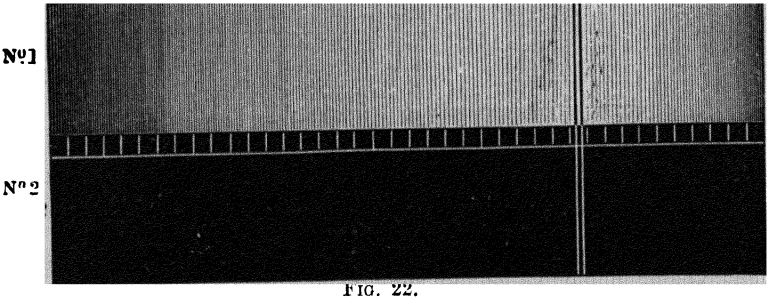


FIG. 22.

spectrum exhibits, at the same temperature, a continuous absorption, whilst those bodies the emission spectra of which are broken or discontinuous yield, under similar conditions of temperature, absorption spectra which are in like manner broken or discontinuous. This selective absorptive action of glowing gases is strikingly shown in the case of sodium vapour. If a small piece of this metal is burnt in an iron cap in front of the slit of the spectroscope the bright yellow sodium lines will at first be seen (No. 2, Fig. 22), but they will soon be replaced by two dark lines which are exactly coincident with the bright yellow lines, and are seen upon a background of a bright continuous spectrum (No. 1, Fig. 22). The sodium spectrum has thus been *reversed*, inasmuch as the yellow rays in passing through the sodium vapour have been absorbed, whilst the particles of glowing oxide of the metal yield a continuous spectrum. Sodium vapour is opaque to the yellow D rays. In a similar way the

bright lines of the emission spectra of lithium, calcium, strontium, barium, as well as of magnesium, copper, and several other heavy metals, have been reversed, or the absorption spectra of these metals have been obtained. The numerous fine black lines seen in the solar spectrum, known as *Fraunhofer's lines*, are produced by the reversal of the spectra of hydrogen, sodium, calcium, iron, magnesium, and other metals which are present in the state of luminous gas in the solar atmosphere.

This selective absorption is exhibited by nearly all substances in some portions of the spectrum, although in many cases it is confined to the non-visible region. The dark absorption bands seen when white light passes through the vapour of iodine (No. 1, Fig. 23), and those first observed by Brewster in the red

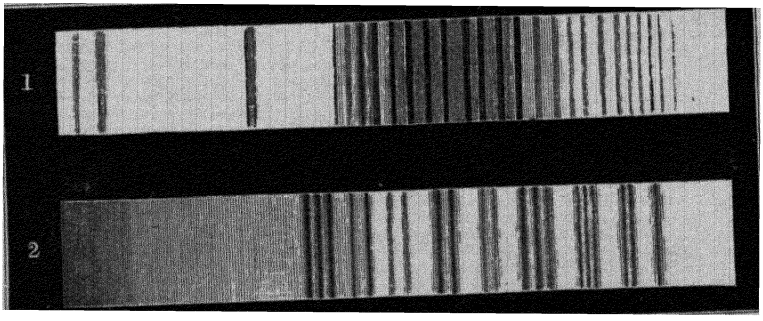


FIG. 23.

fumes of nitrogen peroxide (No. 2, Fig. 23), are good examples of this selective absorptive power of gases. Even some colourless gases, such as aqueous vapour, possess a strong power of selective absorption when a column of sufficient depth is examined (Rain-band).

In addition to the production of bands and lines, there is often a general absorption extending over a considerable extent of the spectrum. The measurement of the exact position, extent, and character of the absorption bands is a matter of considerable difficulty, since they are often diffuse, with badly defined edges. In such cases the position of maximum absorption must be found by photometric measurement, and a series of observations must be made on different thicknesses of the substance in order to ascertain how the bands vary in intensity and extent.

The arrangement shown in Fig. 24 is one which may be used

for examining the absorption spectra of gases by means of a direct-vision spectroscope.

The absorption spectrum of a substance, when examined at a lower temperature than that at which the bright line spectrum is obtained, is not, as a rule, identical with the emission spectrum. Thus the dark absorption lines seen in chlorine are not identical with, or even analogous to, the bright lines of the emission spectrum of chlorine.

The dark absorption bands of iodine, on the other hand, correspond with the emission band spectrum obtained at a low pressure in a Geissler tube and also in the flame.

Characteristic absorption spectra are shown in the visible region also by coloured liquids and solutions, whilst many

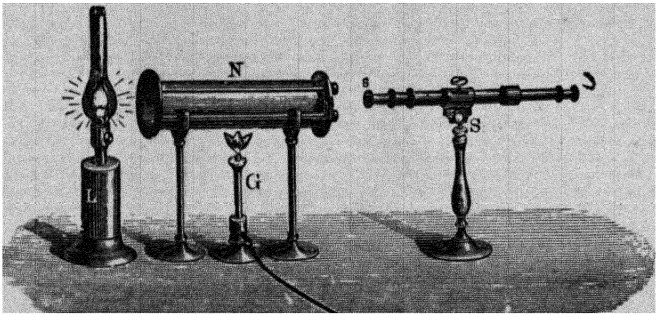


FIG. 24.

liquids which appear perfectly colourless produce selective absorption in the ultra-violet or infra-red.

92 According to the theory of electrolytic dissociation, salts in dilute aqueous solution are almost completely ionised, and Ostwald pointed out that it follows from this that the colour and absorption of dilute solutions must be due to the presence of a particular "colour-producing" ion. The absorption of dilute solutions of all salts yielding the same colour ion should therefore be the same, whilst in more concentrated solutions the absorption would be due both to the undissociated molecules and to the ions, and would therefore be modified in character.

The fact that the different salts of a metal may show absorption spectra which differ in certain respects was observed in 1866 by Bunsen in the case of didymium, and has been established for neodymium and praseodymium, the constituents into which Bunsen's didymium has since been resolved, and for many other

salts. Dilution of the solutions of these salts, however, does not invariably bring about complete identity of absorption, and a striking instance of this is afforded by the metallic nitrates, each of which shows a characteristic absorption spectrum in the ultra-violet, differing according to the metal which is present (Hartley).

In other cases, examples of which are the bromide, chloride, nitrate, and sulphate of copper (Ewan), and the metallic permanganates (Vaillant), the absorption spectra of the different salts are practically identical, and are not greatly altered by dilution, although the dissociation is thereby increased.

It is evident that the absorption produced by aqueous solutions

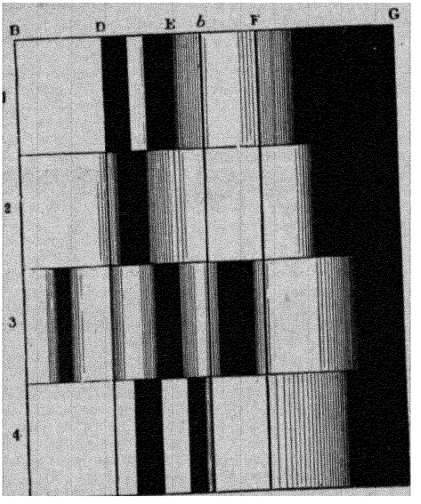


FIG. 25.

of salts is a very complex phenomenon, the complete analysis of which has not yet been effected.[1]

93 Solutions of metallic salts are not the only liquids which exhibit this power of selective absorption. Many organic liquids possess it in a high degree, and by this means complicated liquids of animal and vegetable origin can be easily distinguished when no other method is available. As an example of selective absorption in organic liquids, the spectrum reaction of blood may be cited. No. 1, Fig. 25, exhibits the two dark bands, situated between Fraunhofer's D and E, seen in oxidised blood, and due to oxyhæmoglobin. No. 2 on the

[1] See Baly's *Spectroscopy* (Longmans); also Houstoun, *Proc. Roy. Soc. Edin.*, 1911, **31**, 521–558.

same figure shows the absorption spectrum of deoxidised or venous blood, consisting of one dark band. By the action of an acid on blood, the oxyhæmoglobin is converted into hæmatin, yielding a different absorption spectrum. The hæmatin, like the oxhyæmogolobin, is capable of undergoing oxidation and reduction. The absorption bands of hæmatin are shown in Nos. 3 and 4, Fig. 25. Another interesting fact is that the blood, when it contains very small quantities of carbon monoxide in solution, exhibits a very characteristic set of absorption bands. Carbon monoxide acts, however, as a very violent poison, and these bands are seen in the blood of animals which have been suffocated in the fumes of burning charcoal. In the same way, the peculiar compound which hæmoglobin forms with hydrocyanic acid yields a characteristic absorption spectrum. The instrument with which these absorption spectra can be observed with extremely small quantities of the liquids is a spectroscope placed in connection with a microscope. The eyepiece contains prisms so arranged that the refracted rays pass in a straight line from the object into the eye. Such spectroscopes are termed direct-vision instruments, and are very portable and useful forms of the apparatus. This instrument, in the hands of Sorby, has proved capable of detecting $\frac{1}{100000}$ part of a grain of blood in a blood-stain.

The same observer states that wines of different vintages may be distinguished by a variation in their respective absorption spectra.[1]

Many substances which are transparent to ordinary light show very characteristic absorption bands in the ultra-violet or infra-red portions of the spectrum. Thus Abney and Festing [2] have ascertained the position of the bands and lines produced in the infra-red spectrum by many elements and groups of elements and radicals, whilst Hartley [3] has shown that the aromatic compounds are characterised by well-marked absorption bands in the ultra-violet, the position of the bands being intimately connected with the constitution of the substance. He has even been able to decide between several possible constitutional formulæ for a substance by the character of its ultra-violet absorption spectrum.[4]

[1] *Chem. News*, 1869, **20**, 295. [2] *Proc. Roy. Soc.*, 1881, **31**, 416.

[3] *Journ. Chem. Soc.*, 1885, **47**, 685; 1888, **53**, 641.

[4] See Hartley, "Relation between Absorption and Constitution of Organic Substances," Kayser, *Handbuch der Spectroscopie*, vol. ii., chap. 3 (Hirzel, Leipzig, 1905), where a detailed account of this subject is given; also Baly's *Spectroscopy*.

Considerable advances have been made in this direction by Henri,[1] who has studied absorption quantitatively and, by means of the principles of the theory of resonance, has succeeded in establishing relationships between absorption and chemical constitution.

Loomis [2] has used the absorption spectra of hydrogen chloride to throw light upon the spectra of isotopes. In the case of lead the difference in the atomic weight of the two isotopes is only a very small fraction of the whole, owing to the high atomic weight of lead, but chlorine, which consists, according to Aston, of two isotopes of atomic weight 35 and 37 respectively, shows a greater proportional difference. The effect on the spectra should be correspondingly more marked. Loomis calculates that the absorption spectra of ordinary HCl should consist of pairs of lines separated by 1/1330 of their frequency, those of the shorter wave-length having about 3·35 times the intensity of the others. This refers to the ideal case where the lines are absolutely sharp and perfectly resolved, and he considers that the experimental results of Imes [3] confirm the theory.

COMPOSITION OF THE SOLAR ATMOSPHERE.

94 When sunlight is allowed to fall upon the slit of a spectroscope, the solar spectrum thus obtained is observed to differ essentially from the spectra which we have hitherto considered. A bright band is seen stretching from red to violet, but this band is cut up by a very large number of fine black lines. These lines are always present, and always occupy the same relative position in the solar spectrum—they are, in fact, shadows in the sunlight. They were originally noticed by Wollaston, but first carefully mapped by Fraunhofer, the principal lines being designated by him with the letters of the alphabet. Fig. 26 is a reduced facsimile of Fraunhofer's original map.

The cause of these dark solar lines was long a mystery. Fraunhofer, finding that sunlight, both direct and reflected as moonlight, always gave the same lines, whereas the light of the fixed stars contained different dark lines, came to the conclusion in 1814 that these dark lines were produced in the solar atmosphere, and not by the passage of the light through the intervening space, or through our own atmosphere.

[1] *Étude de Photochimie*, 1919. [2] *Astrophys. Journ.*, **52**, 248 (1920–22).
[3] *Ibid.*, **50**, 251 (1919).

It was not until the year 1860 that the true cause of the production of these lines was first clearly proved by Kirchhoff,

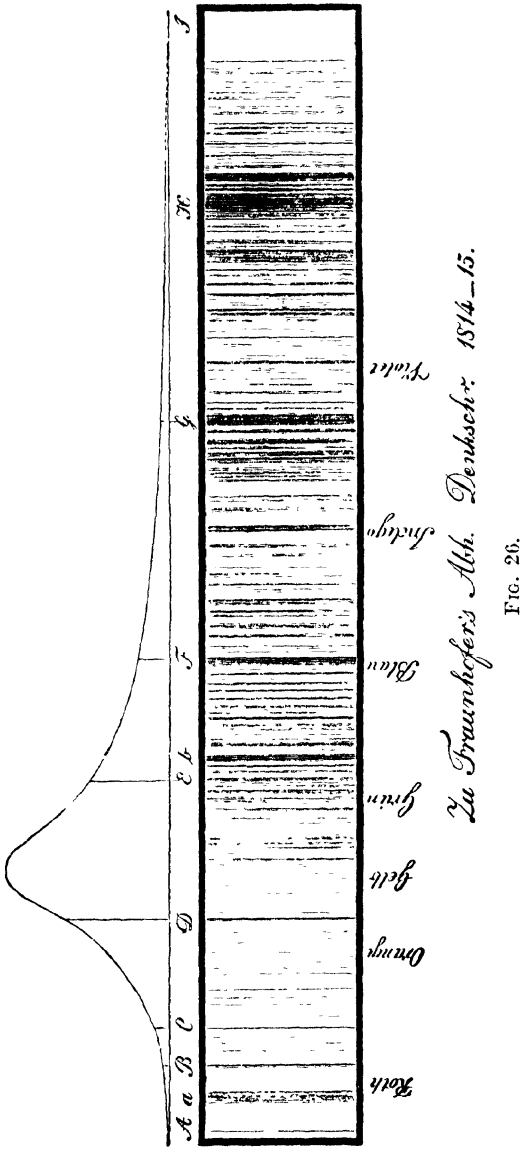


FIG. 26.

although the same cause had already been suggested by Stokes as a possibility. Kirchhoff was engaged in the comparison of the bright lines of certain metallic spectra with the dark lines

in the sun. To his astonishment he found that *all* the bright lines of such metals as iron, calcium, and magnesium have dark representatives of the solar spectrum. Not only has each bright metal line a dark one coincident with it, but the breadth and intensity of the bright metal line are as a rule reproduced in the dark line of the solar spectrum; this may be seen by allowing a solar and a metallic spectrum to fall one below the other in the field of the telescope. Other metals, for instance, gold and antimony, exhibit no such coincidences; not a single bright line of these is found coincident with a dark solar line. It is clear therefore, that there must be some kind of connection between the bright lines of metals of the former class and the dark solar lines. Such coincidences cannot possibly be the result of mere chance.

We have already seen that the spectrum of sodium can be reversed. By passing the light from incandescent sodium through the vapour of the metal, the bright yellow double line is changed to a dark one. If the solar atmosphere contained the vapours of sodium, of iron, of magnesium, of calcium, etc., in the state of glowing gas, and if white light from the incandescent mass beneath passed through these vapours, the effect produced would be exactly that which is in fact observed. The coincidence of the *dark* solar lines with the *bright* iron lines may therefore be attributed to the presence of iron in the sun's atmosphere.

"As this is the only assignable cause, the supposition appears to be a necessary one. These iron vapours might be contained either in the atmosphere of the sun or in that of the earth. But it is not easy to understand how our atmosphere can contain such a quantity of iron vapour as would produce the very distinct absorption-lines which we see in the solar spectrum; and this supposition is rendered still less probable by the fact that these lines do not appreciably alter when the sun approaches the horizon. It does not, on the other hand, seem at all unlikely, owing to the high temperature which we must suppose the sun's atmosphere to possess, that such vapours should be present in it. Hence the observations of the solar spectrum appear to me to prove the presence of iron vapour in the solar atmosphere with as great a degree of certainty as we can attain in any question of physical science" (Kirchhoff).

By observing the coincidences of the dark solar lines with the bright lines of terrestrial elements we may deduce the constitu-

ents of the solar atmosphere. The elements the existence of which in the sun has now been ascertained, thanks to the labours of Kirchhoff, Ångström, Thalén, Lockyer, Kayser, Runge, and Rowland, are the following:

Elements contained in the Sun's Atmosphere.

Aluminium.	Helium.	Palladium.
Barium	Hydrogen.	Rhodium.
Cadmium.	Iron.	Scandium.
Calcium.	Lanthanum.	Silicon.
Carbon.	Lead.	Silver.
Cerium.	Magnesium.	Sodium.
Chromium.	Manganese.	Strontium.
Cobalt.	Molybdenum.	Tin.
Columbium.	Neodymium.	Titanium.
Copper.	Nickel.	Vanadium.
Erbium.	Nitrogen (as	Yttrium.
Germanium.	cyanogen).	Zinc.
Glucinum.	Oxygen.	Zirconium.

Presence Doubtful.

Iridium.	Potassium.	Thorium.
Lithium.	Ruthenium.	Tungsten.
Osmium.	Tantalum.	Uranium.
Platinum.		

The solar corona yields a spectrum of bright lines, none of which have as yet been identified with the lines of any terrestrial spectrum.

STELLAR SPECTRA

95 In a similar way W. Allen Miller and Huggins have succeeded in proving that various elements, including hydrogen, sodium, calcium, magnesium, iron, occur in the atmosphere of the star Aldebaran, whilst other stars have been shown to contain other elements. The photographic mode of record was applied by Huggins to the spectra of stars, and has yielded permanent pictures of the dark lines in the stellar spectra drawn by nature herself.

From the observations of Secchi and others it appears that the stars may be divided into four main classes according to the

general nature of the spectra which they present. In those of the first class, metallic vapours are not conspicuous, the spectra being characterised mainly by strong dark lines corresponding in position to the bright lines of hydrogen, as in the case in Sirius, Vega, and most white stars. In some of the stars of this class, dark lines of helium, oxygen, nitrogen, silicon, and carbon are present. The second group contains the yellow stars such as Pollux, Capella, Aldebaran, etc., the spectra of which resemble that of the sun, containing numerous dark lines due not only to hydrogen, but also to metals. The members of the third group, which comprises the red stars such as Betelgeux and α Herculis, in addition to some dark lines show fluted spectra, which have been found to be due to the presence of titanium oxide [1] in their atmospheres. Stars of the fourth type exhibit fluted spectra due to some compound of carbon in the incandescent state. Apart from the classification just given there are a few stars, such as β Lyra and γ Cassiopeiæ, which exhibit bright line spectra. Nebulæ show, as a rule, very simple spectra of bright lines, among them those of hydrogen and helium, together with others not yet identified.

The simpler a spectrum is, the simpler must be the composition of the body which yields that spectrum. Arguing upon these premisses, Lockyer concludes that the atmospheres of the whiter stars contain the fewer elements and those of smaller atomic weight, and that as the peculiar colour of the star becomes more distinct its atmosphere becomes more complicated. These results, coupled with the well-known fact that dissociation of chemical compounds uniformly takes place if the temperature is only sufficiently high, have led Lockyer to suggest that, the heat being greatest in the white stars, their simple spectra can be best explained by the existence of a temperature sufficient to dissociate the substances to which on this earth we give the name of elementary bodies.[2] More recent research, however, makes it increasingly probable that all the lines in celestial spectra will ultimately be identified with those of terrestrial spectra.[3]

[1] Fowler, Monthly Notices, *Roy. Astronom. Soc.*, 1909, **69**, 508.

[2] See further, Roscoe's *Lectures on Spectrum Analysis* (4th edition, Macmillan, 1885); Lockyer, *Chemistry of the Sun* (Macmillan, 1887), *Inorganic Evolution as Studied by Spectrum Analysis* (Macmillan, 1900), *Proc. Roy. Soc.*, 1887, **42**, 37; 1888, **43**, 117; 1910, [*A*], **84**, 426.

[3] See *Nature*, 1912, **90**, 466.

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CRYSTALLOGRAPHY

96 When a chemical substance passes from the gaseous or the liquid state into that of a solid, it generally assumes a definite geometrical form, and is said to *crystallise.*

A *crystal* is a solid body, formed in this way, and bounded by plane surfaces. As a rule, every chemical substance in the solid state possesses a distinct form in which it usually crystallises and by which it can be distinguished.

The occurrence of various mineral substances in distinct crystalline forms was noticed by the ancients, and they gave the name crystal (κρύσταλλος, ice) to one of these, viz., to quartz or rock-crystal, because they believed that this body owed its formation to the effect of cold. The Latin Geber was aware that crystals can be obtained artificially by the evaporation of a solution of a salt. He describes the production of several chemical compounds in the crystalline condition, and shows how they may be purified by recrystallisation. Many years, however, elapsed before this property of matter was regarded as anything more than an unimportant one. Libavius, it is true, asserted in the year 1597 that the nature of the saline components of a mineral water could be ascertained by an examination of the crystalline forms of the salts left on the evaporation of the water. But so imperfect were the views regarding the formation of crystals that Lemery classified them simply according to their thickness, believing that this was dependent upon the size of the ultimate particles of the acids contained in the salts. In the year 1703, Stahl pointed out that the compounds obtained by the action of acids upon sea-salt crystallise in forms different from those assumed by the corresponding compounds of potash, and hence he concluded that sea-salt contained a peculiar alkali, distinct from the common alkali potash. Guglielmini appears to have held much more rational views than Lemery concerning the formation of crystals. In his *Dissertatio de Salibus,* published in 1707, he asserts that

the smallest particles possess definite crystalline forms, and that the differences in form which we observe between the crystals of alum, nitre, and sea-salt are caused by similar differences existing between the forms of the smallest particles.

It is, however, to Haüy (1743–1822), that we are indebted for the foundations of the science of crystallography. Haüy was the first to point out the fact that every crystalline substance possesses certain definite and characteristic forms in which it crystallises, and that all these different forms can be derived from one fundamental form which can be ascertained by measurement of the angles of the crystal. Upon this principle he founded in 1801 his celebrated system of the classification of minerals.

General Characteristics of Crystals.—A crystal of any substance is characterised, in the first place, by its special geometrical form, and, in the second place, by its physical properties, both of which we must suppose to be due to the special mode of arrangement of the particles of which the crystal is built up. In an amorphous, or non-crystalline, substance the physical properties are as a rule the same in every direction throughout its mass, whilst in a crystalline substance this cannot be the case for all of them. Thus, for example, under ordinary conditions light travels through a piece of glass at the same rate in whatever direction it may happen to pass, whilst in a crystal of quartz or calcspar the rate is different in different directions. The physical properties are even more characteristic of a crystalline substance than the geometrical form which it assumes, and can be recognised in fragments of the substance in which the characteristic crystalline form may be quite unrecognisable.

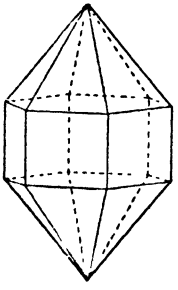


FIG. 27.

Parts of a Crystal; Faces, Edges, Corners, and Zones.—A typical crystal of quartz or rock-crystal, SiO_2, is shown in Fig. 27. The plane surfaces by which the crystal is bounded are termed *faces.* The straight lines formed by the intersection of two contiguous faces are the *edges.* Solid angles or *corners* are made by the intersection of three or more faces at a point, and are sometimes also termed summits. In the given crystal there are evidently two kinds of corners, namely, those in which four faces meet, and those in which six faces meet.

A remarkable feature of the development of crystals is that no matter how great the number of faces, they can be divided

into a relatively small number of *zones*, *i.e.*, sets of faces intersecting in parallel edges; *e.g.*, the six vertical faces in Fig. 27 lie in a zone with vertical edges. There are three other obvious zones, each of which includes two vertical faces and four pyramid faces, the edges of intersection being horizontal. The eighteen faces, then, on the crystal lie in four zones. This predisposition of a relatively large number of faces to lie in a zone greatly simplifies the measurement of a crystal. A line drawn through the centre of the crystal parallel to a zone edge is termed the zone axis.

Distortion of Crystals.—Crystals of alum are bounded by eight faces inclined at the same angles as the regular octahedron of Fig. 28, but the shape of the crystal rarely obtains such an ideal

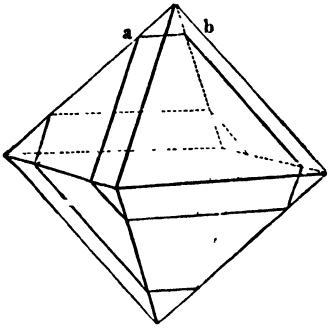


Fig. 28.

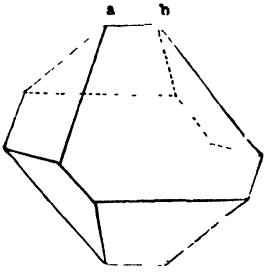


Fig. 29.

development; more often it approximates to that of Fig. 29. A comparison of the two figures will show that the deposition of parallel layers of material on the large pair of faces of the latter figure would transform it into the ideal shape. This deposition does not alter the angles between the faces. Such a departure of the shape from that of the ideal form is termed *distortion*, and is due to the more favoured position of some of the faces of the crystal in the solution during growth. If a small distorted crystal be carefully turned over from time to time so as to rest on different faces during growth, it will gradually assume the ideal form.

97 *Measurement of Crystals.*—The instrument now used for this purpose is the reflecting goniometer invented by Wollaston in the year 1809, a modern form of which is shown in Fig. 30. Suppose the crystal to be measured is the quartz crystal of Fig. 27. By means of a little wax it is placed in a vertical position

with its pointed end on a small pin which fits into a corresponding hole at the upper end of the central axis of the instrument, and is clamped tight by means of the top small screw. The other screws, seen at the upper end of the axis, are for centring and tilting the crystal so as to bring the edges truly vertical. The remaining parts of the instrument are :—the divided circle,

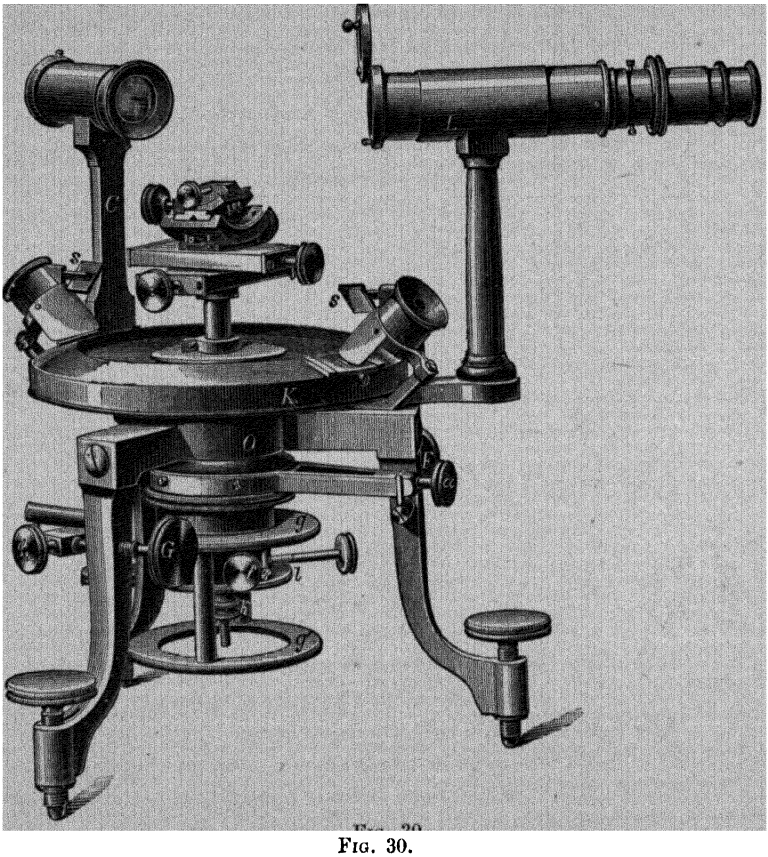


FIG. 30.

K (provided with verniers ss for taking the readings), which is clamped to the central axis, the whole being rotatable by means of the milled ring, g', at the bottom of the instrument. Light from an incandescent burner is sent through a slit at the end of the collimator C and falls on the crystal. The telescope L is fixed at a convenient angle to C (say a little over a right angle), and the crystal is rotated till the image of the slit, reflected from a face, comes on to the cross-wires in the telescope. When

the reading has been taken, the crystal is rotated and successive readings are noted for the various faces till a full rotation of 360° has been carried out. The differences between successive readings will be found to be 60° 0′. The position of one of the faces while a reading is being taken, as viewed from the top of the instrument, is shown in Fig. 31. It is seen that the normal to the face, namely *N*, bisects the angle between collimator and telescope, and in order to bring the next face into the same position it is necessary to rotate the crystal 60°. It follows that the angle actually measured is the outside angle, or the angle between the normals to the two faces, and not the internal angle, which in this case would be 120°. These outside measured angles are the ones usually employed in modern writings, a fact which should be borne in mind. After a complete zone has been measured, the crystal is removed, and adjusted on the wax with another set of faces vertical, and the process is repeated till all the faces have been measured.

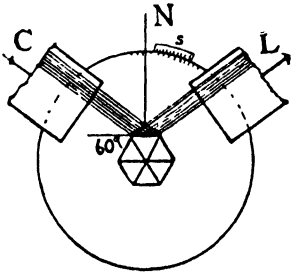


FIG. 31.

As will be shown in the next section, the angles between edges have great theoretical significance. The simple goniometer just described records only the angles between pairs of faces ("interfacial angles"); from them the angles between the various edges can be obtained by simple trigonometrical calculation. In recent years, however, goniometers have been constructed provided with two, or even three, divided circles which admit of a direct measurement of the angles between edges as well as the interfacial angles.

98 *The Fundamental Law of Geometrical Crystallography.*— The difference in appearance between two crystals of the same substance, even when they are of the same crop, may be due to another factor besides distortion, viz., a difference in the number of faces: not only may some faces be suppressed, but in addition to the usual faces a crystal may occasionally exhibit an altogether new set of faces. It is therefore not surprising that the view was formerly held that each individual crystal has its own shape; and it was only after crystals began to be measured that a simple mathematical relationship was discovered between the various shapes. The nature of this relationship will now be discussed.

Crystals of common salt are generally cubes with small triangular facets on the corners (Fig. 32); the latter on measurement are found to be inclined to one another at the same angles as the faces of a regular octahedron. Through the centre, *O*, of the crystal let three axes, *OX*, *OY*, and *OZ*, be drawn parallel to the three cube edges. Now imagine the facet, *p*, extended in space till it meets the axes in the points *A*, *B*, *C*; the lengths *OA*, *OB*, *OC* are the *intercepts* of the face *p* on the axes *OX*, *OY*, and *OZ*. The actual lengths *OA*, *OB*, *OC* obviously depend on the perpendicular distance of the face *p* from the point *O* at the centre of the crystal, and as a crystal grows they will all increase in magnitude. Since, however, during

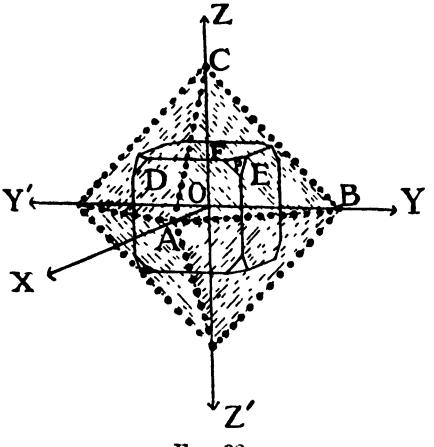


FIG. 32.

growth the face *p* remains parallel to itself, the ratios of the three intercepts, viz. *OA* : *OB* : *OC* remain constant. These ratios, generally denoted by $a : b : c$, are termed the *parametral ratios* (or *axial ratios*) of the crystal, the face *p* the *parametral plane*, and the three axes, *OX*, *OY*, *OZ*, the *crystallographic axes*.

It is thus found that the intercepts of any other face of the crystal can be expressed by the ratios $ma : nb : oc$, where *m*, *n*, and *o* are rational whole numbers (or in some cases infinity). This relation is known as the *Law of Rational Intercepts* and has been verified in every case investigated.

In the instance just considered (viz., salt) $a = b = c$, but in other substances they may be unequal.

If the other three front corner facets be extended in a precisely similar manner it is found that their intercepts have

exactly the same rations $a : b : c$, but when allowance is made for the fact that they intercept certain of the axes towards their negative ends (X', Y', Z'), the intercept ratios of the three facets are seen to be $a : -b : c$, $a : -b : -c$, and $a : b : -c$. The extensions of the four corresponding facets at the back of the crystal are not put into the figure; they have this in common, that they meet the negative end of the axis OX.

The intercepts of the three faces D, E, F must now be considered. To take D. The axes OY and OZ were drawn parallel to the edges between DF and DE respectively, *i.e.*, to two directions lying in the plane D. Since, however, they were drawn through the centre of the crystal which lies at the back of D, it is easy to see that however far the plane D be extended, it will never meet the axes OY and OZ. Its intercepts, then, on these axes are of infinite length. Its intercept on the axis OX is finite and the ratios of the intercepts of the face D are $1a : \infty b : \infty c$. Similarly, the intercepts of the faces E and F are in the ratios $\infty a : 1b : \infty c$, and $\infty a : \infty b : 1c$.

The parametral or axial ratios, $a : b : c$, are calculated by trigonometrical methods from the measured angles. Now, *with the exception of crystals belonging to the cubic system* (p. 202) the angles of no two substances are alike, and it follows that *the parametral ratios have different numerical values for each separate substance.*

Millerian Indices.—It is convenient to replace the system of intercepts by one of "indices," the use of which was introduced by W. H. Miller. The indices of any face are derived from the intercepts by a simple algebraic transformation. For example, the intercepts $1a : \infty b : \infty c$ may be written in the form $\frac{a}{1} : \frac{b}{0} : \frac{c}{0}$ $\left(\text{for } \frac{b}{0} = \infty b, \text{ etc.}\right)$; the denominators 1, 0, 0, enclosed in a bracket, thus (100), are the *indices* of the face D (Fig. 32). Similarly, we obtain E-(010) and F-(001). The intercepts of p, viz., $1a : 1b : 1c$, become $\frac{a}{1} : \frac{b}{1} : \frac{c}{1}$, hence the indices are (111). It will be noted that when a face is parallel to any axis its intercept is ∞, and the corresponding index is 0. In the case of a negative intercept the minus sign is placed over the corresponding index. The indices of all the faces are shown in Fig. 33. The indices of a face constitute its *symbol*, and the symbol determines unambiguously the direction of the face on the crystal: thus

(213) means that the face has intercepts in the ratios $\frac{a}{2}:\frac{b}{1}:\frac{c}{3}$, where a, b, and c are the parametral lengths of the crystal in question.

Form.—This term, in addition to its ordinary meaning "shape," is employed in a very special sense in crystallography, the precise nature of which will now be explained. As has already been stated the physical properties of a crystal vary with the direction; *e.g.*, the cohesion of a crystal is less in certain directions than in others, and the difference is often so pronounced that on subjecting the crystal to fracture it breaks quite easily along certain planes so as to afford brilliantly reflecting *cleavage* surfaces. A crystal of common salt may be easily cleaved into thin flakes parallel to the three faces *D*, *E*, *F*, whilst attempts to break the crystal in other directions, say along the octahedra facets, merely lead to very irregular fractures. The perfection of the cleavage is exactly the same for the three pairs of cube faces, and the same absolute similarity is found to extend to every physical property that has been investigated. Again, the four octahedral planes are similar in every respect. Such a *group of physically similar faces* is known as a *form*; the six cube faces constitute the cube form, the eight octahedron faces the octahedron form. When several forms are developed on the same crystal it is said to exhibit a combination of forms.

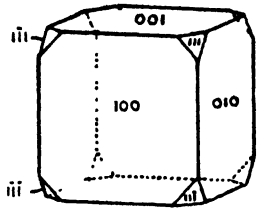


FIG. 33.

It will be noted that the indices of the faces constituting the cube and octahedron forms are permutations of the numbers (100) and (111) respectively, including plus and negative signs. This regularity has really resulted from a wise choice of the three crystallographic axes and parametral plane, and is very desirable, since crystallographic descriptions are much simplified thereby. A complete form is often denoted by enclosing the indices of one of the faces in broken brackets, *e.g.*, {111} designates the whole octahedral form.

SYMMETRY OF CRYSTALS.

99 Symmetry is a property of frequent occurrence in natural objects: the higher forms of life are characterised externally by

bi-lateral symmetry—the two halves bearing a very obvious relationship to each other. But it is in the crystal kingdom that symmetry reaches its highest form, for, as a rule, not only does the external form exhibit symmetry of a high order, but a study of the physical properties discloses the fact that the internal structure is also endowed with symmetry; and the conclusion may be safely drawn that the symmetry of external form is a manifestation of a unique, and regular, molecular arrangement. The form of a crystal often appears to be of a most complicated character, but when viewed in the light of symmetry it never fails to acquire the utmost simplicity. Symmetry again provides a sure basis of classification with regard to both the external form and the physical properties. There are three kinds or "elements" of symmetry to be considered: plane, axis, and centre of symmetry.

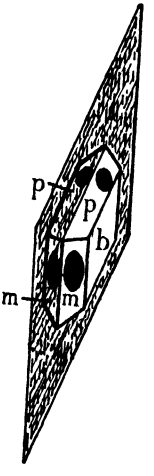


Fig. 34.

Plane of Symmetry.—Any object which can be divided into two halves, so that one half is, as it were, the mirror image of the other across the plane of bisection is said to exhibit a *plane of symmetry*. Thus in Fig. 34, representing a crystal of gypsum, $CaSO_4,2H_2O$, the plane of symmetry which bisects the crystal parallel to the face *b* is indicated by shading, and it is seen that the two faces, *mm*, occupy mirror image positions with respect to that plane: the same holds for the other faces, *pp* and *bb*, as well as all the edges on the crystal. Such a crystal is said to have a plane of symmetry parallel to *b*. The symmetrical character of the crystal about this plane in regard to physical properties can be proved by means of a simple experiment. On pressing the point of a red-hot needle against the faces, dehydration commences and as a result of a difference of the conductivity for heat in different directions, elliptical, and not circular, opaque rings of plaster of Paris are formed, which show up very well against the clear, unaffected parts of the crystal. Now on examination it is found that not only are the ellipses on the faces *mm* similar in curvature but also in orientation with respect to the plane of symmetry. Further proof of the existence of the same plane of symmetry in the physical sense is afforded by the relative orientation and curvature of the ellipses on the faces *pp*.

Axes of Symmetry.—If the crystal of potassium periodate, KIO_4 (Fig. 35), be rotated about the vertical axis, Z through an angle of 90°, the face o_1 will come into the position of o_2, o_3 into o_4, d_1 into d_2, etc. Further rotations of 90° serve to bring every part of the figure again into coincidence. Such an axis of rotation is termed an *axis of symmetry*, and as complete coincidence occurs four times during a complete rotation of 360°, the axis is designated *four-fold* or *tetragonal*. On the other hand, when rotated about the axis Y the rotation necessary to bring each face into the position formerly occupied by a similar face is 180°; so that this direction is termed a *two-fold* or *digonal axis of symmetry*. The crystal of apatite (Fig. 36) has a vertical axis of *six-fold* or *hexagonal symmetry* emerging through the centre of the top face, whilst in the crystal of sodium periodate, $NaIO_4,3H_2O$

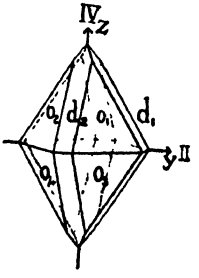


Fig. 35.

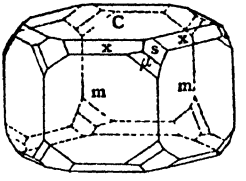


Fig. 36.

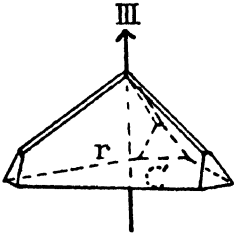


Fig. 37.

(Fig. 37), the vertical direction is one of *three-fold* or *trigonal symmetry*.

Alternating Axes of Symmetry.—Crystals of urea, $CO(NH_2)_2$, Fig. 38, appear at first sight to have a vertical axis of two-fold symmetry. But consider the face p_1: if it be rotated 90° about the vertical axis and subsequently reflected across the horizontal, shaded plane it comes into the position of p_2, and the same coincidence holds for the crystal as a whole. An axis of symmetry of this peculiar character is termed an *alternating axis of four-fold symmetry*. An *alternating axis of six-fold symmetry* is exhibited by the mineral calcite, $CaCO_3$, a rare form of which is shown in Fig. 39. The crystal appears to have a vertical six-fold axis of ordinary symmetry. If, however, the crystal be immersed in a dilute solution of hydrochloric acid for a few seconds, then washed free from the acid and viewed with a lens, etched figures are seen. These figures are due to the fact that the solubility of a crystal is different along different directions,

but the same along similar directions; the etched figures have, moreover, a similar form and a symmetrical orientation on similar faces. Although the form of the figures is the same on all the vertical faces, yet the orientation is only similar on alternate faces; if the etched figures be rotated 60° about the vertical axis and then inverted by reflection across a horizontal plane, coincidence becomes complete: the vertical axis is really an alternating six-fold axis of symmetry. Reliance on the geometrical form often suggests too high a symmetry; the method of exploring crystal structures by means of etched figures is most valuable in unmasking the true symmetry.

Centre of Symmetry.—When the physical and geometrical

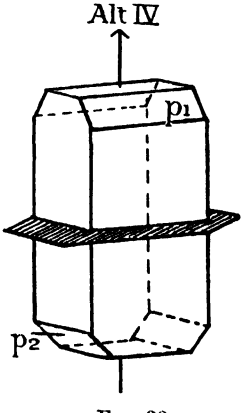


FIG. 38.

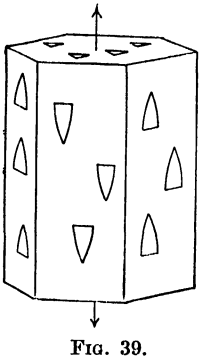


FIG. 39.

properties of a crystal are the same along both directions of each and every line in the crystal, the crystal is said to possess a *centre of symmetry.* The presence of a centre of symmetry is shown geometrically when each and every face is accompanied by a similar parallel face; *e.g.*, the crystal of copper sulphate, $CuSO_4,5H_2O$, shown in Fig. 40.

It must be remarked that a crystal need not necessarily possess any of the above elements of symmetry. Such a crystal is completely asymmetric in the fullest sense. Calcium thiosulphate, $CaS_2O_3,6H_2O$, is an example (Fig. 41); it will be noticed that several of the faces have no corresponding parallel faces at the back.

100 *The Thirty-two Classes of Crystals.*—The various elements of symmetry which have been described are the only kinds

exhibited by crystals, and it is easy to show that no other elements of symmetry are possible in a body obeying the law of rational intercepts: *e.g.*, a five- (seven- eight-, etc.) fold axis of symmetry would lead to the development of faces with irrational intercepts. Now most of the crystals used as illustrations in the preceding section possess more symmetry than was actually mentioned; most of those containing axes of symmetry also exhibit one or more planes of symmetry, and also a centre of symmetry. The following question then arises: "What combinations of the various elements of symmetry are possible in a crystal obeying the law of rational intercepts?" This mathematical problem

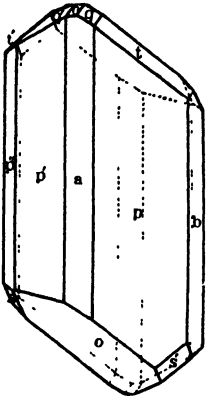


Fig. 40.

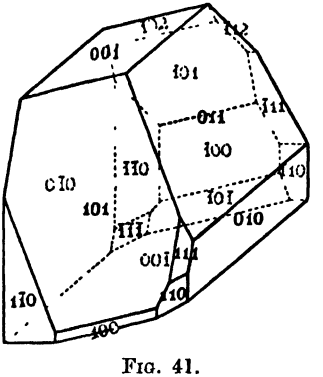


Fig. 41.

has been completely solved, and the number of classes, or combinations of symmetry, is thirty-one; adding to this the asymmetric class, the number thirty-two is finally obtained. Of the thirty-two classes theoretically possible, representatives of at least thirty have been recognised amongst the substances already measured. The number of substances crystallising in each class is very disproportionate; one or two of the classes are hitherto only represented by a single substance, whilst others include many thousands. A reference-list of the thirty-two classes is given on page 209.

The word *form* has already been defined as the collection of faces having similar physical properties; it must be added that they must also be similar in the geometrical sense. Now, even in the same crystal, the number of faces constituting the various forms is not the same. In the crystal of sodium periodate (Fig. 37, p. 192) the vertical three-fold axis is the only element

of symmetry, and it is perpendicular to the base *C*. On rotating the crystal through angles of 120° about this axis, the face *C* never occupies any other direction in space; but a face like *r* on such rotation gives rise to two other similar faces. The form *r* therefore consists of three faces, whilst the form *C* is represented by one face. It may be stated that the number of faces constituting the form depends on the relative position of the faces with regard to the elements of symmetry. In those classes where there are several elements of symmetry, the possibility of variation is naturally greatly increased.

101 *The Seven Systems.*—In addition to the division into the thirty-two classes according to symmetry there has long been in use another classification of a coarser character, viz. into the seven "systems." The latter classification was already in use before the question as to the possible number of classes of symmetry had been exhaustively studied. When the crystallographic axes and parametral face have been chosen so that the various faces of a form obtain similar intercepts, or in other words similar indices, it is found that the relative inclination of the axes and their parametral lengths correspond to one of the following seven cases, or *systems*, and the crystal is reckoned as belonging to that system :

Crystallographic Axes and Parameters.	System.
1. Three axes unequally inclined; with unequal parameters	Triclinic, Anorthic or Asymmetric.
2. Three axes, one perpendicular to the other two; with unequal parameters	Monoclinic or Monosymmetric.
3. Three axes, all at right angles; with unequal parameters	Rhombic or Orthorhombic.
4. Three axes, all at right angles; with two out of the three parameters equal	Tetragonal or Quadratic.
5. Three axes, mutually inclined at equal angles (not a right angle); with all three parameters equal	Rhombohedral or Trigonal.
6. Four axes, one perpendicular to the remaining three, which are mutually inclined at 60°; with parameters of the last three axes equal	Hexagonal.
7. Three axes, mutually perpendicular; with all three parameters equal	Cubic, Tesseral or Regular.

In this way the thirty-two classes may be distributed into seven systems. The classes which fall within one and the same system bear a pronounced family likeness : the class with highest symmetry contains all the elements of symmetry exhibited by the other classes in the same system and, except in the trigonal system, is the most common class. In the following short description of the various systems, the most common class

will be the one selected to represent each system; a few of the remaining, less symmetrical, classes which are of chemical interest will be discussed subsequently.

It can be proved that the direction (1) of an axis of symmetry or (2) of a line perpendicular to a plane of symmetry, is a possible edge, *i. e.* an edge between faces having rational intercepts; and it is therefore permissible to use such directions as crystallographic axes although they may not be actually developed as edges. It should be noted that axes of symmetry and crystallographic axes are not interconvertible terms; the latter are as a rule chosen parallel to the former, but this is not always so. Moreover, there is often a greater number of axes of symmetry than of crystallographic axes, the number of the latter being only three, with the single exception of the hexagonal system, which has four.

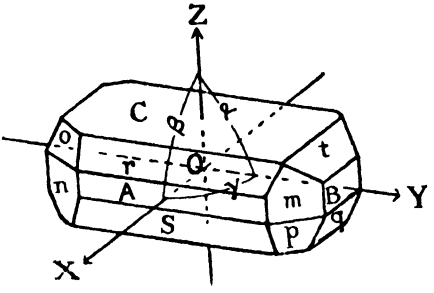


Fig. 42.

1. The Triclinic, Anorthic, or Asymmetric System.

102 The three crystallographic axes, OX, OY, OZ, may be selected parallel to any three edges on the crystal, and are in any case inclined at different angles, usually denoted by α, β, and γ. The parametral lengths of these three axes are unequal.

Example.—Potassium dichromate, $K_2Cr_2O_7$. (Fig. 42.)

$a : b : c = 1{\cdot}0116 : 1 : 1{\cdot}8146$; $\alpha = 98° 0'$, $\beta = 96° 13'$, $\gamma = 90° 51'$.

Symmetry: A centre of symmetry; each form therefore consists of a pair of parallel faces.

The edges selected for the directions of the three crystallographic axes, OX, OY, and OZ, are those between the faces B and C, C and A, A and B respectively, from which it follows that the faces A, B, C will have the indices (100), (010), (001) respectively. The parametral face chosen is p, and since it cuts the axis OZ

at its negative end, the indices of p must be $(11\bar{1})$. The ratios of the parameters $a : b : c$, as also the angles α, β, and γ, are calculated from the angles which these four faces make with each other. The remaining faces are then found to have the following indices: s $(10\bar{1})$, r (101), m (110), n $(1\bar{1}0)$, q $(01\bar{1})$, t (012), o $(1\bar{1}1)$.

2. The Monoclinic or Monosymmetric System.

103 One of the crystallographic axes, namely OY, is taken parallel to the only edge on the crystal which is found to be perpendicular to two other edges, and the latter are chosen for the directions of the two crystallographic axes, OX and OZ.

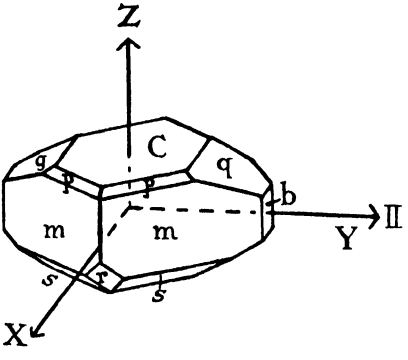


Fig. 43.

The latter axes are not inclined at 90°, but at some other angle, β.

Example.—Rubidium magnesium sulphate,

$$Rb_2Mg(SO_4)_2,6H_2O \text{ (Fig. 43).}$$
$$a : b : c = 0{\cdot}7400 : 1 : 0{\cdot}4975; \beta = 105° 59'.$$

Symmetry (Class 5).—One plane of symmetry containing the axes OX, OZ, perpendicular to which is a two-fold axis of symmetry (the axis OY); also a centre of symmetry.

The axis OX is parallel to the edge cq, OZ to mm. The axis OY is a possible edge, since it is parallel to the two-fold axis of symmetry; it is the edge in which c and r would intersect. The parametral plane is p (111), the remaining forms being m {110}, s {11$\bar{1}$}, and q {011}, each consisting of four faces; and c {001}, b {010} and r {20$\bar{1}$}, each consisting of two faces. There is an imperfect cleavage parallel to the last-mentioned face.

Another example of a monoclinic crystal is gypsum (Fig. 34, p. 191).

3. The Rhombic or Orthorhombic System.

104 The three crystallographic axes, *OX*, *OY*, and *OZ*, are taken parallel to a particular set of edges (or possible edges) mutually perpendicular to one another. A face which is inclined to all these directions is selected as parametral plane, and gives three unequal parameters.

Example.—Potassium sulphate, K_2SO_4 (Fig. 44).

$$a : b : c = 0{\cdot}5727 : 1 : 0{\cdot}7418.$$

Symmetry (Class 8).—Three planes of symmetry at right angles to one another (Fig. 45), intersecting in three two-fold axes of symmetry; also a centre of symmetry.

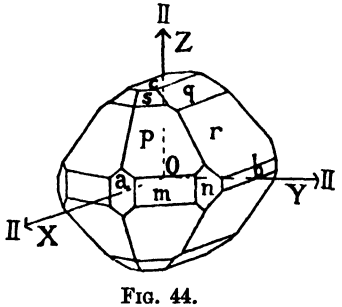


Fig. 44.

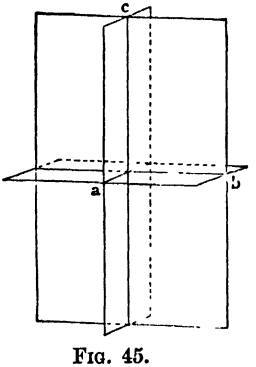


Fig. 45.

The crystallographic axes, *OX*, *OZ*, are taken parallel to the edges *cq* and *am* respectively. The axis *OY* is not developed as an actual edge, but this direction, as well as those of *OX* and *OZ*, is one of two-fold symmetry. The parametral plane is *p* and has therefore the indices (111). The forms *a* {100}, *b* {010}, and *c* {001}, which are parallel to two of the axes, consist of a pair of parallel faces; forms like *m* {110}, *n* {130}, *q* {011}, and *r* {021}, which are parallel to one axis and intersect the other two, consist of four faces; finally, forms like *p* {111}, and *s* {112}, which intersect all three axes, consist of eight faces.

Other examples are aragonite, $CaCO_3$ (Fig. 46), and potassium perchlorate, $KClO_4$, a crystal of which is shown in Fig. 47.

The forms in the first mentioned are :—the parametral plane *o* {111}, *b* {010}, *p* {110} and *q* {011}; and the parametral ratios

are $a : b : c = 0{\cdot}623 : 1 : 0{\cdot}721$. In potassium perchlorate the forms are: c {001}, a {100}, b {010}, q {011}, m {110} and r {102}. In this crystal there is no face intersecting all three axes, so recourse must be had to two parametral faces, viz., m, which

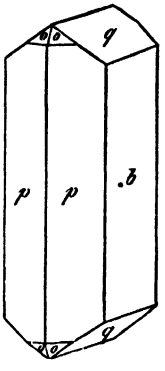


Fig. 46.

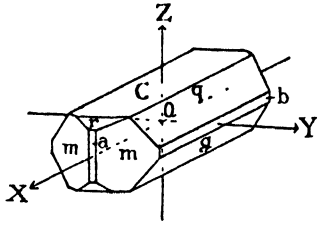


Fig. 47.

decides the ratio $a : b$, and q, from which the ratio $b : c$ is calculated; $a : b : c = 0{\cdot}7815 : 1 : 1{\cdot}2805$.

4. The Tetragonal or Quadratic System.

105 The crystallographic axes, OX, OY, and OZ, are mutually perpendicular, OZ being taken parallel to the unique axis of

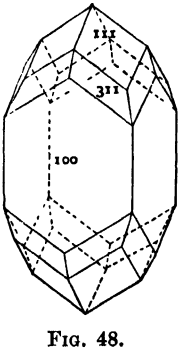


Fig. 48.

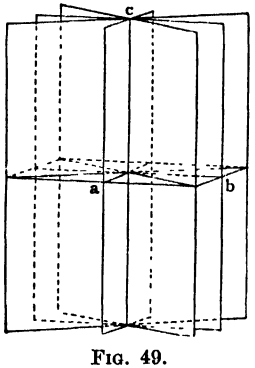


Fig. 49.

four-fold symmetry (or of the alternating axis of four-fold symmetry). The parametral lengths of the axes OX and OY are equal, but have a different value from that of the axis OZ.

Example.—Zircon, $ZrSiO_4$ (Fig. 48).

$$a = b;\ a : c = 1 : 0{\cdot}640.$$

Symmetry (Class 15).—One vertical four-fold axis which is perpendicular to four two-fold axes intersecting at angles of 45°. These five axes of symmetry are respectively perpendicular to the horizontal and the four vertical planes of symmetry shown in Fig. 49.

In Fig. 48, the parametral plane is (111), which is seen to consist of eight faces. The form {100} consists of four faces, and the form {311} consists of sixteen faces.

5. The Rhombohedral or Trigonal System.

106 The most characteristic form of this system is the rhombohedron (Fig. 50), and the three crystallographic axes, *OX*, *OY*, and *OZ*, are drawn parallel to the three edges of this form. The parametral lengths are equal. The angles between the three axes, *OX*, *OY*, and *OZ*, are equal, but not right angles; these angles are denoted by α, and are calculated from the measured angles between the faces of the rhombohedron.

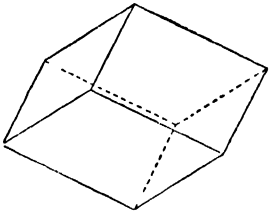


Fig. 50.

Example.—Sodium nitrate, $NaNO_3$; $\alpha = 102° 47'$. Form, the simple rhombohedron (Fig. 51).

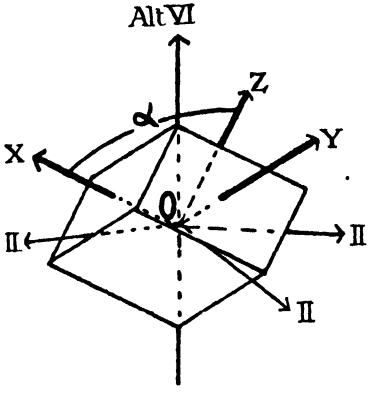


Fig. 51.

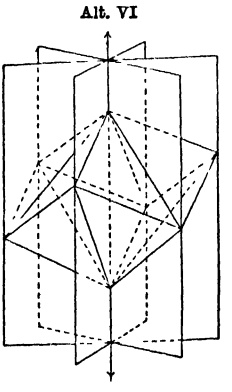


Fig 52.

Symmetry (Class 21).—Three vertical planes of symmetry (Fig. 52), perpendicular to each of which there is a two-fold axis of symmetry, emerging at the middle point of each of the zig-zag edges (Fig. 51), and further a vertical axis of alternating six-fold symmetry. It will be noted that none of the crystallographic axes is chosen either parallel to an axis of symmetry,

or perpendicular to a plane of symmetry. Although somewhat arbitrary, it is only by means of this choice that similar faces acquire similar intercepts and indices.

Other examples are the minerals of the calcite group.

6. The Hexagonal System.

107 Here, again, the choice of crystallographic axes is peculiar, since it is found advisable to select no fewer than four. The

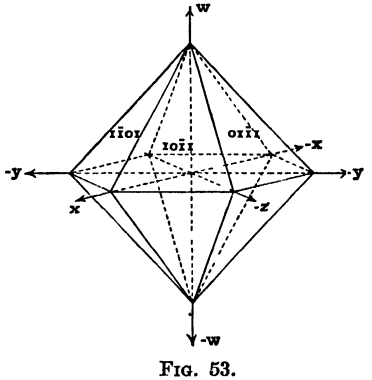


Fig. 53.

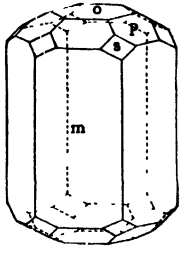


Fig. 54.

disposition of the three axes X, Y, Z, intersecting at angles of 120°, and of the fourth axis W, which is perpendicular thereto, is shown in Fig. 53. The parameters a_1, a_2, a_3 of the axes X, Y, Z are equal, but the parameter c of the fourth axis has a different value. The parametral ratio $a : c$ is calculated from the angles between the faces shown on the figure.

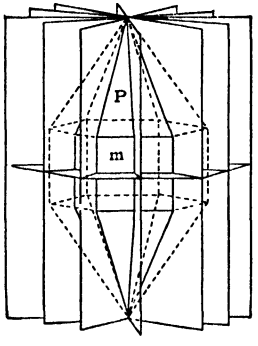


Fig. 55.

Example.—Beryl (emerald), $a : c = 1 : 0{\cdot}4989$ (Fig. 54).

Symmetry (Class 27).—A vertical axis of six-fold symmetry and six two-fold axes of symmetry, intersecting at angles of 30° in the horizontal plane; each being respectively perpendicular to the single horizontal and the six vertical planes of symmetry shown in Fig. 55; also a centre of symmetry.

Since there are four crystallographic axes, each face has four intercepts.

The forms in Fig. 54 are $m\{10\bar{1}0\}$, $p\{01\bar{1}1\}$, $s\{11\bar{2}1\}$, and $c\{0001\}$.

7. The Cubic, Tesseral, or Regular System.

108 Crystals of this system are referable to three mutually perpendicular crystallographic axes, with equal parameters, *i.e.*, $a = b = c$.

Examples:—Fluorspar, CaF_2; cubes with octahedral facets

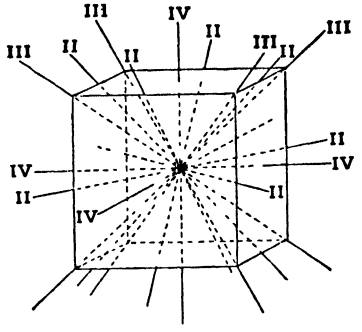


Fig. 56.

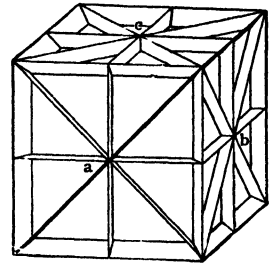


Fig. 57

(Fig. 33, p. 190). Senarmontite, Sb_2O_3; regular octahedra (Fig. 32, p. 188). Garnet: Rhombic dodecahedra (Fig. 59).

Symmetry (Class 32).—The symmetry is the highest possible in all crystals and is identical with that of a cube, viz., four three-fold axes emerging through the corners, *i.e.*, perpendicular to the octahedron faces; three four-fold axes parallel to the

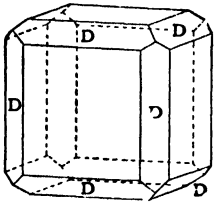


Fig. 58.

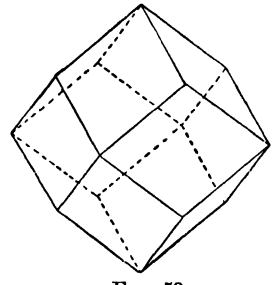


Fig. 59.

cube edges, *i.e.*, perpendicular to the cube faces; six two-fold axes emerging at the mid-point of the cube edges, *i.e.*, perpendicular to the dodecahedral faces (Fig. 56). Further, three planes of symmetry parallel to the cube faces, and six diagonal planes of symmetry parallel to the dodecahedral faces (Fig. 57); also a centre of symmetry.

The relationship of the rhombic dodecahedron to the cube will become clear from an inspection of Figs. 58 and 59. In

the first figure the dodecahedral faces are seen to truncate the twelve edges of the cube. If the twelve facets be extended in space, so as to eliminate the cube faces, they ultimately yield the simple rhombic dodecahedron of Fig. 59.

ENANTIOMORPHISM.

109 Many natural objects are not identical with their mirror images; the reflection of a right hand in a plane mirror appears to be a left hand; so that although the two hands are certainly similar, the one is easily distinguishable from the other. Bodies which can exist in two non-superposable forms which are the mirror images of each other are termed enantiomorphous. The study of geometry has led to the recognition that only those bodies can exist in enantiomorphous forms which are devoid of the following three elements of symmetry: plane, centre, and alternating axis of symmetry. The only elements of symmetry compatible with enantiomorphism are the ordinary axes of symmetry. These conditions are satisfied by eleven out of the thirty-two classes of symmetry, and examples of enantiomorphism have been discovered in crystals belonging to all these classes.

Geometrical Evidence of Enantiomorphism in Crystals.—The more important faces on crystals of magnesium sulphate, $MgSO_4,7H_2O$, are shown in Fig. 60. The crystals are orthorhombic with $a : b : c = 0{\cdot}9901 : 1 : 0{\cdot}5709$, and appear to have three planes of symmetry (shaded), and three two-fold axes of symmetry as indicated. The development of the crystals, however, is sometimes of a less symmetrical character, and two kinds of crystals may be distinguished (Figs. 61 and 62). Of the eight terminal faces in Fig. 60, only half are developed on the first crystal, the remaining half on the other crystal. The effect of this "*hemihedral*" development of the terminal faces is to indicate the absence of the three planes of symmetry; nor is there a centre of symmetry, for the faces no longer all appear in parallel pairs. The crystals still possess the three two-fold axes of symmetry, and are enantiomorphous, one being the non-superposable mirror image of the other. It may be noted that the enantiomorphism is outwardly indicated on the crystals by the p faces; each set of four p faces constitutes a form, the two forms being symbolised by p {111} and p' {1$\bar{1}$1} respectively. When both these forms are developed, Fig. 60 is obtained, and

the crystal appears to have both planes, and a centre of symmetry. The form *m* {110} consists of four faces on all the three crystals and does not afford any clue to the class of symmetry. In fact, only faces like *p*, which consist of half the usual number of faces, really unmask the true symmetry and exhibit geometrical enantiomorphism. In certain classes of the cubic and tetragonal systems a form may consist of only a *quarter* of the usual number of faces, and on this account is termed *tetartohedral.*

The first known example of enantiomorphism was quartz. The usual development of this mineral is that already shown in Fig. 27, p. 184, which appears to have a centre, as well as several

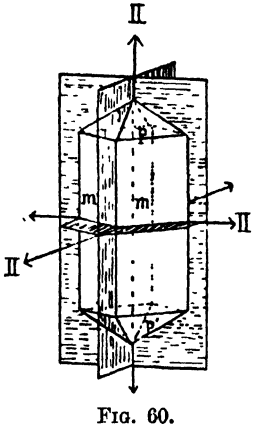


Fig. 60.

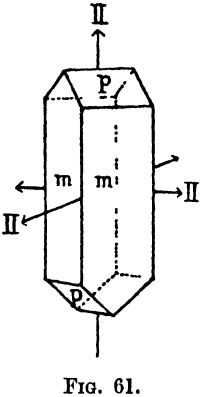


Fig. 61.

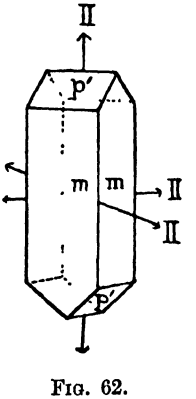


Fig. 62.

planes, of symmetry; but etched figures prove the absence of all these elements of symmetry. Moreover, the enantiomorphism is sometimes demonstrated by the appearance of hemihedral facets, labelled *x* on Figs. 63 and 64, which distinguish the two kinds of crystal; the two crystals are called right- and left-handed respectively, or dextro- and lævo-crystals.

110 *Optical Activity or Rotatory Polarisation.*—The enantiomorphous development of a crystal is due to a corresponding enantiomorphism of its internal structure, or in other words, to the fact that the arrangement of the molecules is devoid of a centre, plane, or alternating axis of symmetry. The structure is of course the same for a given substance, whether hemihedral faces are developed or not. It has been discovered that most substances crystallising in enantiomorphous forms are endowed with optical activity, *i.e.*, the power of rotating the plane

of polarised light. This property was found in quartz by Arago, and soon after it was proved by Herschel that a crystal having the development of Fig. 63 effects a clock-wise or *dextro*-rotation whilst the quartz of Fig. 64 is optically active in the opposite sense (*laevo*). Whether a given quartz crystal, devoid of hemihedral facets, is dextro or lævo can be easily settled by a simple optical determination.

The fact that certain enantiomorphous crystals are devoid of optical activity has received a satisfactory theoretical explanation, which cannot be entered into here. An example is sal-ammoniac (cubic system, class 29).

Certain substances preserve their optical activity when dissolved, liquefied, or vaporised: not so the remainder. An

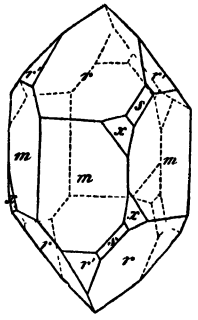


Fig. 63.

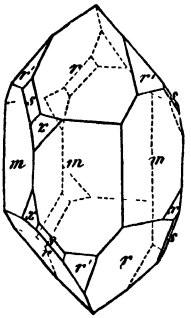


Fig. 64.

example of the first kind is tartaric acid; quartz and magnesium sulphate, on the other hand, are examples of the second kind. In the latter cases, the seat of the activity must lie in an enantiomorphous grouping of molecules in the crystal edifice. In the former case, the primary cause is evidently an enantiomorphous grouping of atoms within the molecule (see p. 227).

Twin Crystals or Macles.—Sometimes two ("*twins*") or more ("*trillings*," "*fourlings*," etc.) crystals are grown together in a symmetrical manner, so that the various individuals present a recognisable regularity of orientation. Cassiterite, SnO_2, for example, often occurs in the elbow form of Fig. 65, which is clearly a combination of two crystals, each being the reflection of the other across a plane—"*twin plane*"—which happens to be the plane of contact. The couplet of fluorspar crystals (simple cubes of Fig. 66) is an interpenetration twin, and the orientation of one crystal is derivable from that of the other by

a rotation of 180° about the diagonal emerging through the common corner; this direction of rotation is called the *twin axis*. Such groups of crystals are regarded as twins only when the plane of reflection (or the axis of rotation) is parallel to a possible face (or a possible edge); and other groupings are regarded as accidental.

The twinning of enantiomorphous crystals deserves especial mention. Combinations are sometimes observed in which the two individuals are symmetrical about a plane. Now reflection of a dextro-crystal across a plane yields a lævo-crystal; such "twins," then, are really combinations of dextro- and lævo-individuals. If the two individuals interpenetrate each other

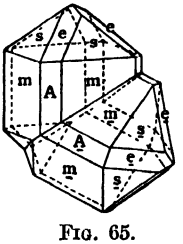


FIG. 65.

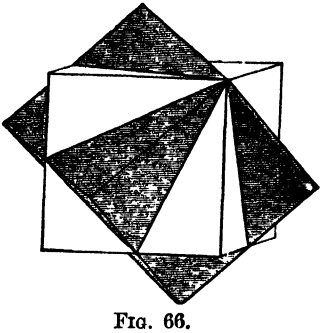


FIG. 66.

very thoroughly the result may appear to be a single crystal, and if the conditions have been favourable for the development of hemihedral facets, both sets will appear. This interesting property is of quite frequent occurrence in quartz, apparently single crystals of which sometimes exhibit both sets of x faces; when subjected to optical examination they are found to be composed of dextro- and lævo-material. Kipping and Pope [1] have shown that this mutual interpenetration provides a simple explanation of the general behaviour of "pseudo-racemic" substances.

OPTICAL, THERMAL, AND ELECTRICAL PROPERTIES OF CRYSTALS.

111 In general it may be stated that the physical properties of a crystal vary with the direction; but directions which are similar in the geometrical sense are also physically equivalent,

[1] Kipping and Pope, *Journ. Chem. Soc.*, 1897, **71**, 989.

so that the investigation of the physical properties often sheds valuable light on the symmetry.

Optical Properties of Crystals.—The relations of crystals to light are of great importance, as enabling us to determine crystalline symmetry in cases in which the usual methods either give uncertain results or fail entirely. Transparent crystals belonging to the regular system exert no peculiar action on a ray of light; they behave in this respect like glass or any other amorphous substance. The incident ray gives rise to one refracted ray, and the crystal possesses one refractive index.[1]

All other crystals are doubly refractive, and they are further subdivided into uniaxial and biaxial crystals.

The uniaxial crystals comprise those of the rhombohedral, hexagonal and tetragonal systems. In one direction, termed the optic axis, which is parallel to the principal axis of symmetry, no double refraction occurs, but in all others the incident ray is doubly refracted, forming two plane-polarised rays, one of which, the ordinary ray, follows the ordinary law of refraction, whilst the other, the extraordinary ray, does not in general follow this law.

The biaxial crystals comprise those of the rhombic, monoclinic, and triclinic systems. In them, incident light is doubly refracted, yielding two extraordinary plane-polarised rays. They possess, however, two directions in which a ray is singly refracted, and these are called the optic axes. The angle between the optic axes of a biaxial crystal is an important constant of the crystal. Thus, for example, with sodium light it is 69° 5′ for rhombic sulphur, 47° 54′ for the monoclinic potassium magnesium sulphate, and 76° 36′ for the triclinic albite.

Thermal Properties.—Crystals which belong to the cubic system expand equally in every direction when heated, but for crystals belonging to other systems the expansion in general varies with the direction. A sphere cut out of a cubic crystal remains a sphere, but one cut out of a crystal belonging to the uniaxial systems (rhombohedral, tetragonal, and hexagonal) becomes an ellipsoid of rotation, the axis of rotation being coincident with the principal axis of symmetry; while in the case of the biaxial systems (rhombic, monoclinic, and triclinic), the sphere

[1] Cases have indeed been observed by Brewster and others in which a crystal belonging to the cubic system exhibits double refraction, but this is due to unequal tension in the mass of the crystal, and resembles the case of double refraction by unequally heated or compressed glass.

expands into an ellipsoid with three unequal, rectangular axes. As a result of the unequal expansion a small change is noted in at any rate some of the interfacial angles on raising the temperature. Cubic crystals, however, retain their angles unchanged.

Similar relationships hold good for heat conduction. The conducting power of crystals can be studied by covering the face of a crystal with a thin coating of melted wax, allowing the wax to solidify, and then bringing the point of a hot needle through the wax coating into contact with the crystal. If the crystals contain water of crystallisation, wax may be unnecessary (see p. 191). If the crystals conduct equally in all directions in the plane of the face, the wax will melt in a circle of which the hot point is the centre; this is the case with all cubic crystals. If the conduction be unequal, the melted wax assumes the form of an ellipse. The ellipses on similar faces have similar curvature and orientation.

Pyro-electric Behaviour of Crystals.—Certain badly conducting crystals when heated exhibit a peculiar development of electricity, one end of the crystal becoming negatively electrified, whilst the other end exhibits positive electricity. Such crystals are termed pyro-electric.

This phenomenon can naturally occur only in crystals which have no centre of symmetry, for the latter involves a similarity of physical properties in opposite directions along every line. If the polar ends of the crystal correspond to the two ends of an axis of symmetry, that axis is said to be polar. Polarity along an axis conclusively proves the absence of a plane of symmetry perpendicular thereto, and pyro-electricity is therefore a valuable help in the determination of symmetry. Examples of crystals possessing one polar axis are the minerals hemimorphite and tourmaline (classes 7 and 20 respectively); quartz exhibits three, and boracite four, polar axes.

Certain enantiomorphous crystals exhibit pyro-electricity, *e. g.* tartaric acid (class 4); the dextro- and lævo-forms are antipodal with respect to their pyro-electric behaviour.

Reference List of the Thirty-two Classes of Crystal Symmetry.

112 In the annexed list the following abbreviations are employed: "*II*-A" = a two-fold axis, "*III*-A" a three-fold axis, etc.; "*Alt*" = alternating, "*Pol*" = polar (used in con-

System.	Class No.[1]	Symmetry.	Example.
Triclinic .	E. 1	No symmetry	Calcium thiosulphate.
	Hol. 2	Centre of symmetry . .	Potassium dichromate.
Monoclinic	3	$1P$	Potassium tetrathionate.
	E. 4	1 II-*A* (*Pol.*) . . .	Tartaric acid.
	Hol. 5	1 II-*A*, $1P$	Rubidium magnesium sulphate.
Rhombic .	*E.* 6	(1+1+1) II-*A* .	Magnesium sulphate.
	7	1 II-*A* (*Pol*), (1+1)P .	Hemimorphite, $ZnSiO_3$,$Zn(OH)_2$.
	Hol. 8	(1+1+1) II-*A*, (1 + 1 + 1)P . .	Potassium sulphate.
Tetragonal	*E.* 9	1 IV-*A* (*Pol.*) . .	Barium antimonyl tartrate.
	10	1 IV-*A* (*Alt.*) . . .	No example known.
	E. 11	1 IV-*A*, (2+2) II-*A* . .	Strychnine sulphate.
	12	1 IV-*A*, $1P$	Scheelite, $CaWO_4$.
	13	1 IV-*A*, (*Pol.*), (2+2)P	Iodosuccinimide.
	14	1 IV-*A*, (*Alt.*), 2 II-*A*, $2P$	Urea.
	Hol. 15	1 IV-*A*, (2+2) II-*A*, (1+2 + 2)P	Zircon, $ZrSiO_4$.
Rhombohedral . .	*E.* 16	1 III-*A* (*Pol.*)	Sodium periodate.
	17	1 VI-*A* (*Alt.*)	Dioptase, CuH_2SiO_4.
	E. 18	1 III-*A*, 3 II-*A* (*Pol.*) . . .	Quartz, SiO_2.
	19	1 III-*A*, $1P$	No example known.
	20	1 III-*A* (*Pol.*), $3P$ . . .	Tourmaline (complex silicate).
	21	1 VI-*A* (*Alt*), 3 II-*A*, $3P$ . .	Calcite, $CaCO_3$.
	Hol. 22	1 III-*A*, 3 II-*A*, (3 + 1)P .	Benitoite, $BaTiSi_3O_9$.
Hexagonal	*E.* 23	1 VI-*A* (*Pol.*)	Strontium antimonyl tartrate.
	E. 24	1 VI-*A*, (3+3) II-*A*	Barium antimonyl tartrate + potassium nitrate.
	25	1 VI-*A*, $1P$	Apatite, $Ca_5F(PO_4)_3$.
	26	1 VI-*A* (*Pol.*), $6P$	Silver iodide.
	Hol. 27	1 VI-*A*, (3+3) II-*A*, (1+3+3)P	Beryl, $Be_3Al_2(SiO_3)_6$.
Cubic . .	*E.* 28	4 III-*A*, 3 II-*A*	Sodium chlorate.
	E. 29	4 III-*A*, 3 IV-*A*, 6 II-*A* . . .	Sal-ammoniac.
	30	4 III-*A*, 3 II-*A*, $3P$	Iron pyrites, FeS_2.
	31	4 III-*A* (*Pol.*), 3 II-*A*, $6P$ . .	Zinc blende, ZnS.
	Hol. 32	4 III-*A*, 3 IV-*A*, 6 II-*A*, (3+6)P	Fluorspar, CaF_2.

[1] The numerical order of the classes is that adopted by Tutton in his *Crystallography and Practical Crystal Measurement*, p. 137 (Macmillan, 1922).

nection with axes), "*P*" = plane of symmetry. The numbers refer to the number of planes or of axes of symmetry. Where there are several planes of symmetry, they are divided up into groups, the members of each group occupying similar positions in the crystal; thus, (3 + 1) *P* signifies that there are altogether four planes of symmetry, three of which are similar (*i. e.* are parallel to faces belonging to the same form), but different from the fourth. The same procedure is adopted for the axes. Those eleven classes in which enantiomorphism is possible are indicated by the letter *E*. The class in each system with highest symmetry is often termed *holohedral* ("*Hol*") since the number of faces belonging to each form is the greatest possible.

POLYMORPHISM.

113 In his celebrated system of classifying minerals devised in 1801, Haüy propounded the following two principles: (1) a given substance always crystallises in the same form, (2) similarity of form of two substances, except in crystals of the cubic system, indicates a complete identity of chemical composition. It was, however, soon found that his principles could not be applied in all their generality, for exceptions to both of these statements were known even at that time, and many more were soon discovered and established by careful investigation.

In 1821, Mitscherlich proved that the property of crystallising in two distinct forms, *i.e.*, forms which are not referable to the same parameters, is common to many substances both elementary and compound, and he termed such substances *dimorphous*.

It has since been found that other substances are capable of existence in three or even four distinct crystalline forms, as, *e.g.*, titanium dioxide and ammonium nitrate respectively. These are termed *trimorphous* and *tetramorphous*, whilst the general term *polymorphous* is applied to all substances which possess more than one crystalline form.

The different modifications of polymorphous substances are not only distinguished by their crystalline form, but also differ in their other physical properties, such as specific gravity, hardness, cleavage, refractive power, etc. In fact, they behave physically like distinct substances. These differences, however, exist only in the crystalline condition, the various forms yielding identical solutions, fusions, and vapours. The differences there-

fore would seem to be due solely to a difference in the arrangement of the chemical molecules in the crystal structure. Substances of the same composition which preserve their individuality when dissolved are not polymorphous modifications but *isomerides*.

Sulphur is an excellent example of a polymorphous substance. At least four crystalline modifications are known, as well as several amorphous varieties; only two of the crystalline modifications will be considered. One of these occurs in nature, and is rhombic (class 6), with $a : b : c = 0{\cdot}8130 : 1 : 1{\cdot}9030$ (Fig. 67), the specific gravity being 2·07. It is also formed on evaporation of a solution at the ordinary temperature. The second modification was discovered by Mitscherlich by allowing fused sulphur to cool; it is monoclinic (class 5), with $a : b : c =$

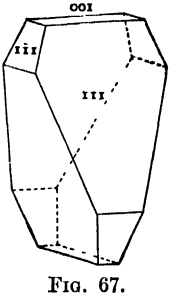


Fig. 67.

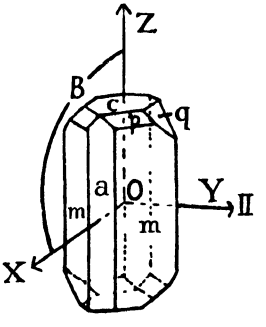


Fig. 68.

$0{\cdot}9958 : 1 : 0{\cdot}9998$; $\beta = 95° 46'$, and the specific gravity is 1·96 (Fig. 68). The rhombic form is stable at the ordinary temperature, but at 95·6° it changes with absorption of heat into the monoclinic variety, which is stable from this temperature up to the melting point. The reverse change, accompanied by evolution of heat, occurs when the monoclinic crystals are cooled below 95·6°. This "transition temperature" is influenced by change of pressure, and Tammann [1] has found that under a pressure of 1288 atmospheres the transition point is 151°. This is also the melting point of the monoclinic modification under the pressure mentioned, so that under higher pressures and temperatures it ceases to have any stable existence. Similar cases are known in which under the ordinary atmospheric pressure the transition temperature is above the melting point of one of the two modifications.

[1] Tammann, *Ann. Physik*, 1899, [3], **68**, 633.

The exceptions to Haüy's second statement are isomorphous substances (page 230).

CRYSTALLOCHEMICAL ANALYSIS.

114 Since, with the exception of substances belonging to the cubic system, no two substances are alike, the possibility of identifying a given unknown substance by measurement becomes obvious, provided the substance has already been examined crystallographically. Such a process of identification has been termed "Crystallochemical Analysis" by Fedorov,[1] who has succeeded in classifying all the available crystallographic material so as to permit of easy reference. The classification depends on the principle that the angles in the most important zone of a crystal approximate either to 90° or to 60°, or in other words crystals are either pseudo-tetragonal or pseudo-hexagonal. A good example is potassium dichromate, which is triclinic with $a : b : c = 1{\cdot}0116 : 1 : 1{\cdot}8146$; $a = 98° 0'$, $\beta = 96° 13'$, $\gamma = 90° 51$. Now these values are not far removed from the hypothetical values, $1 : 1 : 1{\cdot}8146$; $a = \beta = \gamma = 90°$, which would be characteristic parameters for a tetragonal crystal. Each substance hitherto measured (the total being about ten thousand) has been given a "correct setting," *i.e.*, has been set up so that the important 90° or 60° zone is placed in the vertical direction. An index of all these correct settings has been compiled, the values of certain characteristic angles, never exceeding five in number and usually only two or three, being taken as the basis of the sub-arrangement.

An unknown substance can be quickly identified by measuring one or two crystals; an examination of the various angles leads to the discrimination of the correct setting, and the characteristic angles can then be selected. A substance having these angles is sought for in the index, and identification is effected. Apart from its great theoretical interest, the new method is likely to be of the utmost practical utility, especially in those cases where only a small amount of material is available.

[1] Fedorov, *Zeit. Kryst. Min.*, 1912, **50**, 513; Barker, *Chem. News*, 1912, **106**, 199; *Lancet*, 1917 (May 26th), 798.

CRYSTAL STRUCTURE.[1]

115 *Theories of Crystal Structure.*—The first real theory of crystal structure is due to Haüy, who advanced the idea that a crystal is built up of minute units having the form of the cleavage figure, and packed together so as to fill space completely. The structure of a crystal of sodium (or potassium) chloride on this

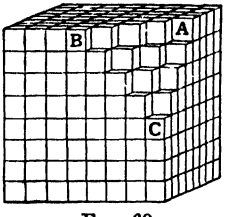


FIG. 69.

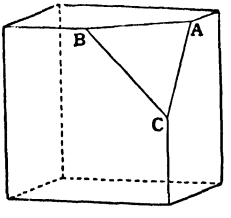


FIG. 70.

theory is shown in Figs. 69 and 70, which also illustrate the development of an octahedral facet at one of the corners. This, as well as any other inclined facets (for example, the dodecahedral facet replacing a cube edge), presents a step-like character, which distinguishes it from a cube facet; but no experimental evidence of this distinction is looked for, as the irregularity is premised to be of molecular dimensions.

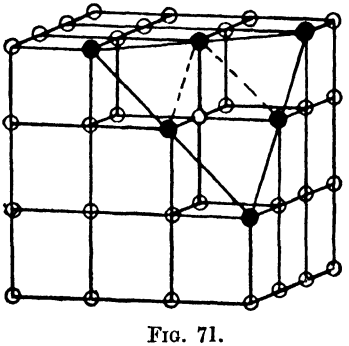


FIG. 71.

The next theory of crystal structure is essentially due to Bravais, who discarded the idea that a crystal is built up of solid units in favour of an open structure, *i.e.*, one in which discrete particles are arranged at regular intervals throughout space. If each cubelet of Fig. 69 be replaced by a structural particle

[1] Consult *Brit. Assoc. Report*, 1901, 297; *Annual Reports Chem. Soc.*, 1913 onwards; W. H. and W. L. Bragg, *X-Rays and Crystal Structure.*

(represented by a point) placed at its centre, the Bravais " space-lattice " structure of Fig. 71 is obtained. It will be seen that the irregular character of the octahedral facet disappears, the latter being now represented by a smooth plane of points. The cube and octahedral planes (as also the dodecahedral plane represented on a vertical edge of Fig. 72) can, however, still be distinguished from each other in no less than three ways. In the first place, the pattern is different, being a square in a cube plane, an oblong in a dodecahedral plane and a 120°-rhomb in an octahedral plane. The second way in which the three planes differ is in closeness of texture (or, as it is generally termed, " reticular density "). This can be conveniently measured by the area of the typical parallelograms (square, oblong, and 120°-

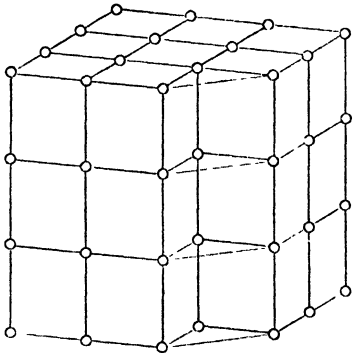


FIG. 72.

rhomb respectively reproduced in Fig. 73), which simple geometrical considerations prove to be in the ratios $1 : \sqrt{2} : \sqrt{3}$. Texture is therefore closest in the cube planes. The third point of difference refers to the perpendicular distances between successive layers. A glance at Fig. 71 will show that this distance in the case of the cube planes is given by the edge of the tiny cubical cell. The corresponding distances between dodecahedral and octahedral layers can be proved to have the following comparative values (illustrated true to scale by Fig. 74), d (cube) : d (dodec.) : d (octah.) $= 1 : 1/\sqrt{2} : 1/\sqrt{3}$.

The distances between successive layers of particles have recently acquired a great practical importance, since they can be actually measured by the X-ray method of exploring crystal structure. They will therefore receive further notice, but in the meantime it may be observed that the relatively great

distances between cube layers can scarcely be compatible with strong forces of attraction. An easy separation (cleavage) parallel to the cube planes is therefore to be expected. Bravais also sought to explain the development of specific faces on a crystal in terms of the space lattice structure. In the case of rock salt (or of sylvine) the faces of common occurrence (namely, the cube, dodecahedron, and octahedron) are precisely those that are distinguished by a close texture. This simple correlation between the structural texture of a plane and its actual development as a crystal face is not limited to the case of rock salt or

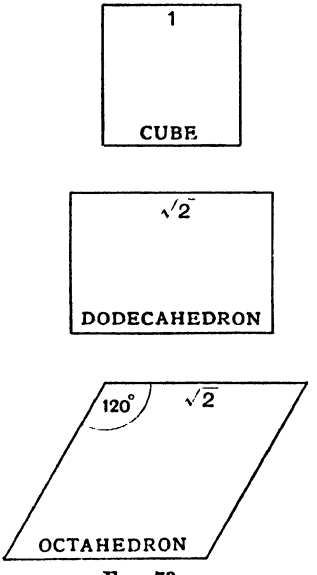


FIG 73.

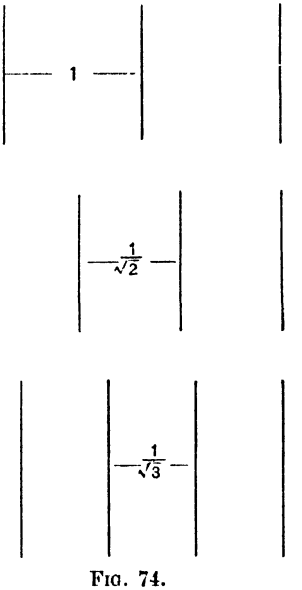


FIG. 74.

sylvine, but can be extended to the whole of the crystal kingdom. It can therefore be regarded as a general law of nature ("The Bravais Law").

The various space lattices were studied thoroughly by Bravais, who showed that fourteen types are distinguishable, falling under the seven crystalline systems. The symmetry, however, is always that of the holohedral class of each system; thus the existence of the lower classes of symmetry necessitates a further assumption. Bravais met the requirement by employing small, symmetrically shaped particles instead of mere points, the shape and orientation of these particles being such as to produce the lowering of symmetry requisite in each case.

Subsequent geometricians have shown, not only that it is possible to account for the thirty-two classes without having recourse to Bravais particles, but also that a new method of treatment reveals possible cases of crystal structure which are not capable of representation by his method. There are two stages in this final development.

The first advance is due in its completed form to Sohncke.[1] It will be observed that the space lattice is homogeneous, every part of the structure being the same as any other part. Sohncke showed that sixty-five types of arrangement of points in space (" point-systems ") are possible which fulfil the following definition of " homogeneity "; the system of points, regarded as unlimited, is such that the arrangement around any one of the points is the same as around any other.

The second and final advance consisted in enlarging Sohncke's definition of homogeneity in the following sense : the assemblage around a selected point may be the same as, or the mirror image of, the assemblage around other points. By introducing this principle of enantiomorphous similarity, it was discovered independently by Fedorov, Schoenflies, and Barlow [2] that there are in all 230 generalised types of point systems, which can be allocated to the thirty-two classes according to their symmetry.

Whilst leaving nothing to be desired in the way of general principles, the completed theory of crystal structure is necessarily lacking in precise details. However reasonably sure, for example, it is that the general lines of the structure of rock salt (or of sylvine) are presented by Fig. 71, the question whether each point represents the centre of gravity of an atom or of a molecule or of a congery of molecules obviously requires for its solution a suitable method of investigation. It was not till quite recently (1912) that the proper instrument was discovered in the form of *X*-rays, but the results already obtained are sufficiently precise to deserve as full a description as space will allow.

116 *The X-Ray Method of Exploring Crystal Structure.*—This remarkable development is due to Laue's happy inspiration that the regular structure of a crystal might act as a three-dimensional diffraction grating towards *X*-rays, in much the same way as lines drawn at appropriate intervals on a plane surface

[1] Sohncke, *Entwickelung einer Theorie der Krystallstruktur*, Leipzig, 1879; *Zeit. Kryst. Min.*, 1888, **14**, 423.

[2] Consult H. Hilton, *Mathematical Crystallography* (Oxford, Clarendon Press, 1903).

react towards ordinary light. A crystal of copper sulphate was first tried,[1] and specially ground sections of zinc blende were then examined. The arrangement of the apparatus used is shown in Fig. 75, where A is the X-ray tube, B_1—B_4 are diaphragms allowing a narrow beam of rays about 0·75 mm. diameter to fall on the crystal, Kr, which is adjusted on a goniometer. The screen, S, and the box, K, are made of lead. The photographic plates were placed in positions P_4—P_5 and treated to a very long exposure.

The results obtained from sections of zinc blende, ZnS, parallel respectively to the cube and octahedral planes, are reproduced

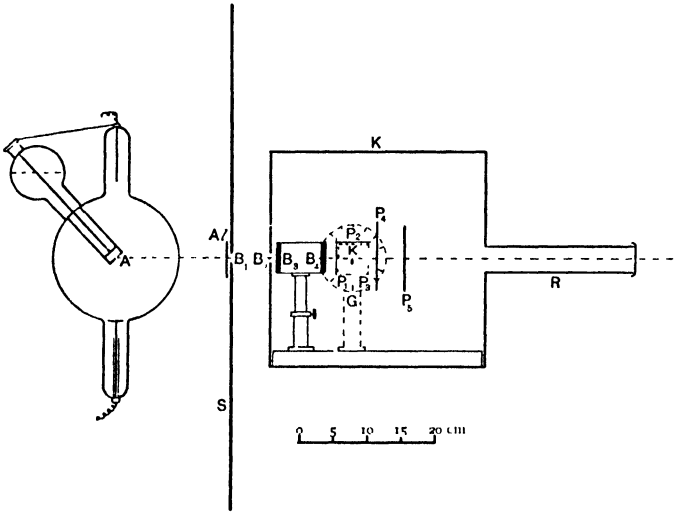


FIG. 75.

in Figs. 76 and 77. The symmetry in the first figure consists of four planes intersecting at angles of 45°, and an axis of four-fold symmetry. In the second figure there are three planes of symmetry intersecting at 120°, and a three-fold axis. Now this symmetry is precisely that which a cubic lattice would exhibit when viewed perpendicularly to a cube and an octahedral face respectively, and the photographs undoubtedly reveal the space lattice nature of the structure.

W. L. Bragg's Theoretical Interpretation.—The above results are simply explained by W. L. Bragg [2] as an interference effect

[1] Friedrich, Knipping and Laue, *Sitzungsber. Bayer. Akad. Wiss.*, 1912, 303; *Ann. Physik*, 1913, [iv], **41**, 971.

[2] W. L. Bragg, *Proc. Camb. Phil. Soc.*, 1913, **17**, 43.

of trains of waves, reflected from successive layers of particles. A consideration of the effects observed when a beam of monochromatic light is allowed to fall on a pile of excessively thin

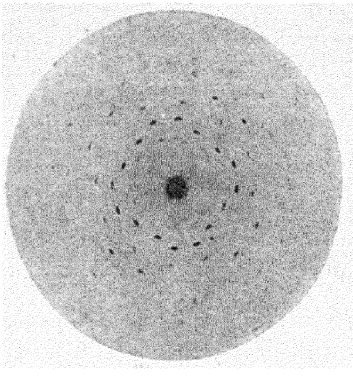


FIG. 76.

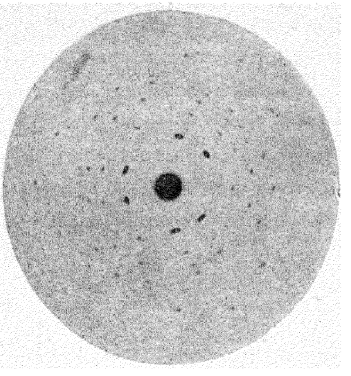


FIG. 77.

plates will help the explanation. The light is partly reflected at the various parallel surfaces (only two of which are shown in trace in Fig. 78). If now the light be allowed to graze the surface and the angle of grazing incidence, θ, be gradually increased,

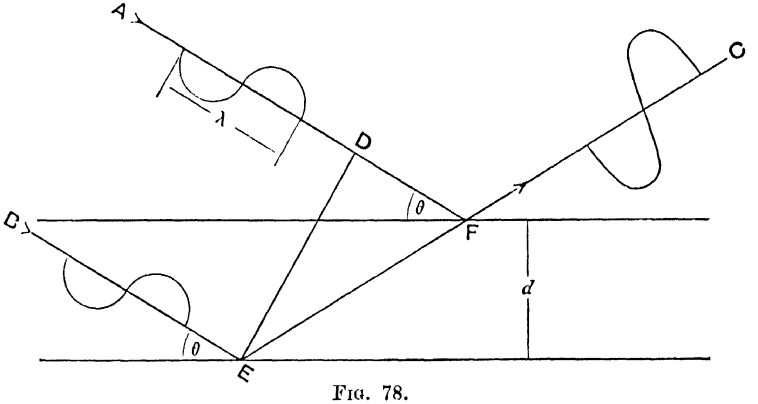


FIG. 78.

the intensity of the reflected beam will acquire successive maxima at certain definite angles, which obey the series of equations, $\lambda = 2d \sin \theta_1$, $2\lambda = 2d \sin \theta_2$, $3\lambda = 2d \sin \theta_3$, . . . or, in general, $n\lambda = 2d \sin \theta$ . . . where λ is the wave-length of light, and d the common thickness of the individual plates. The mechanism of the first of this series of intense reflections (at the angle θ_1) is illustrated by Fig. 78. Two waves, *A* and *B*, *initially in the*

same phase, are disposed so that their reflections, at the first and second surfaces respectively, ultimately pass along the same direction *FC*. As the two waves are initially in the same phase at *D* and *E*, it is clear that any eventual phase-difference will be measured by the difference of path, $EF - DF$. If, as in Fig. 78, this difference happens to be equal to λ (or to 2λ, 3λ . . . $n\lambda$) then the waves travelling along *FC* will be in the same phase, and will unite to form a single wave of increased amplitude. Geometrical considerations show that these conditions are expressed by the above equations. A new set of plates of a different thickness (or a change of wave-length of the light employed) would, of course, involve intense reflections at a new set of angles.

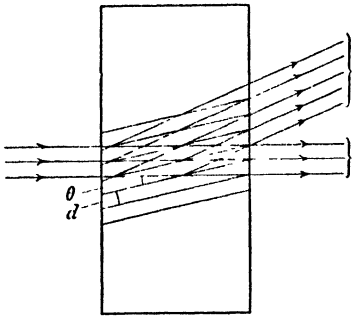


FIG. 79.

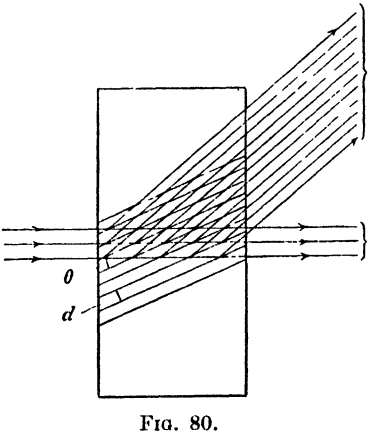


FIG. 80.

The application of the above principle to the interpretation of the Laue-radiogram is quite straightforward. The "pile of plates" lies close to hand in a crystal, the particles being laid down in parallel layers at equal distances. *X*-Rays are electromagnetic waves of very short wave-length. The incident pencil of *X*-rays largely traverses the crystal unchanged, giving rise to the central spot of the photograph (cf. Fig. 79), but part of the energy is cumulatively reflected at a series of *internal* structural layers (owing to a proper coincidence of the three variables λ, d, and θ) and gives rise to a secondary spot; another set of structural layers (see Fig. 80) gives rise to another spot, and so on, the number of spots being limited by the stringent conditions subsisting between λ, d, and θ.

The X-Ray Spectrometer.—The above explanation made it advisable to arrange the crystals so that the *X*-rays do not

impinge at normal incidence as in Laue's experiments, but at small angles of grazing incidence. The general conditions of Fig. 78 are thereby exactly simulated, the problem being simplified to a study of a single set of structural layers (those parallel to the crystal surface). An apparatus was especially devised for this purpose by W. H. Bragg. This "*X*-ray Spectrometer" is essentially a goniometer in which the telescope is replaced by an "ionisation chamber," the office of which is to absorb the reflected *X*-rays and allow of an accurate determination of their strength by an electrical method. A representative series of crystals (including substances of such complexity as potassium ferrocyanide and sodium ammonium tartrate) was tested and found to behave in the same way. Any crystal surface gives a series (2, 3, or even 4) of intense reflections at angles which are related to each other by the fundamental equations, each series of angles being of course characteristic of the substance, since the "grating distance" d has a specific value in every case. The same is also true for different faces of the same substance, on the same structural grounds.

The *X*-ray spectrometer also allows of the proof that the wave-length of *X*-rays depends on the metal used as their source (anti-cathode). The regular march in wave-length of this characteristic radiation has been thoroughly explored by Moseley with results of supreme theoretical importance (see p. 72).

117 *The Structure of Rock Salt and Sylvine.*—These two substances (the chlorides of sodium and potassium respectively) are so similar in all their crystallographic properties that a determination of one structure implies a knowledge of the other. The first intense *X*-ray reflections from the cube, dodecahedron, and octahedron faces of sylvine occur at the angles 5° 13′, 7° 18′, and 9° 3′ respectively (Palladium *X*-rays). Further, as the fundamental equation, $\lambda = 2d \sin\theta$ can be transformed into the form $d = \lambda/2 \sin\theta$, we have : d (cube) : d (dodec.) : d (octah.) = $\lambda/2 \sin 5° 13′ : \lambda/2 \sin 7° 18′ : \lambda/2 \sin 9° 3′$, and as the term $\lambda/2$ cancels throughout, we are finally left with $1/\sin 5° 13′ : 1/\sin 7° 18′ : 1/\sin 9° 3′$, which by evaluation gives the ratios $1/1 : 1/\sqrt{2} : 1/\sqrt{3}$. Now we have previously seen (p. 214) that these values are demanded by the structure of Figs. 71 and 72; and as they are not recomcilable with any other conceivable structure, it follows that this structure is, indeed, that of potassium chloride.

There now remains the question as to the nature of the structural particles that are distributed in this regular cubical

way throughout the crystal. No information on this point is afforded by the actual angles at which the intense reflections occur, such angles merely serving to elucidate the geometrical side of the problem, but not its physical or chemical aspect. In the case of an element, necessarily consisting of like atoms, the problem is fundamentally simpler, being purely geometrical; but in the case of a compound like sylvine the structural particles revealed by *X*-rays may either be molecules or alternately atoms of potassium and atoms of chlorine (as is represented, for example, by Fig. 81). The solution of this part of the problem is to be sought in a general examination of the properties of *X*-rays. As long ago as 1908 it was discovered by Barkla and Sadler [1] that whenever a metal is struck by *X*-rays, new rays are given off

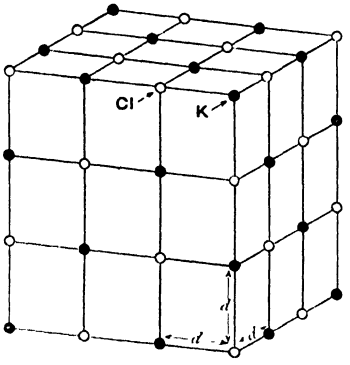


FIG. 81.

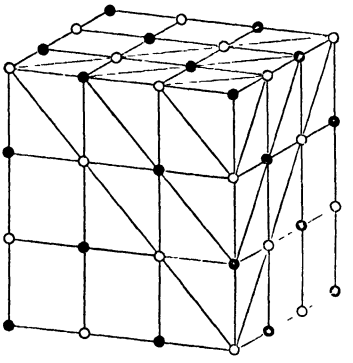


FIG. 82.

having a characteristic penetrative power; and it was subsequently shown by others that this characteristic radiation is independent of the circumstance whether the metal is or is not in a state of chemical combination. This independent behaviour of atoms (as opposed to molecules) suggests that the " structural particles " of sylvine (as revealed by *X*-rays) are, indeed, the individual atoms alternately arranged as in Fig. 81. This interpretation is supported by other evidence. The examination of Fig. 81 will show that each cube and dodecahedral plane contains potassium and chlorine atoms in equal amounts (granted that the structure is indefinitely extended), but the octahedral layers are alternately wholly potassium and wholly chlorine (as shown in Fig. 82). A similar singularity will necessarily hold for the octahedral plane of rock salt, but any resulting *X*-ray

[1] *Phil. Mag.*, 1908, [6], **16**, 550.

effect in this case might be expected to be greater, since the difference in atomic weight of sodium and chlorine is much greater than that between potassium and chlorine. As a matter of fact, experiment reveals something of the nature of an irregularity in the intensity of the various reflections from the octahedral plane of rock salt, which could not be easily interpreted if the structural layers consisted of similar molecules.

Calculation of Absolute Atomic Distances.—The elucidation of the rock salt (or sylvine) structure by W. L. Bragg first made it possible to calculate both the absolute distances between atomic centres in a crystal, as also the wave-length of any given kind of *X*-rays. The calculation involves a knowledge of the mass of an atom of hydrogen (estimated by other methods to be $1{\cdot}64 \times 10^{-24}$ gm.), the molecular weight of sodium chloride (say, 58·5) and the specific gravity of rock salt (say 2·15).[1] Since the structure of rock salt is the close-packed stack of cubic shells of Fig. 69 alternately containing atoms of sodium and atoms of chlorine, it follows that the average mass of matter associated with each shell is half the mass of a molecule of sodium chloride, *i. e.* $(58{\cdot}5/2)1{\cdot}64 \times 10^{-24} = 47{\cdot}97 \times 10^{-24}$ gm. Now we can obtain another expression for this average mass, for the edge length of each shell is equal to d, the distance between consecutive cube layers of Fig. 81, and its volume is therefore d^3. Further, as 1 c.c. of rock salt contains 2·15 gm. of material, it follows that d^3 c.c. contains 2·15 d^3 gram. Equating this to $47{\cdot}97 \times 10^{-24}$ obtained above, and extracting the cube root, we obtain, $d = 2{\cdot}814 \times 10^{-8}$ cm.—or, as generally stated, 2·814 Å.U. (where Å.U. signifies "Ångström unit," 10^{-8} cm.).

Rock Salt as a Standard.—The distance between consecutive cube layers in rock salt has been generally adopted as a standard in all determinations of *X*-ray wave-lengths or of atomic distances in crystals. Thus, if it be required to determine the wave-length of the rays emitted by a rhodium anticathode, it is only necessary to determine the first angle of intense reflection, θ, from the cube face of rock salt, and evaluate the equation $\lambda = 2d \sin \theta$ (where $d = 2{\cdot}814$ Å.U.). Then, if it be required to know the structural distance, d, characteristic of the cleavage plane of calcite, a determination of the special glancing angle, θ, with Rh-rays allows of an evaluation of the equation $\lambda = 2d \sin \theta$

[1] Slightly different values were adopted by Moseley (*Phil. Mag.*, 1913, **26**, 1027), namely, 1·65 (actually cited in the form of the quotient 10/6·05), 58·46, and 2·167, but the small differences happen to cancel each other, the result being a value which is identical with that of Bragg.

for the term d. The technique of such comparative determinations has been greatly improved by Siegbahn,[1] who gives the values $d = 3{\cdot}029$ and $8{\cdot}408$ Å.U. respectively for the cleavage planes of calcite and potassium ferrocyanide. The abnormally high value in the latter case is of course in harmony with the extraordinarily perfect character of the cleavage.

The Powder Method of Experimentation.—The fact that any beam of X-rays is only intensely reflected from the structural layers of a crystal when it meets them at a proper angle, has been ingeniously applied by Debye and Scherrer and by Hull independently [2] to substances which cannot be obtained in large crystals. In any fine grained crystalline material there must always be a number of minute crystals which happen to be correctly orientated, and this fraction of the whole will therefore behave as a single crystal, the remainder of the minute crystals being inactive so far as reflection is concerned. The method has made it possible to determine the structure of many crystalline elements. It has also been recently worked in conjunction with the X-ray spectrometer in the investigation of derivatives of benzene and naphthalene.[3]

118 *Some Results of the X-Ray Method.*—The structures of about 70 elementary and compound substances have already been elucidated by the X-ray method, some of which are of a somewhat complicated nature and difficult to follow in absence of a model, but the majority are quite simple. A representative selection of the latter will now be described with a view to showing how far the new method is able to illuminate the innermost recesses of a crystal.

The Structure of the Alkali Halides.—Although all these substances (as well as the closely allied ammonium salts) crystallise in the cubic system, they have long been known to exhibit certain dissimilarities, pointing to corresponding differences of structure. Consideration of molecular volume, for example, had led to a division into two groups,[4] one consisting of the cæsium salts and ammonium chloride and bromide, the other containing ammonium iodide and the salts of sodium, potassium, and rubidium. Recent X-ray work [5] has confirmed these anticipations,

[1] *Phil. Mag.*, 1919, **37**, 601.

[2] For a full account consult *Annual Report Chem. Soc.*, 1919, 199.

[3] (Sir W. H.) Bragg, *Proc. Phys. Soc.*, 1921, **34**, 33.

[4] Barker, *Min. Mag.*, 1907, **14**, 235.

[5] W. H. and W. L. Bragg, *X-Rays and Crystal Structure*; Bartlett and Langmuir, *J. Amer. Chem. Soc.*, 1921, **43**, 84; Davey and Wick, *Phys. Review*, 1921, **18**, 102.

and shown that the fluorides of lithium, sodium, and potassium belong to the larger group, typified by rock salt or sylvine. The structure of the smaller group, containing ammonium chloride, is that shown in Figs. 83 and 84. The positions of the hydrogen atoms cannot be determined on account of their low resistance to *X*-rays, but the NH_4 groups as a whole can be accurately placed. Each lies at the centre of a small cube at the eight corners of which are located chlorine atoms (as shown in Fig. 83). A more general view of the structure is given by Fig. 84. It is seen that the ammonium groups on the one hand, and the halogen atoms on the other, are arranged according to the simple cubic design of Fig. 71, and that the two lattices interpenetrate each other so that the particles of one lie at the cell-centres of the other.

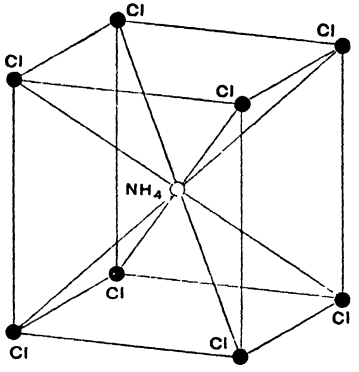


FIG. 83.

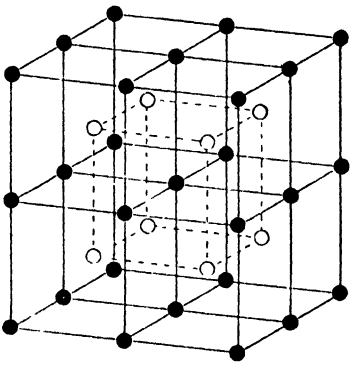


FIG. 84.

Dimorphism in the Cubic System.—It has long been recognised that the simple geometrical form of a cube may cloak a large number of distinct structures, hence the possibility arises that a substance may exist in two modifications, both cubic in form but different in structure, specific gravity, refractive index, and so on. Such a case is represented by ammonium chloride, for Lehmann [1] was able to obtain a second cubic modification from aqueous solution under certain well defined conditions. This existence in two cubic modifications has been recently confirmed by the *X*-ray method,[2] for it has been found that both ammonium chloride and bromide adopt the rock salt structure at high temperatures, the transformation being accompanied by a considerable expansion. This would seem to indicate that all the

[1] Lehmann, *Zeit. Kryst. Min.*, 1885, **10**, 321, 328.

[2] Bartlett and Langmuir, *J. Amer. Chem. Soc.*, 1921, **43**, 84.

alkali halides are potentially capable of existence in both structures, the rock salt structure being no doubt favoured by high temperatures and the ammonium chloride structure (as being the denser of the two) by high pressures.

119 *The Structure of Some Elements.*—The powder method of *X*-ray analysis has been particularly successfully applied (especially by Hull) to the study of the elements, many of which have long been known to crystallise in the cubic or hexagonal system. Lithium, sodium, chromium, iron, nickel, molybdenum, tantalum, and tungsten all adopt the structure represented by the ammonium chloride type of structure, *i.e.*, the structure represented by Figs. 83 and 84, in which both NH_4-groups and chlorine atoms have been replaced by metallic atoms. This arrangement is one of the fourteen structures foreseen by Bravais and termed by him the "centred cube lattice." Another of Bravais' structures (the "face-centred lattice") is now known to be

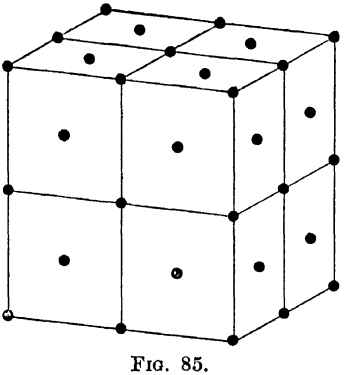


FIG. 85.

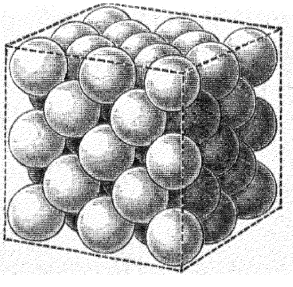


FIG. 86.

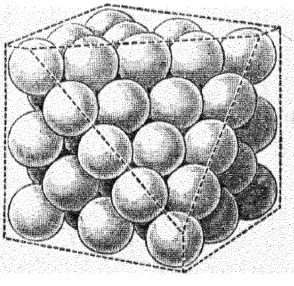


FIG. 87.

adopted by aluminium, calcium, cobalt, nickel, copper, rhodium, palladium, silver, cerium, iridium, platinum, gold, lead, and thorium. This structure is represented by Fig. 85. A comparison with Fig. 81 will show that it is simply the rock salt (or sylvine) structure in which, as it were, all the halogen atoms have been eliminated. Now the residual metallic atoms, if represented by relatively larger spheres than those of Fig. 85, present the arrangement shown in Figs. 86 and 87. The latter

figure is designed to reveal the structure of an octahedral layer. It is seen that the spheres are as close packed as possible, each sphere touching six of its neighbours. This is true of all the octahedral strata : moreover, the various layers fit on each other as closely as possible, so that the structure as a whole is the most closely packed system possible.

The way in which one (octahedral) layer of spheres rests in a set of cavities provided by the layer beneath, is shown in Fig. 88, but a glance at Fig. 89 will show that an upper layer can alternatively be fitted into a second set of cavities (the two sets of cavities are numbered 1 and 2 in the drawings). Similarly, there are alternative ways in which a third layer can be fitted on the second (and so on), for the cavities in any layer are twice as numerous as the spheres that can be accommodated. It must

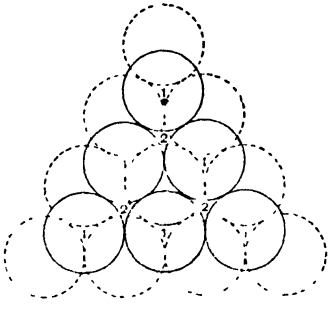


FIG. 88.

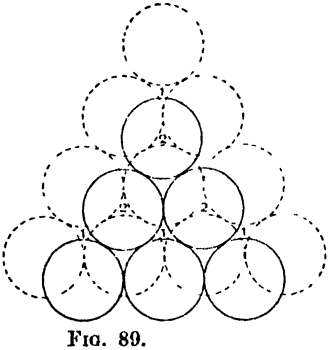


FIG. 89.

now be observed that from the point of view of the principle of close-packing it does not matter how these layers are fitted on each other, but in a crystal the successive arrangement of the layers is by no means fortuitous. In the structure of Figs. 86 and 87 the layers adopt an arrangement by which the 4th comes vertically above the 1st, the 5th above the 2nd, and so on. A simpler type of repetition would be that in which the 3rd is above the 1st, the 4th above the 2nd; and it may be mentioned that this strictly alternating type of closest-packed structure is actually presented by magnesium, titanium, cobalt, zinc, zirconium, ruthenium, cadmium, cerium, and osmium, which present one and the same form and crystallise in the hexagonal system.

Another fairly simple type of structure is that presented by carbon (the diamond), silicon, and white tin, all belonging to the fourth group of the periodic classification. Each atom is tetra-

hedrally surrounded by four other atoms. The structure is interesting as belonging to a type which, although not provided for by Bravais, was foreseen by later contributors to the theory of crystal structure.

Dimorphous Elements.—The *X*-ray method has already been successfully applied to the investigation of elements which have long been known to exist in two crystalline forms (a notable example is afforded by the diamond and graphite). But it has gone a step further by proving that certain other elements, hitherto unsuspected of dimorphism, really exist in two forms, the relative amounts in any given specimen depending on the circumstance whether the metal has been hammered, tempered, annealed and so on. Cobalt, nickel, and cerium are examples. It therefore seems probable that the *X*-ray method will have a wide field of application in metallurgical problems.[1]

CHEMICAL CRYSTALLOGRAPHY.

120 The study of the correlation of chemical composition with crystalline form and structure is a subject of great interest, and is termed chemical crystallography. Any change in the arrangement of the atoms in the molecule (isomerism) is found to lead to a profound difference in the form of the crystals; more than this, under different conditions of temperature and pressure one and the same compound may crystallise in entirely different forms (polymorphism). These two facts go far to prove that the crystalline form is a highly constitutive property, and is a direct outcome of the forces mutually operative between the various atoms in the molecule. This deduction is confirmed by the observation that the closer the chemical similarity of two given compounds, the more striking is the similarity of crystalline form: optical antipodes crystallise in enantiomorphous forms, and substances of very similar composition and constitution generally yield "isomorphous" crystals (see p. 230).[2]

Enantiomorphism of Molecule and of Crystalline Form.—Although it had long been recognised that optical activity is

[1] Andrews, *Phys. Review*, 1921, **18**, 245.

[2] For further information on this subject, see Fock, *An Introduction to Chemical Crystallography*, translated by W. J. Pope (Oxford, Clarendon Press, 1895); Groth, *Einleitung in die chemische Krystallographie* (Leipzig, Engelmann, 1904); English translation by H. Marshall (Gurney, 1906); also Tutton, *Crystallography and Practical Crystal Measurement* (Macmillan, 1922).

the result of a certain asymmetry of arrangement, the greatest discovery of all was reserved for Pasteur, who in the year 1848 showed that substances endowed with optical activity in solution crystallise in enantiomorphous forms. He also recognised that in such cases the seat of the optical activity lies in the unsymmetrical character of the atomic groupings in the chemical molecule. On allowing the sodium ammonium salt of racemic acid to crystallise, the two kinds of crystals of Figs. 90 and 91 were deposited, which could be distinguished by means of the hemihedral facets p and p', and separated from each other. On dissolving in water, the two kinds of crystals gave oppositely active solutions, from one of which Pasteur obtained ordinary *d*-tartaric acid, but from the other a new acid—*l*-tartaric acid.

It was suggested by Pasteur that the atomic grouping is of a

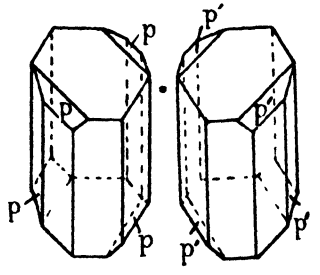


Fig. 90. Fig. 91.

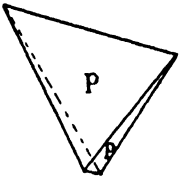


Fig. 92.

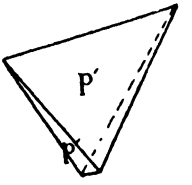


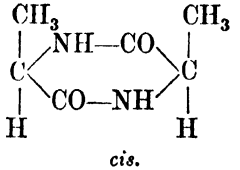
Fig. 93.

spiral or, perhaps, tetrahedral character. The latter idea may have been suggested to him by the fact that the hemihedral facets of Figs. 90 and 91, when extended in space, form the tetrahedra of Figs. 92 and 93, one of which is the non-superposable mirror image of the other.

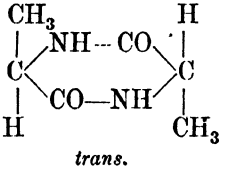
Somewhat later, by giving a spacial extension to the Kekulé hypothesis of quadrivalent carbon, it was pointed out by van't Hoff and Le Bel independently that the enantiomorphous character of the molecular configuration of tartaric acid, as well as that of many other optically active organic compounds, is due to the presence of one or more "asymmetric" carbon atoms, *i.e.*, atoms directly combined to four dissimilar groups. Further, the asymmetric carbon atom may be supposed to be placed at the centre of a tetrahedron, the four groups being at the corners. Subsequently, optically active compounds containing selenium, tin, sulphur, phosphorus, and nitrogen united to different groups have been obtained, and there has been a disposition to ascribe

the activity to the presence of the asymmetric atoms. A more satisfactory view, however, is to ascribe the activity to the enantiomorphous configuration of the molecule as a whole. Optically active compounds have been prepared by Werner [1] which, perhaps, do not contain an asymmetric atom, *e.g.*, potassium chromium oxalate, $K_3Cr(C_2O_4)_3,H_2O$; the atomic configuration, however, is of such a character that it is non-superposable on its mirror image.

The true test for enantiomorphism of molecular structure is not the presence or absence of any particular atom united to dissimilar groups, but the absence of plane, centre, and alternating axes of symmetry in the molecule as a whole, the presence of any one of these elements of symmetry being sufficient to cause identity of the molecule with its mirror image. For example, 1 : 4-diketo-2 : 5-dimethylpiperazine [2] exists in two forms, *cis-* and *trans-* :—



cis.



trans.

Now the *cis*-form only possesses a two-fold axis and has therefore a non-superposable mirror image; but the *trans*-form, although devoid of a plane of symmetry, has a centre of symmetry, since a line passing through the centre of the ring meets similar groups or atoms at the two ends (the carbonyl oxygen and the imido-nitrogen being in the plane of the ring). The former may therefore exist in two optically active forms, the latter does not.

The numerical values of all properties of antipodal crystals are identical; thus, the specific gravity, molecular volume, and refractive indices are the same, as well as the angles and the parametral ratios; and it is only by means of such properties as pyro-electricity, the sign of the rotatory power, the development of hemihedral facets, and the orientation of etched figures that the crystals can be distinguished.

Racemic substances, or compounds of the two antipodes in equal molecular proportions, do not bear a very close crystallographic relationship to the antipodes themselves.

[1] *Ber.*, 1912, **45**, 3061. [2] Fischer, *Ber.*, 1906, **39**, 467. 3981.

Pseudo-racemic compounds have practically the same parameters as the pure antipodes, and are to be looked upon as mixed crystals or intimate intercalations of active material of the two kinds (see p. 206).

121 *Isomorphism.*—Haüy's second principle, that identity of crystalline form implies identity of composition, was soon found to be inconsistent with facts. As long ago as 1781, Leblanc had shown that crystals of an identical form could be obtained from solutions containing sulphate of copper and sulphate of iron mixed in very different proportions. He likewise states that crystals of alum, a sulphate of aluminium and potassium, may frequently be found to contain a considerable quantity of iron, although no alteration in the crystalline form can be noticed. Vauquelin, too, showed in 1797 that common potash alum may contain large quantities of ammonium, and yet the crystalline form of the substance does not undergo any change. It is well known also that many minerals which are identical in crystalline form may possess a very different chemical composition. Thus the common garnet, crystallising in the cubic system, sometimes contains much iron and little aluminium and sometimes large quantities of aluminium and little iron. Berthollet considered facts like these to be in accordance with his views on chemical combination, but Proust explained them by supposing that we have here to deal, not with chemical compounds, but rather with mechanical mixtures.

In the year 1816, Gay-Lussac made the remarkable observation that when a crystal of common potash alum is suspended in a saturated solution of ammonia alum it grows exactly as if it had been placed in the solution from which it was originally obtained. From this fact he drew the conclusion that the molecules of these two alums possess the same form. Later on, in 1819, Beudant noticed that if solutions containing two of the following salts, sulphate of zinc, sulphate of iron, or sulphate of copper, are crystallised, the deposited crystals always possess the form of one of these salts, although they contain a considerable quantity of the other salt, which, when crystallised by itself, possesses a totally different form.

In order to explain these and similar well-recognised facts Haüy supposed that certain substances possess the power of crystallisation to such a degree that even when present in small quantities they compel other substances to adopt their crystalline form.

Clear light was thrown on this subject by the researches of Mitscherlich, published in 1819. Mitscherlich showed that the compounds of various elements possessing a similar composition have also identical crystalline form, as ascertained by the measurement of their angles. The first substances examined by Mitscherlich were the arsenates and phosphates of sodium, potassium, and ammonium. He showed not only that the crystals of the phosphate and arsenate of the same metal contain the same amount of water of crystallisation, and crystallise in the same form, but also that when the two salts are mixed in varying quantities the crystals which such solutions deposit are of the same form as those obtained from solutions of the pure salts, whilst the proportions of the ingredients in the crystal vary according to their proportions in the solution. Hence Mitscherlich concluded that analogous elements or groups of elements can replace one another in compounds without any alteration of crystalline form. Such substances are said to be *isomorphous* (ἴσος, equal, μορφή, shape). Many other compounds were shown by Mitscherlich to conform to the above law.

Mitscherlich was at first of the opinion that the geometrical similarity of isomorphous substances is complete, that is, that they have absolutely the same angles. He was not aware of the work of Wollaston,[1] who some seven years previously had measured very carefully the rhombohedral cleavage angle of the following naturally occurring carbonates and obtained the values :—calcite, $CaCO_3 = 74° 55'$; dolomite, $CaMg(CO_3)_2 = 73° 45'$; and spathic iron ore, $FeCO_3 = 73° 0'$. All subsequent measurements have confirmed these values, and they are the ones actually accepted at the present day. After obtaining a Wollaston goniometer, Mitscherlich found that isomorphous substances are not identical, but merely very similar, in angles. All subsequent work has confirmed this view, except, of course, in the case of cubic substances, the angles of which are constant for all, being, in fact, determined by the symmetry.

122 *The Relation of Isomorphism to Chemical Constitution.*—The necessity for a similar arrangement of atoms in the molecules of isomorphous compounds was appreciated by Mitscherlich, but its full importance became apparent only after the development of the structure theory—a product of organic chemistry which was subsequently applied to inorganic substances. It was recognised that isomorphous substances have a similar

[1] *Phil. Trans.*, 1812, **102**, 159.

atomic arrangement: for example, the constitutional formulæ of potassium sulphate and selenate are completely analogous. The formulation of the periodic classification provided a further stimulus to the study of isomorphism. It now became evident that in most simple isomorphous compounds the replaceable elements belong to the same sub-group of Mendeléev's arrangement, *e.g.*, potassium, rubidium, and cæsium; chlorine, bromine, and iodine; iron, nickel, and cobalt. In the more complicated compounds, however, especially in the large class of double salts, a considerably greater degree of freedom exists: elements which are not in the same sub-group of the periodic classification can replace each other isomorphously, provided that the degree of oxidation (valency) is the same, *e.g.*, the metals copper, zinc, cadmium, manganese, iron, nickel, and cobalt are capable of isomorphously replacing the metal magnesium in rubidium magnesium sulphate (see p. 26).

The very striking similarity of calcite and sodium nitrate has long been known, but as a direct result of the development of the structure theory in chemistry there has been a tendency to dispute the isomorphism on account of the dissimilarity of constitution when the two compounds are formulated on the conventional lines of valency, viz.,

$$O=C<\begin{matrix}O\\O\end{matrix}>Ca \qquad\qquad \begin{matrix}O\\O\end{matrix}\!\!>N-O-Na.$$

It has, however, been pointed out [1] that this case is by no means isolated, for there are many other isomorphous series of compounds which present similar peculiar features of chemical constitution. The following four series will serve as illustrations:

Tetragonal System.		
Potassium periodate (Fig. 35, p. 192)	KIO_4	$a:c = 1:1\,5534.$
Scheelite (calcium tungstate)	$CaWO_4$	$= 1:1{\cdot}5268.$
Potassium osmiamate	$KOsO_3N$	$= 1:1{\cdot}6319.$
Rhombic System.		
Potassium perchlorate (Fig. 47, p. 199)	$KClO_4$	$a:b:c = 0{\cdot}7817:1:1\,2792.$
Barytes (barium sulphate)	$BaSO_4$	$= 0{\cdot}8152:1:1{\cdot}3136.$
Potassium borofluoride	KBF_4	$= 0{\cdot}7898:1:1{\cdot}2830.$
Rhombic System.		
Potassium sulphate (Fig. 44, p. 198)	K_2SO_4	$a:b:c = 0{\cdot}5727:1:0{\cdot}7418.$
Potassium glucinum fluoride	K_2BeF_4	$= 0\,5708:1:0{\cdot}7395.$
Tetragonal System.		
Xenotime	YPO_4	$a:c = 1:0{\cdot}6177.$
Zircon (Fig. 48, p. 199)	$ZrSiO_4$	$= 1:0\,640.$
Cassiterite or tinstone	SnO_2 or $SnSnO_4$	$= 1:0{\cdot}6726.$

[1] Barker, *Journ. Chem. Soc.*, 1912, **101**, 2484.

It will be seen that although in each series there is a complete analogy of composition with respect to the total number of the atoms in the molecule, yet the constitutions as ordinarily accepted are quite different. A possible explanation appears to be that the theory of co-ordination advanced by Werner is applicable to the compounds enumerated, a view which derives a considerable amount of support from recent *X*-ray work, for the positions of the various atoms are now known in crystals of calcite and sodium nitrate. In neither case is there any distinction in the positions of the various oxygen atoms, which affect a symmetrical grouping round the carbon or nitrogen atoms, as the case may be. Moreover, the metallic atoms are relatively remote, so that the constitution of the crystals must be written $Ca[CO_3]$ and $Na[NO_3]$ respectively. It will be observed that the latter formula expresses the ionic condition of sodium nitrate in an aqueous solution, and it has therefore been suggested that a crystal of any electrolyte may really be built up of positive and negative ions instead of neutral molecules. Tubandt's[1] researches on electrolytic conductivity are significant in this connexion: the observation that the cubic form of silver iodide, at a temperature close to the melting point, has a higher specific conductivity than the fused substance suggests that the cubic form is largely if not completely ionised.

123 *Mutual Affinities of Isomorphous Substances.*—It has been mentioned that all cubic substances are isomorphous in the literal sense of the word, but to designate substances like alum and potassium platinichloride isomorphous, merely because they both crystallise in regular octahedra, would be entirely misleading. On this account the term isomorphism has long been restricted to those substances whose similarity of form is unquestionably due to a far-reaching similarity of internal structure, which is in turn the result of a close correspondence of atomic and molecular constitution. Owing to the similarity of structure, isomorphous compounds in this narrow sense are endowed with very special properties: (1) they form mixed crystals or isomorphous mixtures in variable proportions; (2) they are capable of forming regular overgrowths or "parallel growths" on each other; (3) a crystal fragment, when introduced into a supersaturated solution of another substance isomorphous with it, immediately relieves the supersaturation and causes a

[1] *Zeit. Elektrochem.*, 1920, **26**, 360.

copious separation of crystals.[1] These three properties have been employed to test the character of the isomorphism in suspected cases, but recent investigations have proved that pairs of admittedly isomorphous substances fail to respond to the three tests when the molecular volumes are not sufficiently close in value.

Isomorphous Mixtures.—The properties of isomorphous mixtures are a continuous function of the percentage composition (Retgers), and in many cases this function is practically linear; so that the values of a property of the mixture can be very simply calculated. Many isomorphous substances, however, are not miscible in every proportion, each being capable of taking up only a limited amount of the other; others, again, do not mix at all. Thus, according to Wulff,[2] ammonium sulphate (molecular volume = 74·63) mixes in all proportions with rubidium sulphate (73·77), and also completely with potassium sulphate (65·33) and with cæsium sulphate (85·17). Potassium and cæsium sulphates, however, are completely immiscible.

Parallel Growths.—This subject has been especially studied by Barker,[3] who in addition to observations on many other substances has found that potassium and cæsium sulphates yield quite irregular deposits on each other, whilst all other possible pairs of the sulphates mentioned above always give parallel growths.

Relief of Supersaturation.—Our knowledge concerning the state of supersaturation has been greatly enlarged by the work of Miers and Isaac,[4] who from observations of the change of refractive index of a cooling, supersaturated solution have arrived at the conclusion that there are two states of supersaturation, viz., the *metastable* and the *labile* states. A solution in the metastable condition, although supersaturated, is not capable of crystallising spontaneously (*i.e.*, unless inoculated with a crystal of the solute), no matter how violently it is agitated. If the solution is protected from the introduction of crystal nuclei from outside, it will on further cooling pass into the labile

[1] Gernez, *Compt. rend.*, 1865, **60**, 833, 1027; 1866, **63**, 843; Lecoq de Boisbaudran, *Ann. Chim. Phys.*, 1866, [4], **9**, 173; Thomson, *Journ. Chem. Soc.*, 1879, **35**, 196; Thomson and Bloxam, *ibid.*, 1882, **41**, 379.

[2] Wulff, *Zeit. Kryst. Min.*, 1906, **42**, 558.

[3] Barker, *Journ. Chem. Soc.*, 1906, **89**, 1120; *Min. Mag.*, 1907, **14**, 235; 1908, **15**, 42.

[4] Miers and Isaac, *Journ. Chem. Soc.*, 1906, **89**, 413; Isaac, *ibid.*, 1908, **93**, 384.

condition and crystallise spontaneously. A sudden shower of crystals then appears, the shower being preceded by a sudden fall in the value of the refractive index of the solution (p. 130).

Miers and Chevalier have found that calcite (molecular volume = 36·8) induces crystallisation in a metastable solution of sodium nitrate (37·8), whilst the remaining rhombohedral carbonates (see below), with molecular volumes ranging between 28·2 and 31·0, have no action.

Isomorphous Mixtures in Minerals.—Cases of isomorphous mixtures are very common among minerals, and the following serve as an excellent illustration of isomorphous replacement:

Apatite (Fig. 36) . . .	$Ca_5F(PO_4)_3$
Pyromorphite	$Pb_5Cl(PO_4)_3$
Mimetite	$Pb_5Cl(AsO_4)_3$
Vanadinite	$Pb_5Cl(VO_4)_3$.

The isomorphously replaceable chemical elements in these minerals are:

(1) Phosphorus, Arsenic, Vanadium; (2) Calcium and Lead; (3) Chlorine and Fluorine. Not infrequently both chlorine and fluorine occur in the same specimen of apatite, and phosphorus and arsenic often replace one another in pyromorphite.

Another well marked case is that of the rhombohedral carbonates of the metals calcium, magnesium, iron, zinc, and manganese. These minerals all crystallise in similar rhombohedra, the values of the rhombohedral angle between cleavage planes being:

Calcium carbonate, or calcite, $CaCO_3$ . . .	74° 55′
Magnesium carbonate, or magnesite, $MgCO_3$.	72° 35′
Ferrous carbonate, or spathic iron ore, $FeCO_3$.	73° 0′
Zinc carbonate, or calamine, $ZnCO_3$ . . .	72° 20′
Manganese carbonate, or rhodochrosite, $MnCO_3$	73° 55′.

The various metals enumerated can replace each other in varying proportions, as is well illustrated by the following percentage analysis of spathic iron ore:

Ferrous oxide, FeO	45·55
Manganese oxide, MnO	12·50
Lime, CaO	1·57
Magnesia, MgO	1·80
Carbonic acid, CO_2	38·58
	100·00

If we now divide the percentage of oxide by its combining weight, thus $\frac{45{\cdot}55}{71{\cdot}84}$ for ferrous oxide, etc., etc., we obtain the following numbers representing the proportion between the number of equivalents of the several constituents present:

FeO = 0·6340, MnO = 0·1762, CaO = 0·0280, MgO = 0·0446.

The sum of these amounts (0·8828) is, however, very nearly the proportion which must be present in order to unite with $\frac{38{\cdot}58}{44{\cdot}00} = 0{\cdot}8768$ equivalent of CO_2, the difference being due to errors of experiment. In other words, the number of molecules of the basic oxides present is the same as that of the carbon dioxide; hence the formula for the spathic iron ore may be written $(Fe,Mn,Ca,Mg)CO_3$, signifying that the relative quantities of the metals in question present are indeterminate, but are in the aggregate such as are needed to combine with CO_2. Hence we have the following as the composition of the mineral:

Ferrous carbonate, $FeCO_3$	73·45
Manganese carbonate, $MnCO_3$ . . .	20·25
Calcium carbonate, $CaCO_3$	2·80
Magnesium carbonate, $MgCO_3$ . . .	3·76
	100·26

124 *Comparison of Isomorphous Substances by means of Topic Axes.*—The parametral ratios of a crystal furnish merely the relative lengths of the three edges of Haüy's structural unit, the actual lengths themselves remaining unknown. It has been ingeniously suggested by Becke[1] that in the case of two isomorphous substances the volumes of Haüy's units are proportional to the molecular volumes, *i.e.*, the molecular weight divided by the specific gravity. The volumes and also the ratios of the edge-lengths of the units being known, it is a simple matter to calculate the edge-lengths themselves; these three lengths are termed the *topic parameters* or *topic axes*, and are denoted by the letters χ, ψ, ω. When the pile of units is supposed to be replaced by molecular points at their centres, so that the structure becomes a space lattice, the topic axes then represent the distances between contiguous molecules in the three principal directions of the structure.

[1] Becke, *Anzeiger Akad. Wiss. Wien*, 1893, **30**, 304.

The following table includes the topic axes of the isomorphous series consisting of the sulphates of potassium, rubidium, cæsium, and ammonium, which have been very carefully investigated by Tutton.[1] One of the most important results of the investigations of this author is that, with regard to the geometrical and general physical properties, the rubidium compounds take up an intermediate position between the corresponding compounds of potassium and cæsium.

Crystallographic axes, a b . c.	Density	Mol. vol.	Topic Axes.		
			χ	ψ	ω
K_2SO_4 . . . 0·5727 : 1 : 0·7418	2 666	64·91	3 8810	3 8574	4·9964
Rb_2SO_4 . . 0 5723 : 1 : 0 7485	3 615	73·34	4·0304	4·0039	5 2366
Cs_2SO_4 . . . 0·5712 : 1 : 0·7531	4 246	84·58	4·2187	4·1849	5 5175
$(NH_4)_2SO_4$. 0·5635 : 1 : 0·7319	1·772	74·04	4·0792	4 0051	5·2020

It is interesting to note that the effect on the structure of the crystal of replacing the potassium atom by the ammonium radical, NH_4, is almost exactly the same as that produced by its substitution by rubidium.

The values of the topic axes shed some light on the relations of the first three salts with respect to miscibility and capacity of forming parallel growths. It must be inferred that these two properties depend on the possibility of a fitting together of the two structures—in no other way does the rôle played by the molecular volume admit of interpretation. The large difference between the molecular volumes of the potassium and cæsium salts leads to correspondingly large differences in the values of the topic axes, which, it will be remembered, furnish a measure of the relative distances between contiguous molecules of the space lattices. Apparently these differences have overstepped the limit of mutual accommodation and the two substances will neither mix nor form parallel growths. The limit is not exceeded, however, when either the rubidium or the ammonium salt is compared with the potassium and cæsium salts. These considerations illustrate the value of the conception of topic axes in comparisons of the members of an isomorphous series—a value which has not been diminished by the results of X-ray work.[2]

[1] See Tutton, *Crystalline Structure and Chemical Constitution* (Macmillan, 1910).

[2] Tutton, *Proc. Roy. Soc.*, 1917, [*A*], **93**, 72.

Isodimorphism.—When two substances are isomorphous with one another and one of them is dimorphous, crystallising in two distinct forms, it is often found that the second substance is also dimorphous, and that each of its two forms corresponds with one of the forms of the first substance, a double isomorphism being thus exhibited. Such substances are said to be *isodimorphous*, and cases of *isotrimorphism* are also known. The trioxides of arsenic and antimony serve as a striking example of isodimorphism. For a long time these compounds were known to occur only in forms which were not isomorphous, and this was the more remarkable as their elementary constituents exhibit such a close analogy. It was afterwards found that arsenious oxide, As_4O_6, which usually crystallises in regular octahedra (arsenolite), is occasionally met with in rhombic crystals (claudetite), exactly identical in form with those in which antimonious oxide, Sb_4O_6, commonly occurs in nature (valentinite). A mineral consisting of this latter oxide, and called senarmontite, was next discovered. The crystals of this are octahedral, so that the isodimorphism of these substances is now completely proved, especially since it has been found possible to produce the octahedral crystals of antimonious oxide artificially.

SYSTEMATIC DESCRIPTION OF THE METALS AND THEIR DERIVATIVES.

125 In the following systematic description of the metals, the latter are classified in groups according to the periodic system, each of these groups being further divided into two or more sub-groups. The members of each sub-group are described in the order of their atomic weight.

GROUP I.

Sub-group (a).
The Alkali Metals.
- Lithium
- Sodium
- Potassium
- Rubidium
- Cæsium

Sub-group (b).
The Copper Group.
- Copper
- Silver
- Gold

The metals of this group all form characteristic series of salts in which the metal is apparently monovalent, and except in the cases of copper and gold this series of salts is by far the most important. The division into sub-groups is more sharply defined than is usually the case, the metals copper, silver, and gold, which, as already pointed out, fall near the centre of the " double periods " (p. 54), showing only a limited resemblance to the alkali metals. The resemblance is most prominent in the case of the two typical elements, lithium and sodium, the salts of which are frequently isomorphous with the corresponding silver salts. In the exact classification according to the periodic system, sodium belongs to the sub-group (*b*), for like copper, silver, and gold it is a member of one of the " odd " periods; in its properties, however, it so closely resembles the metals of the sub-group (*a*) that it is described together with these.

THE ALKALI METALS.

126 The above name is given to this group because the two most important members, sodium and potassium, are constituents of the substances which have been long known by the name of *alkalis*. The name alkali is first found in the works of the Latin Geber, and is the name there given to the soluble salt obtained by the lixiviation of the ashes of sea-plants. We find the same word employed to designate also the carbonate of potash obtained by a similar treatment of the ashes of land-plants. The difference between the alkalis potash and soda was at that time not understood, and in order to distinguish them from the carbonate of ammonia, the volatile alkali, they were both termed the fixed alkali. The distinction between the mild and caustic alkalis had long been known, and the mode of converting the former into the latter by boiling their solutions with lime was a well-recognised process. We have seen (Vol. I., p. 16) that Black, in the year 1755, was the first to explain this change, as he proved that the mild alkalis contain fixed air or carbon dioxide.

The first clear distinction between the two alkalis, potash and soda, appears to have been made by Duhamel in the year 1736, although Stahl pointed out that the alkali contained in common salt is different from that contained in wood-ashes, and this difference was indicated by the first being termed the mineral and the second the vegetable alkali. Marggraf showed in 1759 that the salts of the two alkalis possess totally distinct properties, and that whilst those of the common alkali tinge the flame of a spirit-lamp violet, those containing the base of common salt impart a yellow colour to the flame. It was, however, pointed out by Klaproth that the vegetable alkali potash was contained in several minerals, such as leucite; the special name *potash* in English, *potasse* in French, and *kali* in German, was given to this particular alkali. Klaproth suggested for the mineral alkali the name *natron*, in English *soda*, in French *soude*. These names had formerly been used indiscriminately for any alkali.

Up to the year 1807 the alkalis were considered to be simple substances. Lavoisier had indeed considered that they probably contained oxygen, from analogy with other well-known metallic oxides, but Davy was the first to isolate the metals.

A few years later (1817), the lithium compounds were discovered by Arfvedson, and in 1860 the two remaining metals, rubidium and cæsium, were isolated by Bunsen and Kirchhoff. Careful search has been made for an alkali metal of higher atomic weight than cæsium, without result, and it seems probable that no such element exists.[1]

The alkali metals are all soft, silvery metals, which may be readily fused and volatilised, the melting and boiling points becoming lower with increasing atomic weight. The specific gravity increases with, but less rapidly than, the atomic weight, the atomic volume therefore becoming greater as we ascend the series. They are the most strongly electro-positive of the metals, their hydroxides being the most powerful bases known; within the group itself the basicity increases with atomic weight, that of cæsium hydroxide being the greatest.

The alkali metals form only one series of stable salts, and in these they are monovalent; a few halogen derivatives are known in which they have a valency of 3, 5, 7, or even 9, but these readily decompose into the free halogens and the monovalent halide. With very few exceptions all the salts are soluble in water, those of lithium being the least soluble.

They combine with oxygen to form oxides of the general formula M_2O, which correspond to the stable salts; these are, however, difficult to prepare in the free state, since they combine very readily with oxygen, forming higher oxides, and with water, forming the characteristic hydroxides MOH, which are produced also by the action of the metals on water.

These metals all unite directly with hydrogen, forming crystalline hydrides, $(MH)_n$, which are decomposed by water.

LITHIUM, Li = 6·94. At.No. 3.

127 Lithium was discovered in 1817 by Aug. Arfvedson whilst he was working in the laboratory of Berzelius.[2] He obtained a new alkali, and Berzelius gave to it the name *lithia*. It was first found in several minerals from the iron mines of Uto in Sweden, especially petalite and spodumene.

Lithium is derived from λίθεος, stony, as it was then believed to be an alkali whose presence was confined to mineral matter

[1] See, *e.g.*, Baxter, *J. Amer. Chem. Soc.*, 1915, **37**, 286; Dennis and Wyckoff, *Ibid.*, 1920, **42**, 985.

[2] *Schweigger's Journal*, 1817, **22**, 93; *Ann. Chim. Phys.*, 1819, **10**, 82.

in contradistinction to the other alkalis which were found in vegetable and animal bodies. Since that time, however, lithium has been shown to be very generally distributed throughout the animal and vegetable kingdoms, this fact having been first ascertained by Bunsen and Kirchhoff in their earliest research on spectrum analysis in 1860 (p. 168).[1]

Sources of Lithium.—The most important minerals containing this element are *triphylite*, $(LiNa)_3PO_4 + (FeMn)_3(PO_4)_2$, or $(LiNa)(FeMn)PO_4$, containing from 1·6 to 3·7 per cent. of lithium; *petalite*, $LiAl(Si_2O_5)_2$, containing 2·7 to 3·7 per cent. of lithium; *lepidolite* or *lithia-mica*, 1·3 to 5·7 per cent.; *spodumene* or *triphane*, $LiAl(SiO_3)_2$, 3·8 to 5·6 per cent. Smaller quantities of lithium, whose presence can be ascertained by the spectroscope, are found in a large number of minerals. The water of certain mineral springs also contains large quantities of dissolved lithium salts. Thus Berzelius [2] in 1822 detected this element in the water of Egger-Franzensbad, and in 1825 in the springs at Karlsbad and Marienbad. The spectroscope has since shown that lithium occurs in most mineral waters, in sea-water, and in that of almost every river [3] and surface spring. Some mineral springs contain lithium in considerable quantity. Thus Bunsen found 295·2 mgrm. of lithium chloride in one litre of the water of the Murspring at Baden-Baden,[4] and W. A. Miller [5] found 372 mgrm. in one litre from a spring in the Wheal Clifford mine at Redruth in Cornwall.

By the decomposition of rocks containing lithium this metal finds its way into the soil. It has been detected in that of the Limagne d'Auvergne, and can be traced in the ashes of the plants which grow in that district (Truchot).[6] It is widely distributed throughout the vegetable kingdom, occurring in the ash of the vine, and in that of many cereals, in sea-weed and in tobacco (Bunsen and Kirchhoff). It has been found especially in the leaves of many plants, in cacao, coffee, and sugar-cane as well as in the residues from the extraction of beet-sugar.[7] It appears that lithium salts cannot replace potassium salts in plants; indeed, when added in quantity they generally seem to act as a poison. In certain plants, however, such as for instance

[1] *Phil. Mag.*, 1860, (4), **20**, 97. [2] *Pogg. Ann.*, 1825, **4**, 245.
[3] *On Thames Water.* A. and F. Dupré. *Phil. Mag.*, 1860, [4], **20**, 373.
[4] *Jahresb.*, 1861, 1091. [5] *Chem. News*, 1864, **10**, 181.
[6] *Ber.*, 1874, **7**, 653; *Compt. rend.*, 1874, **78**, 1022.
[7] Lippmann, *Ber.*, 1897, **30**, 3037. See also Tschermak, *Journ. Chem. Soc.*, 1900, Abstr., ii. 235.

the *Samolus Valerandi*, lithium appears to act beneficially, inasmuch as the stronger plants contain most lithium.

From the vegetable world lithium finds its way into the animal kingdom; thus Bunsen and Kirchhoff observed its presence in the ashes of milk and in human blood and muscular tissue.[1] Nor is lithium a metal which is confined to terrestrial matter, for Bunsen [2] detected it in two meteoric masses, one of which fell at Juvenas in France on May 15th, 1821, and the other at Parnallee in Southern India on February 28th, 1857, and Engelback [3] found lithium in a meteorite from the Cape.

128 *Extraction of Lithium Salts.*—1. From petalite and lepidolite. The first method of extraction, proposed by Berzelius,[4] consists in fusing the powdered mineral with double its weight of lime. On dissolving the fused mass in hydrochloric acid, and evaporating with sulphuric acid, the lithium is obtained in solution as sulphate, together with some aluminium sulphate and gypsum. The first salt is precipitated by addition of chalk, and the second by ammonium oxalate. This method was improved by Regnault and again much simplified by Troost.[5] This latter chemist fuses the following mixture at a very high temperature in a wind furnace: finely powdered lepidolite, 10 parts; barium carbonate, 10 parts; barium sulphate, 5 parts; potassium sulphate, 3 parts. The heavy silicate and sulphate of barium sink to the bottom, and a layer of the sulphates of potassium and lithium is found at the top of the fused mass. These can be extracted by simple lixiviation. The sulphates are then converted into chlorides by the addition of barium chloride, the chlorides evaporated to dryness, and the lithium chloride extracted by treatment with a mixture of absolute alcohol and ether, or preferably, with pyridine.

An alternative method for the preparation of lithia from lepidolite, described by Schieffelin and Cappon,[6] is to decompose the finely powdered mineral with concentrated sulphuric acid by careful ignition at a temperature which is gradually raised from 120° to 340°. The mass is digested with water, the silica removed by filtration, and the aluminium sulphate converted into potash alum by the addition of potassium sulphate. A portion of the alum separates as crystals on standing, and the

[1] See also Hermann, *Pfluger's Archiv*, 1905, **109**, 26.
[2] *Annalen*, 1861, **120**, 253.
[3] *Pogg. Ann.*, 1862, **116**, 512.
[4] *Traité*, **2**, 89.
[5] *Compt. rend.*, 1856, **43**, 921.
[6] *J. Soc. Chem. Ind.*, 1908, **27**, 549.

remainder is removed by the successive addition of calcium carbonate and freshly precipitated aluminium hydroxide; the last traces of aluminium are separated by the addition of calcium carbonate, the solution being made alkaline by slaked lime. The filtrate is concentrated, the calcium salts are precipitated as calcium oxalate, and traces of iron and manganese by potassium hypochlorite. The solution of lithium sulphate thus obtained is separated, and converted into carbonate by treatment with a slight excess of potassium carbonate solution.

2. For the purpose of extracting lithium salts from triphylite, a process proposed by Hugo Müller [1] is the best. This consists in dissolving the mineral in hydrochloric acid, oxidising with nitric acid, precipitating the phosphoric acid with a ferric salt, evaporating to dryness, and extracting with hot water. Chlorides of manganese and lithium are thus dissolved. The manganese is precipitated by barium sulphide, and the excess of barium removed by sulphuric acid. Lithium oxalate is obtained by evaporating with oxalic acid, which on ignition gives the carbonate.

129 *Preparation of Lithium.*—The attempts made by Arfvedson and Gmelin to prepare metallic lithium were fruitless. They endeavoured to separate the metal by the electrolysis of its salts, but the battery they used was not powerful enough. Later on, the decomposition of lithia was tried by heating it with iron and carbon; these experiments also proved abortive. Then Davy succeeded in obtaining a small quantity of the metal by electrolysis, but was unable to examine its properties. In 1858 Bunsen and Matthiessen were the first to obtain lithium in quantity by electrolysis and to examine its properties carefully. Bunsen thus described the process: [2] "Pure chloride of lithium is fused over a Berzelius' spirit-lamp (or Bunsen's gas lamp), in a small thick porcelain crucible and is decomposed by a zinc-carbon battery consisting of four to six cells. The positive pole is a small splinter of gas-coke, and the negative an iron wire about the thinness of a knitting-needle. After a few seconds, a small silver-white regulus is formed under the fused chloride round the iron wire and adhering to it, which after two or three minutes attains the size of a small pea: to obtain the metal the wire pole and the regulus are lifted out of the fused mass by a small flat spoon-shaped iron spatula. The wire can then be withdrawn from the still melted metal, which is protected from ignition by the chloride of lithium, with which

[1] *Annalen*, 1853, **85**, 251. [2] *Journ. Chem. Soc.*, 1856, 143.

it is coated. The metal may now be easily taken off the spatula with a pen-knife, after having been cooled under rock oil. As this operation can be repeated every three minutes, an ounce of chloride of lithium may be reduced in a very short time."

For the preparation of the metal on a somewhat larger scale it is advisable to employ a mixture of the chlorides of potassium and lithium in equal weights,[1] or preferably lithium bromide to which 10—15 per cent. of the chloride has been added.[2] The metal can be obtained also by electrolysing solutions of the chloride in pyridine,[3] and in various alcohols.[4]

Lithium cannot be obtained in a similar manner to that by which sodium and potassium are prepared, viz., by heating the carbonate with charcoal, or the hydroxide with iron (Troost), but it distils over when pieces of magnesium are added to lithium hydroxide heated in an iron retort.[5]

Properties.—Lithium is a solid, possessing a silver-like lustre, but tarnishing on exposure to the air. It is much less oxidisable than potassium or sodium. It is not so soft as these metals, but is softer than lead, and makes a grey streak on paper. Lithium can be pressed into wire, and can be welded at ordinary temperatures. It melts at 180·1°,[6] and if the melted metal be pressed between two sheets of glass, a surface is obtained which exhibits the colour and brilliancy of polished silver. Lithium floats on petroleum, and is the lightest of all known bodies which are solid at the ordinary temperature, its specific gravity varying from 0·5891 to 0·5983 (Bunsen).

Heated in the air lithium ignites at a temperature above its fusing point, burning tranquilly with a bright white light. It burns also when heated in hydrogen, chlorine, bromine, iodine, dry carbon dioxide, or sulphur vapour; it combines readily with nitrogen on heating, and slowly absorbs the gas even at the ordinary temperature, forming the nitride. When thrown on to water it oxidises, but does not fuse like sodium. Nitric acid acts on lithium so violently, that it fuses and often ignites. Sulphuric acid attacks it slowly, but dilute sulphuric and hydro-

[1] Guntz, *L'Electrochimie*, 1896, October.

[2] Ruff and Johannsen, *Zeit. Elektrochem.*, 1906, **12**, 186.

[3] Kahlenberg, *J. Physical Chem.*, 1899, **3**, 602.

[4] Patten and Mott, *J. Physical Chem.*, 1904, **8**, 153.

[5] Warren, *Chem. News*, 1896, **74**, 6.

[6] Bernini and Cantoni, *Nuovo Cim.*, 1914, [6], **8**, ii, 241; cf. Ruff and Johannsen, *Zeit. Elektrochem.*, 1906, **12**, 186; Bernini, *Physikal. Zeit.*, 1905, **6**, 74.

chloric acids quickly. Silica, glass, and porcelain are attacked by lithium at a temperature below 200° (Bunsen and Matthiessen). Lithium is more electro-negative than sodium. It amalgamates readily with mercury, but the highest compound formed is $LiHg_3$.[1]

COMPOUNDS OF LITHIUM.

130 *Lithium Hydride*, LiH.—Lithium combines with hydrogen slowly at a dull red heat, and rapidly at a bright red heat with incandescence, forming the white solid hydride, density 0·816, which melts at 680°. It decomposes partially when slowly heated, and at 600° has a dissociation pressure of 27 mm. At a red heat the hydride burns in chlorine, yielding hydrogen chloride and lithium chloride, whilst with hydrogen chloride it forms the chloride and hydrogen (Guntz). It slowly alters in the air; with water it gives hydrogen and the hydroxide.[2] Lithium hydride acts as a salt on electrolysis, yielding lithium at the cathode and hydrogen at the *anode*.[3]

Lithium Oxide, Li_2O, *and Lithium Hydroxide*, LiOH.—Dry oxygen does not act upon lithium at the ordinary temperature. Indeed the metal may be melted in dry air without losing its brilliancy. Heated much above 180°, lithium takes fire and burns brilliantly in the air with the formation of lithium oxide, or lithia, which is coloured yellow by a small quantity of a higher oxide and volatilises slowly at 600°.[4] It may be prepared in a purer state by heating nitrate of lithium in a silver basin, and also by heating the hydroxide or carbonate in a current of dry hydrogen at 780°. It forms a white crystalline mass which dissolves slowly in water with the formation of a hydrated form of the hydroxide, LiOH. The anhydrous hydroxide can only be prepared from the hydrate, $LiOH,H_2O$, by heating the latter in a current of hydrogen below 140°. It forms a white, porous mass. The hydrate is prepared by adding the calculated quantity of barium hydroxide to lithium sulphate and concentrating the resulting solution after filtering off the barium sulphate; crystals are thus obtained which are freed from water by heating

[1] Smith, *Zeit. anorg. Chem.*, 1912, **74**, 172.
[2] Guntz, *Compt. rend.*, 1896, **122**, 244; **123**, 694.
[3] Moers, *Zeit. anorg. Chem.*, 1920, **113**, 179.
[4] Lebeau, *Compt. rend.*, 1903, **136**, 1256.

to 33° in a current of pure hydrogen.[1] A second crystalline hydrate, $2LiOH,H_2O$, has also been obtained.[2]

Lithium Peroxide, Li_2O_2.—When hydrogen peroxide and alcohol are added to a solution of the hydroxide, the compound $Li_2O_2,H_2O_2,3H_2O$ is precipitated in hard, colourless crystals, which yield the anhydrous peroxide, Li_2O_2, when they are kept over phosphoric oxide.[3]

131 *Salts of Lithium.*—Many of the salts of lithium are isomorphous with those of sodium and silver, whilst in the alums this element can replace potassium and the other alkali metals. Lithium differs in a marked manner from sodium, potassium, etc., by forming a sparingly soluble carbonate, phosphate and fluoride.

Lithium Fluoride, LiF, is a white crystalline salt, less soluble than the carbonate (2·7 gm. per litre), and its precipitation by means of pure ammonium fluoride is the best method for the purification of lithium salts.[4]

Lithium Chloride, LiCl.—This salt is formed when lithium burns in chlorine, or when lithia or the carbonate is dissolved in hydrochloric acid. Its preparation from spodumene and petalite has already been described. By evaporating the aqueous solution above 15·5°, or the alcoholic solution over sulphuric acid, the chloride is obtained in octahedra. The fused salt has a specific gravity of 2·068 at 25°, and melts at 606° (Ruff and Johannsen)[5] to a mobile liquid; it is one of the most deliquescent salts known, and is also very soluble in many of the alcohols and pyridine. When its aqueous solution is evaporated to dryness traces of hydrochloric acid are given off, a little lithia being formed, and on redissolving, the liquid has an alkaline reaction. Three hydrated chlorides are known, viz., $LiCl,H_2O$, $LiCl,2H_2O$, and $2LiCl,3H_2O$.

One hundred parts of water dissolve :

At	0°	20°	65°	80°	140°	160°	
LiCl	63·7	80·7	104·2	115	139	145	parts

The saturated solution boils at 171° (Kremers).

The chloride forms a series of unstable additive compounds with 1, 2, 3, and 4 molecules of ammonia.[6]

[1] Dittmar, *J. Soc. Chem. Ind.*, 1888, **7**, 731; de Forcrand, *Compt. rend.*, 1907, **144**, 1321 and 1402.

[2] Muretow, *Ber.*, 1872, **5**, 331; Göttig, *Ber.*, 1887, **20**, 2912.

[3] de Forcrand, *Compt. rend.*, 1900, **130**, 1465.

[4] Richards, *J. Amer. Chem. Soc.*, 1910, **32**, 19.

[5] *Zeit. Elektrochem.*, 1906, **12**, 186.

[6] Bonnefoi, *Ann. Chim. Phys.*, 1901, [7], **23**, 317.

Lithium Iodotetrachloride, $LiICl_4,4H_2O$, is obtained by the action of chlorine on a solution of lithium chloride and iodine in dilute hydrochloric acid, and crystallises in needles.[1]

Lithium Perchlorate, $LiClO_4,3H_2O$, is readily obtained by evaporating lithium chloride with perchloric acid. The anhydrous salt melts without decomposition at 236° and contains a higher proportion of available oxygen than any other known compound. It was for this reason selected by Richards [2] for the determination of the atomic weights of silver and lithium.

Lithium Sulphate, Li_2SO_4,H_2O, is obtained by dissolving the carbonate in dilute sulphuric acid, and crystallises in thin monoclinic plates which dissolve readily in water and alcohol. It forms double salts with other alkali sulphates: $Li_2SO_4,3Na_2SO_4,12H_2O$; Li_2SO_4,K_2SO_4; $Li_2SO_4.(NH_4)_2SO_4$.[3] The *acid sulphate*, $LiHSO_4$, is also known.[4]

Lithium Nitride, Li_3N.—Lithium absorbs nitrogen at the ordinary temperature. The reaction takes place with incandescence when the metal is heated in a stream of the gas,[5] with formation of the nitride, Li_3N, which is, however, best prepared pure by heating the metal very gently in an iron dish in a slow stream of nitrogen.[6] It fuses at 840—845°, and attacks most substances when in the molten state.[7]

Lithiumamide, $LiNH_2$, is formed slowly by the prolonged action of liquid ammonia on metallic lithium at the ordinary temperature in a sealed tube.[8] It is obtained also by heating the nitride in either hydrogen or ammonia at temperatures between 340° and 480°.[9] The amide forms white, shining crystals which melt at 373—375° when heated in a sealed tube.

Lithiumimide, Li_2NH, is obtained by heating lithiumamide from 360° to 450° in a silver dish, as a white, partially fused mass which is decomposed at 600°. On exposure to sunlight it is decomposed with the formation of the nitride and amide.[10]

[1] Wells and Wheeler, *Zeit. anorg. Chem.*, 1891, **2**, 255.
[2] *J. Amer. Chem., Soc.* 1910, **32**, 8.
[3] Spielrein, *Compt. rend.*, 1912, **155**, 346.
[4] Schultz, *Pogg. Ann.*, 1868, **133**, 137.
[5] Deslandres, *Compt. rend.*, 1895, **121**, 886.
[6] Guntz, *Compt. rend.*, 1896, **123**, 995.
[7] Dafert and Miklauz, *Monatsh.*, 1910, **31**, 981.
[8] Ruff and Georges, *Ber.*, 1911, **44**, 502.
[9] Dafert and Miklauz, *Monatsh.*, 1912, **33**, 63.
[10] *Ber.*, 1911, **44**, 502; *Monatsh.*, 1912, **33**, 63.

Lithium Azoimide, LiN_3, crystallises with $1H_2O$ in colourless hygroscopic needles and explodes between 115° and 298°.[1]

Lithium Nitrite, $LiNO_2,H_2O$, is prepared by the action of silver nitrite on aqueous lithium chloride.[2]

Lithium Nitrate, $LiNO_3$, is prepared by dissolving the carbonate in nitric acid, and is very soluble in water or alcohol. It crystallises in anhydrous rhombohedra, isomorphous with sodium nitrate (Troost).

The solid salt in equilibrium with a saturated solution contains $3H_2O$ up to a temperature of 29·6° and a concentration of 57·5 per cent., $\frac{1}{2}H_2O$ from 29·6° to 61·1°, and above this temperature is the anhydrous salt.[3]

Normal Lithium Phosphate, Li_3PO_4, is distinguished from the phosphates of the other alkali metals by its slight solubility in water, in this respect resembling the phosphates of the next group of metals. It is precipitated as a crystalline powder by adding a lithium salt to sodium phosphate together with caustic soda.[4] It may be obtained also by acting on lithium carbonate with phosphoric acid. It dissolves in 2,539 parts of water, and in 3,920 of water rendered alkaline by ammonia. In presence of ammonium salts it is much more soluble, and is precipitated from the solution by heating with caustic potash. It is readily soluble in hydrochloric and nitric acids; baryta water precipitates the phosphoric acid from the solution as barium phosphate, the whole of the lithium salt remaining in solution (W. Mayer). When a nitric acid solution of the normal salt is evaporated and the excess of free acid driven off, the dihydrogen salt, LiH_2PO_4, remains. Evaporation over sulphuric acid deposits deliquescent crystals.

Lithium Carbide, Li_2C_2, is formed when a mixture of the carbonate with sugar charcoal is heated in the electric furnace,[5] and when metallic lithium is heated with carbon, or in a current of carbon monoxide or dioxide.[6] It is a transparent, colourless, crystalline mass of sp. gr. 1·65 at 18°, and is a powerful reducing agent. It inflames in fluorine and chlorine at the ordinary temperature, and is readily attacked by bromine, iodine, oxygen,

[1] Dennis and Benedict, *Zeit. anorg. Chem.*, 1898, **17**, 18; Curtius and Rissom, *J. pr. Chem.*, 1898, [2], **58**, 261.

[2] Oswald, *Ann. Chim.*, 1914, [9], **1**, 32.

[3] Donnan and Burt, *Journ. Chem. Soc.*, 1903, **83**, 335.

[4] Compare Quartaroli, *Gazz.*, 1907, **37**, [1], 598.

[5] Moissan, *Compt. rend.*, 1896, **122**, 362; 1898, **126**, 302.

[6] Guntz, *Compt. rend.*, 1896, **123**, 1273; 1898, **126**, 1866.

sulphur, phosphorus, and arsenic. Water decomposes it, forming lithium hydroxide and pure acetylene. It can be prepared also by acting on lithium dissolved in liquid ammonia with acetylene at −40° to −80°, and heating the crystalline compound, $C_2Li_2,C_2H_2,2NH_3$, which is formed.[1]

Heated in nitrogen at 925° lithium carbide forms lithium cyanamide, with some dicyanamide and cyanide; the nitrogen absorption is more rapid than for calcium carbide.[2]

Lithium Cyanide, LiCN, is obtained by the action of hydrocyanic acid on lithium hydroxide in absolute alcohol or benzene.[3] It forms an *argenticyanide*, $LiAg(CN)_2$, and *ferro-* and *ferricyanides*, $Li_4Fe(CN)_6,6H_2O$ and $Li_3Fe(CN)_6,4H_2O$.

Normal Lithium Carbonate, Li_2CO_3.—This salt, unlike the carbonates of the other alkali metals, is but slightly soluble in water, thus more nearly resembling the carbonates of the next group of metals. It forms a crystalline powder when a concentrated solution of lithium chloride is poured into a solution of ammonium carbonate in aqueous ammonia, the mixture being heated so long as the precipitate increases in bulk.

The carbonate commences to decompose at about 600° into carbon dioxide and lithium oxide, which slowly volatilises;[4] when heated in a current of hydrogen at 780° the whole of the carbon dioxide is expelled.[5]

One hundred parts of water dissolve at :

0°	10°	20°	50°	75°	100°
1·539	1·406	1·329	1·181	0·866	0·728

parts of lithium carbonate.[6] The solubility is increased by various sodium and potassium salts, and still more by ammonium salts.[7]

If the solution is slowly evaporated crystalline crusts or small transparent crystals of the salt separate out, and if these are suspended in water and carbon dioxide is passed in, *lithium hydrogen carbonate*, $LiHCO_3$, is formed. On evaporation the solution loses carbon dioxide, again depositing the normal salt.

[1] Moissan, *Compt. rend.*, 1898, **127**, 911.
[2] Tucker and Moody, *J. Amer. Chem. Soc.*, 1911, **33**, 1478.
[3] Meyer, *Zeit. anorg. Chem.*, 1920, **115**, 203.
[4] Lebeau, *Compt. rend.*, 1903, **136**, 1256.
[5] Dittmar, *J. Soc. Chem. Ind.*, 1888, **7**, 731; de Forcrand, *Compt. rend.*, 1907, **144**, 1402.
[6] Bewad, *J. Russ. Phys. Chem. Soc.*, 1884, i, 591.
[7] Geffcken, *Zeit. anorg. Chem.*, 1905, **43**, 197.

Lithium carbonate is employed in medicine, especially in gouty affections, since it acts as a solvent for uric acid.

Lithium Silicide, Li_6Si_2, is prepared by heating lithium and silicon together in a vacuum, and removing the excess of lithium by liquid ammonia or by heating to 500° *in vacuo*. It forms small lustrous crystals of a deep indigo blue colour, has the sp. gr. 1·12, and decomposes into its elements above 600°. This compound acts as a vigorous reducing agent, burns when heated in the air or oxygen, and is decomposed when heated in hydrogen and the halogens. Concentrated hydrochloric acid decomposes it, forming silicoethane, Si_2H_6, and water produces a violent reaction, the silicoethane, which is probably the first product, being decomposed by the lithium hydroxide also formed.[1]

Lithium Orthosilicate, Li_4SiO_4, prepared by fusing lithium carbonate with the requisite quantity of silica, crystallises in the same form as olivine; the *metasilicate*, Li_2SiO_3, has the same form as hypersthene. The *orthosilicate* melts at 1215°, the *metasilicate* at 1180° (Rieke and Endell)[2] or at 1202° (Jaeger).[3] Both silicates are partly decomposed by water, but the latter has been obtained as a monohydrate, Li_2SiO_3,H_2O, insoluble in water.[4] The systems formed by each of these silicates with the corresponding aluminium silicate, and the system $LiAlO_2$–SiO_2 have been investigated and evidence has been obtained of the existence of the compounds :[5] $2Li_2SiO_3,Al_2(SiO_3)_3$, m. p. 965°; $Li_2SiO_3,Al_2(SiO_3)_3$, m. p. 1275°; $Li_4SiO_4,Al_4(SiO_4)_3$, m. p. 1330°; $LiAlSi_3O_8$, m. p. 1250.°; $LiAlSi_4O_{10}$, m. p. 1200°. Lithium can also, like sodium and potassium, form soluble silicates containing excess of acid over base.[6]

Detection and Estimation of Lithium.

132 The presence of extremely small traces of lithium compounds ($\frac{9}{10,000,000}$ of a milligram) can be ascertained with certainty by means of the spectroscope. The luminous vapour of lithium, obtained by bringing a trace of a salt on a fine platinum wire into the non-luminous gas flame, gives, when examined

[1] Moissan, *Compt. rend.*, 1902, **134**, 1083.
[2] *Sprechsaal*, 1910, **43**, 683.
[3] *J. Washington Acad. Sci.*, 1911, **1**, 49.
[4] Vesterberg, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 30.
[5] Balló and Dittler, *Zeit. anorg. Chem.*, 1912, **76**, 39.
[6] Vesterberg, *loc. cit.*

by the spectroscope, two sharply defined lines—the one a very weak yellow line, Liβ (wave-length = 6104), the other a bright red line, Liα (wave-length = 6708). Not only do all the lithium salts when thus heated give this reaction, but ashes of plants and the lithium minerals only require for this purpose to be held in the flame. Natural silicates which contain only traces of lithium must first be subjected to the following treatment. A small portion of the substance is digested with hydrofluoric acid, and the residue moistened with sulphuric acid and heated; the dry mass is then treated with alcohol, and the extract allowed to evaporate in a shallow dish. The solid particles are scraped off and brought into the flame on the platinum wire (Bunsen).

Lithium is separated from all the heavy and earthy metals in the ordinary process of analysis. It may be separated from potassium by precipitating the latter metal as the platinichloride or perchlorate, the corresponding lithium salts being soluble. It can be separated from sodium by the solubility of lithium chloride in a mixture of ether and absolute alcohol, but as by this process a small quantity of sodium chloride is found to be dissolved, it is best to determine the amount of chlorine in a given weight of the mixed chlorides, from which the quantities of lithium and sodium may be calculated. The best method for the separation of lithium chloride from the other alkali chlorides is to digest the solid chlorides repeatedly with pyridine,[1] or, better, *iso*butyl alcohol,[2] in which the lithium chloride only is soluble; the chloride is then recovered from the pyridine solution and converted into and weighed as lithium sulphate.

The atomic weight of lithium was first accurately determined by Mallet in 1856 and 1859, and by K. Diehl in 1862. It was afterwards determined by Stas by converting the chloride into the nitrate, and by the determination of chlorine in lithium chloride, the atomic weight deduced from these numbers being 7·03. Richards and Willard[3] have since redetermined the atomic weight by converting the chloride into silver chloride, and obtained the value 6·94 (Ag = 107·88), which is now (1922) accepted.

[1] Kahlenberg and Krauskopf, *J. Amer. Chem. Soc.*, 1908, **30**, 1104.
[2] Winkler, *Zeit. anal. Chem.*, 1913, **52**, 628.
[3] *J. Amer. Chem. Soc.*, 1910, **32**, 4.

SODIUM. Na = 23.00. At. No. 11.

133 In the writings of the Old Testament (Jeremiah, ii. 22) we find a substance used for washing purposes mentioned as *nether*. This same substance is mentioned in Proverbs as being one which effervesces when vinegar is poured over it, and in our version this substance is called nitre. In Luther's translation the name chalk is given to this body, but there can be little doubt that by the word *nether* was meant trona, or the native carbonate of soda, to which the names *νίτρον* in Greek and *nitrum* in Latin were applied. At a later date the name *nitrum* was given to saltpetre; but up to the fourth century there is no doubt that nitrum signified the carbonate of soda originally obtained from the salt lakes in Egypt, to which the names *flos salis* and *spuma nitri* were given. Reasons for believing this are, amongst others, the facts stated by Pliny, that this nitrum does not decrepitate when thrown on the fire ("igni non exsilit nitrum") as saltpetre does; that it possesses a fatty touch, this property being heightened by boiling it with lime; that the nitrum is used both with and without oil in the baths [" in balneis utuntur (nitro) sine oleo "]; and that it is largely used in the manufacture of glass.

The word nitrum was (p. 240) long applied indiscriminately to both soda and potash. The terms soda and natron came into general use in the fifteenth century to distinguish fixed alkali from nitre.

134 The sodium compounds occur very abundantly and are universally diffused. Vast quantities of sodium chloride, NaCl, are found in extended deposits as rock salt in different parts of the world and in various geological formations, whilst the same compound occurs in solution in sea-water, salt lakes, salt springs, and many mineral waters. The double fluoride of sodium and aluminium, or cryolite, $3NaF,AlF_3$, is found in large quantity in Greenland; sodium nitrate, or Chili saltpetre, $NaNO_3$, is deposited in beds several feet thick in the rainless districts of Southern Peru and Bolivia; the carbonate, Na_2CO_3, and the sulphate, Na_2SO_4, are found either in springs or as deposits in the beds of dried-up lakes. Many minerals, especially nepheline, sodalite, albite, labradorite, contain sodium silicate in considerable quantity, whilst traces of sodium compounds occur in all silicates. Indeed it is difficult to find any substance which does not contain traces of sodium.

Sodium compounds are found also in living organisms of all kinds. The whole of the animal body, especially the juices, is rich in sodium compounds, particularly the carbonate, chloride, and phosphate, with sodium salts of organic acids.

Plants growing in or near the sea contain sulphate, iodide, and chloride of sodium. Sodium salts are, however, not characteristic of vegetable life in the same sense that potassium salts are. Thus, whilst the latter alkali is always present in larger quantities in certain organs of the plant than in others, sodium appears in general to be equally diffused throughout the whole organism. It is also a remarkable fact that the sodium salts contained in the ashes of plants are insoluble in water, as they combine with the phosphates of the alkaline earths to form insoluble compounds. For this reason the presence of sodium compounds in the ashes of plants has often been overlooked.

Duhamel and Cadet have shown that if the plant *Salsola Soda*, which grows near the sea, and which yields an ash rich in soda salts, be transplanted to an inland situation, the ash gradually loses in soda and gains in potash, until the whole of the former disappears. If inland plants are grown near the sea the reverse change takes place (Correnwinder).

135 *Preparation of Metallic Sodium.*—Sodium, like potassium, was first obtained in 1807 by Davy [1] by electrolysis of caustic soda. Some years later sodium was manufactured by a process, proposed by Brunner, of igniting a mixture of sodium carbonate and charcoal, and this method was improved by Deville,[2] who showed that the manufacture of sodium is simpler and easier than that of potassium, as there is no liability to explosions. This process, is however, a costly and an uneconomical one, inasmuch as a considerable quantity of the sodium is volatilised and burns; some adheres to the receiver, and the reduction does not occur completely, so that in a well-conducted operation the sodium obtained is only about one-third of the theoretical yield, and, moreover, as it is necessary to expose the retorts to a white heat, they are rapidly burnt through and rendered useless. An improvement introduced by Castner [3] in 1886 was the replacement of sodium carbonate by caustic soda. The reaction is expressed as follows:

$$6NaOH + 2C = 2Na_2CO_3 + 3H_2 + 2Na.$$

[1] *Phil. Trans.*, 1808, **98**, 1. [2] *Ann. Chim. Phys.*, 1855, [3], **43**, 5.
[3] See Roscoe, *Proc. Roy. Inst.*, 1889, **12**, 453.

By this process, which was successfully worked for some time, the price of sodium was materially reduced, but subsequently Castner [1] introduced another method of manufacture, viz., the electrolysis of caustic soda, which has placed the sodium industry on an entirely new basis, and obviated the great difficulties which necessarily beset all the older processes. The temperature of decomposition rises only a few degrees above 300° and thus the wear and tear of the apparatus is reduced to a minimum, whilst at the same time the whole of the sodium is obtained as metal. In the year 1807, Davy, with his battery of 100 cells,

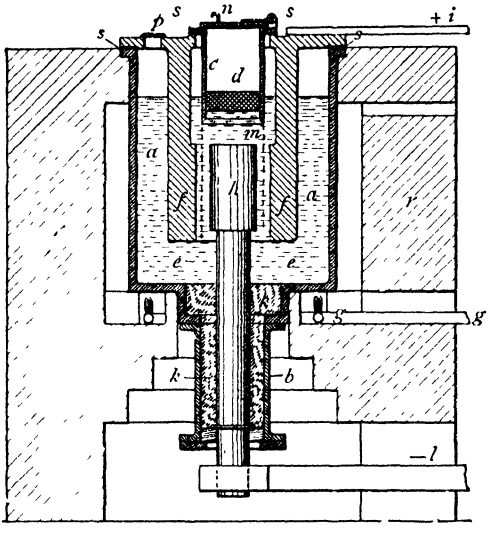


FIG. 94.

found it "impossible to produce the effects of decomposition on pieces of soda of more than fifteen or twenty grains in weight"; the process has now been so amended that very large quantities of sodium are manufactured annually.

The apparatus consists of an iron vessel *a* (Fig. 94) suitably mounted in brickwork *r*, so that the heat applied by the gas burners *g* may be well distributed. The vessel *a* is provided with one or more base pipes *b* adapted to receive the negative electrodes *h*, which are preferably of metal and pass up into the vessel. Suspended directly above the cathode *h* is a tubular iron receptacle *c* which is provided on its upper end with a lid *n*, whilst to its lower edges is secured an iron wire gauze *m*,

[1] *J. Soc. Chem. Ind.*, 1891, **10**, 777; Pat. No. 13356 (1890).

which, when the receptacle *c* is placed in position, completely surrounds the cathode. The positive electrodes *f* are made of such metal as will withstand the oxidising action of the evolved gases, as, for instance, nickel, and either form part of the cover of the vessel *a* or are bolted to it, being so placed that when the cover is adjusted the electrodes are a suitable distance from, and directly surround, the gauze *m*. Electrical connection is made between the cover by the connection *i* with the positive pole of the dynamo, and with the negative pole by the connection *l*. The cover is provided with an opening *p* for the escape of the gases resulting from the electrolysis, this opening serving also for the introduction of a thermometer. Insulation is made at the points *ss*, by means of asbestos. The size and distance apart of the electrodes are both proportioned to the quantity of current to be supplied, the effective action of the apparatus being largely dependent on the accuracy with which this is carried out.

The sodium, being much lighter than the hydroxide, rises together with the hydrogen from the negative electrode and passes into the receiver *c*, the hydrogen escaping around the edges of the cover *n*, while the molten metal continues to collect in quantity. From time to time this collected metal *d* is removed by means of a large finely-perforated spoon, the perforations enabling the molten caustic to flow out whilst the metal remains in the spoon. Caustic is added to the bath from time to time to replace the metal removed, and in this way a continuous process may be carried on in an economical manner.

Any rise of temperature is followed by a proportionate loss of product and waste of electrical energy, but it is possible so to adjust the electrical current and the quantity of caustic alkali forming the electrolyte that the proper temperature will be maintained in a previously melted bath without external heat; or the current may be temporarily increased in order to melt the bath, being subsequently reduced, until the working temperature is attained; if large currents are used the bath and the electrodes may be artificially cooled by air or water circulation. The cathode may be conveniently sealed in the extension *b* by means of molten caustic *k* which is allowed to harden before beginning the process.

In order to secure a fair yield of metal for the current applied it is necessary that the temperature of the electrolyte should not be allowed to rise above 330°, or 20° above the melting

point of caustic soda. The total current for a cell holding 100 kgrm. of molten soda is 1200 amperes, giving a current efficiency of 45 per cent.

The sodium thus obtained is sufficiently pure for ordinary purposes, and only requires to be remelted and then cast into sticks about one inch thick and a foot long. These may be preserved in closed vessels in dry air for a long time without undergoing any considerable oxidation, but it is usual first to moisten the sticks with petroleum. When in smaller masses it is advisable to keep the sodium under petroleum.

In the Griesheim contact electrode process, the cathode consists of a vertical iron rod which can be lowered to make contact with the fused soda electrolyte in the bath. As fast as the sodium is liberated, the cathode is raised and the end of the sodium rod thus formed serves as the cathode. The advantage of this process is that the metal is not so much exposed to the solvent action of the electrolyte as in the Castner process.

Many suggestions have been made for the electrolysis of sodium chloride whereby metallic sodium and chlorine gas would be the products. There appears, however, to be only one plant in successful operation in which direct electrolysis of fused sodium chloride takes place and for this a circular brick-lined furnace, with a circular graphite anode and a hollow iron cathode through which the sodium passes to a collector, are used.

Chemically pure sodium is prepared by distilling pure sodium chloride with metallic calcium *in vacuo*.[1]

136 *Properties.*—Sodium is a white metal possessing a high silver-white lustre. It may be obtained in the crystalline condition by sealing up 100 grams of metal in a glass tube filled with hydrogen. The sodium is melted at one end of the glass tube and then allowed to filter through some wire gauze placed in a narrowed portion of the tube. The melted metal is thus rendered perfectly free from oxide, and must be fused in the clean part of the tube, allowed to cool partially, and then the central liquid portion suddenly poured off from the solidified crust. According to Long,[2] sodium crystallises in the tetragonal system, forming acute octahedra, but it probably exists in two modifications of which the metastable form, β-sodium, is the less dense, and changes exothermically to α-sodium, the trans-

[1] Hackspill, *Ann. Chim. Phys.*, 1913, [8], **28**, 613.
[2] *Journ. Chem. Soc.*, 1861, **13**, 123.

formation occurring most rapidly at about 95°.[1] The density of sodium is 0·9723 at 0°.[2] At −20° sodium is rather hard, at 0° it is very ductile, at the ordinary temperature it has the consistency of wax, at 50° it is semi-fluid, and it melts at 97·6°,[3] forming a liquid resembling mercury in its appearance. Sodium boils at 882·9°,[4] the vapour is colourless when seen in thin layers, but of a peculiar purple colour by transmitted light when seen in quantity (Roscoe and Schuster), and exhibits a green fluorescence.[5] The vapour is monatomic, as shown by the ratio of the specific heats, 1·68°.[6] With the exception of silver, copper, and gold, it conducts heat and electricity better than any other metal. The specific resistance is $4{\cdot}873 \times 10^{-6}$ at 20°, and $9{\cdot}724 \times 10^{-6}$ at 100°, increasing suddenly at the melting point,[7] and next to cæsium, rubidium, and potassium, it is the most electro-positive metal (Bunsen).

Sodium has been obtained in the colloidal state by the electrical method (p. 82), forming an unstable violet-coloured solution in ethyl ether.[8]

When freely exposed to moist air sodium oxidises like potassium, although not quite so rapidly. It burns with a bright yellow flame when heated in the air, forming the monoxide and the dioxide. Thrown on to cold water it floats on the surface, disengaging hydrogen and dissolving, but not evolving heat enough to ignite the hydrogen. With hot water, or a thick paste of starch, or wet filter paper, the evolved hydrogen ignites and burns with a yellow-tinted sodium flame.

Sodium is largely used for the manufacture of cyanides and sodium peroxide, and for the preparation of silicon, boron, and of certain organic substances such as artificial indigo and antipyrin. Sodium amalgam is of great service as a reducing agent in the laboratory. Thermal analysis and microscopic

[1] Cohen and Wolff, *Proc. K Akad. Wetensch. Amsterdam*, 1915, **18**, 91; Cohen and de Bruin, *ibid.*, 1915, **17**, 926, see also Cohen and Heldermann, *ibid*, 1915, **17**, 1238; Cohen, *Trans. Faraday Soc.*, 1915, **10**, 216.

[2] Hackspill, *Ann. Chim. Phys.*, 1913, [8], **28**, 613.

[3] Bernini and Cantoni, *Nuovo Cim*, 1914, [6], **8**, ii, 241.

[4] Heycock and Lamplough, *Proc. Chem. Soc.*, 1912, **28**, 3.

[5] Wiedemann and Schmidt, *Ann. Phys. Chem.*, 1896, [2], **57**, 447; Wood *Phil. Mag*, 1905, [6], **10**, 513; *Physikal. Zeit.*, 1906, **7**, 105; *Phil. Mag.*, 1906, [6], **12**, 499; 1909, [6], **18**, 530; Zickendraht, *Physikal. Zeit.*, 1908, **9**, 593; Dunoyer, *Compt. rend.*, 1911, **153**, 333, 1912, **154**, 815.

[6] Robitzsch, *Ann. Physik*, 1912, [4], **38**, 1027.

[7] Northrup, *Trans. Amer. Electrochem. Soc.*, 1911, **20**, 185.

[8] Svedberg, *Ber.*, 1905, **38**, 3616.

examination of mercury-sodium alloys have shown that these contain compounds of the formulae: Na_3Hg, Na_3Hg_2, NaHg, Na_7Hg_8, $NaHg_2$, and $NaHg_4$.[1]

SODIUM COMPOUNDS.

Sodium and Oxygen.

137 Sodium forms two well-defined oxides, a strong basic monoxide, Na_2O, and a peroxide, Na_2O_2. In addition to these a grey suboxide possibly exists, and also a sesquioxide, Na_2O_3.

Sodium Suboxide, Na_3O, is stated to be formed when a clean surface of the metal is first exposed to air, and when pure air is passed through sodium just above its melting point. It is described as a grey arborescent mass, which burns when heated in the air, and decomposes water with evolution of hydrogen.[2]

Sodium Monoxide, Na_2O.—Sodium does not oxidise in perfectly dry air, but when heated in slightly moist oxygen it takes fire and burns with formation of a mixture of the monoxide and peroxide. If the amount of oxygen be limited and the sodium be not heated above 180°, only the former oxide is obtained,[3] and can be freed from the unaltered metal by distillation in a vacuum.[4]

The monoxide can be prepared also by heating sodium nitrate or nitrite with metallic sodium,[5] the nitrogen being liberated:

$$2NaNO_2 + 6Na = 4Na_2O + N_2.$$

It is a white, amorphous mass (Rengade), having a conchoidal fracture, and a sp. gr. of 2·805. It melts at a dull red heat, and undergoes volatilisation at a still higher temperature (Davy); when heated above 400° it is decomposed into the peroxide and metal, but in a vacuum is dissociated at 300°.[6] When brought in contact with water violent action occurs, sodium hydroxide being formed. Carbon dioxide is not absorbed by sodium monoxide when cold, but sodium carbonate is formed at 300°.[3]

Sodium monoxide is the oxide corresponding to the monovalent sodium salts, to which class, as already stated, all the stable salts belong. They are characterised by the fact that

[1] Vanstone, *Trans. Faraday Soc.*, 1911, **7**, 42.
[2] de Forcrand, *Compt. rend.*, 1898, **127**, 364, 514.
[3] Holt and Sims, *Journ. Chem. Soc.*, 1894, **65**, 442.
[4] Rengade, *Compt. rend.*, 1906, **143**, 1152.
[5] German Patent, 142467 (22/7/1902).
[6] Rengade, *Compt. rend.*, 1907, **144**, 755.

almost all are readily soluble in water, even when the corresponding salts of the remaining alkali metals are sparingly soluble. The least soluble inorganic salt of sodium is the metantimonate.

Sodium Hydroxide, Sodium Hydrate, or *Caustic Soda,* NaOH.—When water is added to sodium monoxide great heat is evolved and the hydroxide is formed; it is obtained also when water is decomposed by sodium. It is best prepared in this way by placing metallic sodium in a pointed funnel of nickel gauze over water contained in a basin, and covering the funnel with a bell jar which stands in the basin, raised from the bottom by some pieces of glass rod. The water vapour attacks the sodium, and a solution of pure caustic soda (of about 40 per cent. strength) is formed, which drips into a platinum or nickel vessel placed under the funnel to receive it. The hydrogen evolved passes out through the water under the edge of the bell jar.[1]

Care is needed in the construction of the apparatus for this preparation, as, if liquid water comes in contact with large pieces of sodium, dangerous explosions sometimes occur. The cause of these is not definitely known, but they are possibly due to the presence of carbide in the metal.[2] The solution may be evaporated, and the caustic soda obtained in a fused state and cast into sticks. The hydroxide thus obtained is free from chloride and sulphate of sodium, and from alumina, silica, and oxide of iron.

The manufacture of caustic soda is described later (pp. 313, 325).

Commercial caustic soda often contains sodium chloride, sodium sulphate, alumina, and frequently silica and ferric oxide. It may be purified by dissolving in pure alcohol, and evaporating the clear solution to dryness in a silver basin (*Soude a l'alcool,* Berthollet). It still contains traces of sodium chloride, carbonate, and acetate, the latter being formed by the action of caustic soda on the alcohol.

Caustic soda is a white opaque solid, with a fibrous texture; it has a specific gravity of 2·13 (Filhol), melts at 310°, is rather less volatile than caustic potash, and decomposes into its elements at the melting point of cast iron; heated in an atmosphere of nitrogen at 400° it becomes quite anhydrous and shows no signs of decomposition when the temperature is raised to 720°.[3] It

[1] Kuster, *Zeit. anorg. Chem.,* 1904, **41**, 474.

[2] Harpf and Fleissner, *Chem. Centr.,* 1906, II. 994; Kuster, *ibid.*

[3] Bergmann, *Ber.,* 1909, **42**, 4728.

deliquesces in the air and when moist absorbs carbon dioxide, and acts as a powerful cautery. It is very soluble in water and in alcohol, one part dissolving in 0·47 part of the former, yielding a strongly alkaline solution. The fused substance rapidly corrodes most metals; cast iron and silver are slightly affected, gold being the only metal which is not attacked. The action on copper is relatively considerable, and it has been shown that in this case, and with iron and nickel, the reaction is essentially an oxidation of the metal.[1]

Hydrates of Caustic Soda.—The equilibrium curve for caustic soda and water is of a very complex character,[2] and indicates the existence of a number of hydrates. Among these the following have been isolated: $NaOH,H_2O$, melting at 64°, is always produced when a hot concentrated solution of the hydroxide is allowed to cool; $NaOH,2H_2O$, melting at about 12°, is obtained from 96·8 per cent. alcohol[3]; $2NaOH,7H_2O$ is deposited in large transparent tabular monoclinic crystals when a solution of soda-ley of specific gravity 1·365 is exposed to a temperature of −8°. These crystals melt at 6°, yielding a liquid having a specific gravity of 1·405 (Hermes),[4] but according to Pickering melt at 15·5°. In addition to these there is evidence for the existence of two isomeric hydrates with $4H_2O$; $NaOH,5H_2O$; $NaOH,7H_2O$, and a complex labile hydrate with $3·11H_2O$. The hydrate, $2NaOH,3H_2O$, has also been described.[5]

The following table gives the specific gravity of caustic soda solutions at 15°/4°, according to the experiments of Bousfield and Lowry:[6]

Percentage of NaOH.	Specific gravity.	Percentage of NaOH.	Specific gravity.
5	1·0555	30	1·3309
10	1·1111	35	1·3830
15	1·1665	40	1·4334
20	1·2218	45	1·4815
25	1·2768	50	1·5290

Caustic soda is a most useful substance, and is largely used for many industrial processes, its chief employment being in the

[1] Wallace and Fleck, *Journ. Chem. Soc.*, 1921, **119**, 1839.
[2] Pickering, *Journ. Chem. Soc.*, 1893, **63**, 890; Dietz, *Wissenschaft. Abhandl. Reichsanstalt*, 1900, **3**, 450.
[3] Gottig, *J. pr. Chem.*, 1889, [2], **2**, 360.
[4] *Pogg. Ann.*, 1863, **119**, 170.
[5] de Forcrand, *Compt. rend.*, 1901, **133**, 223.
[6] *Phil. Trans.*, 1905, [*A*], **204**, 253.

manufacture of soap. A description of the methods used for its preparation on the large scale will be found in the sequel.

Sodium Dioxide, Na_2O_2, is formed when the metal is heated in an excess of air or oxygen, and is prepared on the large scale by placing sodium on aluminium trays, which are in turn placed on tram carriages which are passed through an iron tube heated to about 300°. The air is freed from moisture and carbonic acid before passing through the tube, and as the fully oxidised product is taken from the finishing end of the tube a fresh charge of sodium is placed at the other end, the tram carriages being pushed forward to admit the fresh trays. The finished product contains about 93 per cent. Na_2O_2. About 500 tons are manufactured per annum by this process by the Castner Kellner and other companies.

Pure sodium dioxide is yellow, but becomes white on exposure to the air from absorption of water and carbon dioxide.[1] It dissolves in water with partial formation of caustic soda and hydrogen dioxide, the latter decomposing on heating into water and oxygen, and an analogous decomposition takes place on addition of mineral acids, the corresponding sodium salt being formed. It does not give off oxygen, unless heated to very high temperatures, but acts as a very strong oxidising agent on any substance mixed with it, and is therefore used in the analysis of many minerals, such as iron pyrites, chrome ironstone, etc.; fused with finely divided gold, it forms sodium aurate.[2] It has a very violent action on glacial acetic acid, the whole mass becoming ignited, and in presence of moisture oxidises any readily combustible substances such as wood, paper, etc., and great care must therefore be exercised in dealing with large quantities of the dioxide. It is reduced to metallic sodium by charcoal, coke, or graphite at 300–400°.[3]

It absorbs carbon dioxide with formation of sodium carbonate and liberation of oxygen, and on account of this property its use has been proposed [4] for the regeneration of air in close spaces contaminated by respiration, such as submarines, and in respiratory apparatus for use in atmospheres containing noxious gases. It also absorbs carbonic oxide with formation of sodium carbonate, and nitrous and nitric oxides with formation of sodium nitrate.[5] With ammonium persulphate it forms an

[1] Jaubert, *Compt. rend.*, 1901, **132**, 35.
[2] Meyer, *Compt. rend.*, 1907, **145**, 805.
[3] Bamberger, *Ber.*, 1898, **31**, 451. [4] German Patent, 168717 (3/3/1904).
[5] Harcourt, *Journ. Chem. Soc.*, 1862, **14**, 276.

explosive mixture.[1] When the solution in cold water is allowed to evaporate, large tabular hexagonal crystals of the hydrate $Na_2O_2,8H_2O$ separate out, which on standing over sulphuric acid lose water, forming the hydrate $Na_2O_2,2H_2O$. The first hydrate is formed also when alcohol is added to a mixed solution of caustic soda and hydrogen peroxide,[2] and these two hydrates are also formed when the peroxide is exposed to moist air free from carbon dioxide.[3] When carefully hydrated by means of ice it absorbs carbon dioxide at low temperatures with the formation of percarbonates.[4]

A colourless powder having the composition $Na_2O_2.2HCl$ is formed when sodium dioxide is suspended in carbon tetrachloride and treated with dry hydrochloric acid gas; it is readily decomposed by water, giving hydrogen peroxide.[5]

A solution of the dioxide in hydrochloric acid, consisting of sodium chloride and hydrogen dioxide, is now manufactured on the large scale, and is much used for bleaching straw.

Monosodium Hydrogen Peroxide, NaO.OH.—When sodium peroxide is treated with alcoholic hydrochloric acid or with absolute alcohol at 0°, the dioxide partially dissolves and a white powder remains which has the composition NaO_2H.[6] It dissolves in water at 0°, forming a strongly alkaline solution, which on warming decomposes into caustic soda and oxygen, the same decomposition taking place with explosion when the dry substance is heated. It does not yield salts with mineral acids, but with acetic acid forms a crystalline compound of sodium acetate containing hydrogen peroxide of crystallisation $2CH_3.COONa,H_2O_2$.[7] Its formation from the dioxide is represented by the equation:

$$Na_2O_2 + C_2H_5OH = NaOC_2H_5 + NaO.OH.$$

Monosodium hydrogen peroxide gives oxygen with potassium permanganate, and chlorine with hydrochloric acid; it liberates iodine from potassium iodide at the ordinary temperature.

The dry substance is not acted upon by carbon dioxide, but in presence of a trace of moisture it is decomposed by the gas;

[1] Kempf and Oehler, *Ber.*, 1908, **41**, 2576.

[2] Fairley, *Journ. Chem Soc.*, 1877, **31**, 125. See also de Forcrand, *Compt. rend.*, 1899, **129**, 1246; 1900, **130**, 1555.

[3] Jaubert, *Compt. rend*, 1901, **132**, 86.

[4] Wolffenstein and Peltner, *Ber.*, 1908, **41**, 280; German Patent, 188569.

[5] Jaubert, German Patent, 229572.

[6] Tafel, *Ber.*, 1894, **27**, 816, 2297.

[7] D'Ans and Friederich, *Zeit. anorg. Chem.*, 1912, **73**, 325.

an aqueous solution absorbs carbon dioxide at low temperatures, forming an unstable percarbonate.[1] When treated with absolute alcohol or with hydrogen peroxide, a stable peroxide is formed containing hydrogen peroxide of crystallisation, $2NaHO_2,H_2O_2$;[2] the same substance is formed by treating sodium ethoxide with a mixture of 30 per cent. hydrogen peroxide and absolute alcohol,[3] and by the action of an ethereal solution of anhydrous 100 per cent. hydrogen peroxide on metallic sodium.[4]

Sodium Trioxide, Na_2O_3, is formed according to Joannis,[5] by the action of an excess of oxygen on a solution of sodium in liquid ammonia. It is decomposed by water with evolution of oxygen and formation of the hydrated dioxide, and by carbon dioxide with evolution of oxygen.

Sodium and Hydrogen.

138 *Sodium Hydride*, NaH.—When sodium is heated in hydrogen at 370°, the hydride is produced as a colourless crystalline sublimate. It has the specific gravity 0·92, and is insoluble in organic solvents and in liquid ammonia, but dissolves in fused sodium. When strongly heated in a vacuum it dissociates into its elements. The hydride is at once decomposed by water with formation of caustic soda and hydrogen, burns when heated in dry air, and ignites spontaneously in moist air. It burns brilliantly in fluorine, chlorine, and nitrogen peroxide, and is decomposed by hydrogen chloride, nitric and sulphuric acids, and by solid oxidising agents.[6] When the hydride is heated in carbon dioxide carbon is liberated, whilst it combines with moist carbon dioxide to form sodium formate,[7] $H.CO_2Na$. The absorption of hydrogen by sodium was observed by Troost and Hautefeuille,[8] but they did not obtain the crystalline hydride. The heat of formation of the solid compound is 16·6 cal.[9]

[1] Wolffenstein and Peltner, *loc. cit.*

[2] D'Ans and Friederich, *loc. cit.*

[3] Wolffenstein and Peltner, *loc. cit.*; German Patent, 190369.

[4] D'Ans and Friederich, *loc. cit.*

[5] *Compt. rend.*, 1893, **116**, 1370; *Ann. Chim. Phys*, 1906, [8], **7**, 5.

[6] Moissan, *Compt. rend*, 1901, **133**, 803; 1902, **134**, 71; Holt, *Proc. Chem. Soc.*, 1903, 187; *Mem. Manch. Phil. Soc.*, 1909, **53**, [17], 1.

[7] Moissan, *Compt. rend.*, 1903, **136**, 723.

[8] *Ann. Chim. Phys.*, 1874, [5], **2**, 273.

[9] de Forcrand, *Compt. rend.*, 1905, **140**, 990; compare also Keyes, *J. Amer. Chem. Soc.*, 1912, **34**, 779.

Sodium and the Halogens.

139 *Sodium Fluoride*, NaF, is prepared by neutralising aqueous hydrofluoric acid with caustic soda or sodium carbonate. It crystallises in cubes and sometimes in octahedra,[1] has a specific gravity of 2·766, and melts at 980° (Ruff and Plato). It is sparingly soluble in water, 100 parts of water dissolving 4 parts of the salt at 15° (Frémy). It is sometimes employed as an antiseptic.

Sodium Hydrogen Fluoride, $NaHF_2$, unlike the corresponding potassium salt, is not deliquescent and is, therefore, best suited for the preparation of fluorine by electrolysis of the molten acid fluoride.[2]

Sodium Chloride, or Common Salt, NaCl.—Davy states that sodium takes fire when brought into chlorine gas, but Wanklyn [3] has shown that dry chlorine does not attack sodium even in the melted state. Metallic sodium also retains its brightness in liquid chlorine at — 80°.

Chloride of sodium occurs as rock-salt in large deposits in various geological strata, in solution in sea-water and brine springs, and in small quantities in all running water. The chief European deposits of salt occur in the trias formation. The most important in England are those at Northwich and Winsford in Cheshire, at Fleetwood in Lancashire, and at Middlesboro' in Yorkshire. On the Continent important deposits occur at Weilizca in Galicia, at Reichenhall, Hallein, Berchtesgaden, and other localities in the Tyrol, and at Stassfurt in the north of Germany. Rock-salt occurs also in France, Spain, and Switzerland, and in Asia, Africa, and America, in various localities.

The Cheshire salt-beds occur in the keuper (triassic) beds. They are two in number, separated by about thirty feet of clay: they are together about sixty yards thick, and extend over an area of sixteen miles by ten.

The methods adopted for raising and working the salt differ widely, according to the nature of the deposit and its situation. Sometimes the rock-salt is mined and brought up to the surface; generally, however, salt springs or brine wells are artificially constructed by sinking a bore-hole through the overlying strata

[1] Körbs, *Zeit. Kryst. Min.*, 1907, **43**, 451.

[2] Argo, Mathers, Humiston, and Anderson, *J. Physical Chem.*, 1919, **23**, 348.

[3] *Chem. News*, 1869, **20**, 271.

to the salt-bed, and allowing water to pass down this boring. The water soon becomes saturated with salt, and it is then pumped up and the salt obtained by evaporation, either by means of fuel or by exposure to air.

The process of evaporating the brine, 100 parts by weight of which in Cheshire usually contain 23·3 parts of salt, is of the simplest kind. Indeed it has not been improved since the time of the Romans, and although very numerous patents for the purpose have been taken out, no economy in fuel has been effected. The brine is evaporated in large shallow iron pans heated by means of fires placed beneath. The appearance and quality of the salt deposited depend upon the temperature at which the brine is kept and the rapidity with which the process of evaporation is conducted. The Cheshire brine contains about 1·65 per cent. of calcium sulphate and about 0·05 per cent. of magnesium chloride. The first of these salts is deposited as pan-scale when the brine is boiled down.

In Germany, where fuel is dear, the brine is sometimes evaporated by exposing it to the action of the air by a process termed "graduation." After having been allowed to trickle several times over high walls of fagots and thus become more concentrated, it is boiled down in pans.

Preparation of Salt from Sea-water.—The evaporation of sea-water in salterns, or brine-pans, by the aid of air and the sun's heat has been carried out from very early times. In England, at Hayling Island near Portsmouth, and at Lymington, and in Scotland at Saltcoats on the Ayrshire coast, such salterns have been in use quite recently. In countries more favoured by sunshine, such as the coast of France, Sicily, Portugal, and Spain, these salterns are more numerous. When this salt, termed Bay-salt, is deposited, a mother-liquor called Bittern is left. This consists of the chlorides, sulphates, and bromides of magnesium and potassium, and from this bromine is obtained.

All common salt contains a small quantity of sodium sulphate, calcium sulphate, and magnesium chloride. The presence of the last compound renders the salt liable to become damp in the air, and it often attacks the iron pans, causing the presence of traces of ferric chloride in the salt.

In order to prepare chemically pure sodium chloride from common salt, hydrochloric acid gas is passed into a saturated solution of salt. A precipitate of the pure chloride is thrown down, the alkali sulphates and magnesium chloride remaining

in solution. The precipitate is transferred to a filter, washed with concentrated hydrochloric acid, and then dried and fused in a platinum basin.

Properties.—Sodium chloride crystallises in cubes. Rock-salt is usually found in cubical crystals, sometimes, however, in octahedra and intermediate forms. It possesses an agreeable saline taste and a specific gravity at 0° of 2·16. Rock-salt is highly diathermanous, that is, it permits the heat rays, dark as well as visible, to pass through it; hence it is a valuable substance in thermal researches. Sodium chloride melts at 815·4° (Meyer, Riddle, and Lamb), 808° (Amadori),[1] and begins to volatilise at temperatures not far removed from its melting point; hence it cannot be fused without loss (Stas). It boils at 1750° (Emich).[2] Paal [3] has prepared a colloidal form of sodium chloride.

When heated with silicic or boric acid, sodium chloride is decomposed, with liberation of hydrochloric acid and formation of a silicate or borate.[4] It has been proposed to utilise the former of these reactions for the manufacture of sodium carbonate, but without practical success. Sulphuric acid decomposes it, hydrochloric acid and hydrogen sodium sulphate or the normal sulphate being formed.

According to the experiments of Berkeley,[5] one hundred parts of water dissolve the following quantities of sodium chloride at the corresponding temperatures:

Temp.	0°	10°	20°	30°	40°	60°	80°	100°	107·7°
NaCl.	35·74	35·78	35·94	36·16	36·47	37·19	38·02	39·12	39·65

The boiling point of the saturated solution is 107·7° at 745 mm. pressure (Berkeley). The specific gravity of salt solutions of different strengths is, according to Gerlach,[6] as follows:

Percentage of NaCl.	5	10	15	20	25
Specific gravity at 15°.	1·03624	1·07335	1·11146	1·15107	1·19228

Chloride of sodium is nearly insoluble in absolute alcohol.

When the temperature of a saturated solution of sodium chloride is lowered to −10°, a crystalline hydrate separates out [7]

[1] *Atti R. Accad. Lincei*, 1912, [5], **21**, i. 467.

[2] *Verh. Ges deut. Naturforsch. Aerzte*, 1910, ii. 65.

[3] *Ber.*, 1906, **39**, 1436, 2859; Paal and Kuhn, *Ber.*, 1908, **41**, 51.

[4] For a quantitative investigation of such reactions see Clews and Thompson, *Journ. Chem. Soc.*, 1922, **121**, 1442.

[5] *Phil. Trans.*, 1904, [*A*], **203**, 206.

[6] *Zeit. anal. Chem.*, 1869, **8**, 279.

[7] Lowitz, *Crell. Ann.*, 1793, i. 314.

having the composition $NaCl,2H_2O$; this is obtained also by cooling a solution of sodium chloride in hot hydrochloric acid, in which it is sparingly soluble.[1] When brine is further cooled to −22°, acicular bundles of crystals separate out as a eutectic mixture [2] containing 23·7 per cent. of sodium chloride.

Sodium chloride is frequently found as rock-salt in blue crystals, which become colourless when heated. A similar coloration can be produced by exposing colourless crystals to the vapour of metallic sodium or potassium, to the cathode rays, and to the radiation from radium. The artificial coloration appears to be due to the presence of either the metal or a sub-chloride, but it has not yet been definitely ascertained whether the natural coloration is due to the same cause or to the presence of an organic colouring matter.[3]

Sodium Bromide, NaBr, and *Sodium Iodide*, NaI, are prepared by processes similar to those employed in the case of the corresponding potassium salts, the latter being more largely used (p. 346). Both crystallise from hot concentrated solution in anhydrous cubes, whilst if the solutions be allowed to evaporate at the ordinary temperature, monoclinic prisms are deposited. These contain two molecules of water of crystallisation, $NaBr,2H_2O$ and $NaI,2H_2O$, and are isomorphous with the corresponding hydrate of sodium chloride; hydrates with $5H_2O$ also exist at low temperatures. The bromide melts at 748°, and the iodide at 662°.[4] Both sodium bromide and sodium iodide have been prepared in a colloidal form by Paal.[5] Sodium iodide reacts with liquid sulphur dioxide to form a sulphone, $NaI_3,3SO_2$, which is amorphous.[6]

Sodium Hypochlorite, NaClO, may be prepared by passing chlorine over powdered sodium carbonate slightly moistened with water; it is, however, usually obtained in solution on the small scale by passing chlorine into a solution of caustic soda, which yields a mixture of the chloride and hypochlorite:

$$2NaOH + Cl_2 = NaCl + NaClO + H_2O.$$

Traces of iron render these solutions unstable, but in the absence

[1] Bevan, *Chem. News*, 1877, **35**, 17.

[2] Matignon, *Compt. rend.*, 1909, **148**, 559.

[3] See Wohler and Kasarnowski, *Zeit. anorg. Chem.*, 1905, **47**, 353, where the various possibilities are discussed and references to the literature given; and Siedentopf, *Physikalische Zeit.*, 1905, **6**, 855.

[4] Amadori, *Atti R. Accad. Lincei*, 1912, [5], **21**, i. 467.

[5] *Ber.*, 1906, **39**, 2859; Paal and Kühn, *Ber.*, 1908, **41**, 51.

[6] de Forcrand and Taboury, *Compt. rend.*, 1919, **168**, 1253.

of iron fairly stable solutions, yielding about 30 per cent. of available chlorine, can be prepared. More concentrated solutions are obtained by cooling the original solution to $-10°$, removing the precipitated sodium chloride, replacing this with an equivalent weight of caustic soda, and again saturating with chlorine. By repetition of this process a solution of sodium hypochlorite approximately $5N$ is obtained, from which the crystalline salt is deposited at $-10°$ in fine tetragonal needles, m. p. 18—19°, containing six or seven molecules of water of crystallisation. These crystals are much more stable than the solutions from which they crystallise.[1] They melt to a cloudy liquid which, at the ordinary temperature, deposits large crystals of the penta-hydrate, $NaClO,5H_2O$, which melts at 27° and is also very deliquescent but may be preserved unaltered in well closed vessels.

Sodium hypochlorite in aqueous solution may decompose in either of the following ways :

(i) $2NaClO \rightarrow 2NaCl + O_2$.
(ii) $2NaClO \rightarrow NaCl + NaClO_2$.

Reaction (i) occurs at 25° even in the dark and is much accelerated by light, especially that corresponding to the absorption band in the ultra-violet shown by the solution :[2] reaction (ii) is favoured by rise of temperature and represents the main change at about 50°.[3] The further change to chlorate occurs according to the equation : $NaClO + NaClO_2 \rightarrow NaClO_3 + NaCl$.

Technical Preparation.—Sodium hypochlorite in solution was known about 1790, and in 1820 it was well known as Eau de Labarraque, and subsequently as Eau de Javelle indiscriminately with the potassium hypochlorite solution. The solution was first made by passing chlorine into a soda solution, but afterwards by decomposing bleaching powder by a soda solution or by sodium sulphate; these solutions have been made in large quantities in South Lancashire and France for bleaching purposes; they contain 7 to 15 per cent. of available chlorine.

Still weaker solutions are now prepared in large quantities at a number of paper and bleaching works by electrolysing a solution of common salt under suitable conditions so that the hypochlorite shall not be converted into chlorate, nor yet reduced

[1] Muspratt and Shrapnell-Smith, *J. Soc. Chem. Ind.*, 1898, **17**, 1096; 1899, **18**, 210. Applebey, *Journ. Chem. Soc.*, 1919, **115**, 1106.
[2] Lewis, *Journ. Chem. Soc.*, 1912, **101**, 2371.
[3] Foerster and Dolch, *Zeit. Elektrochem.*, 1917, **23**, 137.

by the escaping hydrogen to chloride. The solutions are therefore made only weak, seldom exceeding 1 per cent. of available chlorine, but as they are manufactured where used, this is no disadvantage. The first practical process was that of Hermite in 1884, since when numerous variations have been introduced; a full account of these has been given by Engelhardt,[1] and the theory of the process has been described by Abel.[2] The solutions frequently contain hypochlorous acid.

The crystals prepared by Muspratt and Smith in their first experiments melted at about 20° and then rapidly decomposed, so that there was little prospect of making this material technically useful; but in 1903 Muspratt, by drying the crystals in a vacuum, obtained a powder melting about 45° and containing from 40 to 60 per cent. of available chlorine.

Sodium Chlorate, $NaClO_3$.—This salt is obtained, according to Muspratt and Eschelmann's process, by saturating milk of magnesia with chlorine and adding sodium carbonate to the resulting solution of magnesium chloride and chlorate. The liquor, after filtering from precipitated carbonate, is boiled down, the sodium chloride fished out as it separates, and the sodium chlorate purified by recrystallisation. In Pechiney's process the solution of calcium chlorate and chloride obtained by passing chlorine into hot milk of lime is evaporated down and as much as possible of the calcium chloride removed by crystallisation, the liquid being then decomposed with salt-cake:

$$CaCl_2 + Ca(ClO_3)_2 + 2Na_2SO_4 = 2CaSO_4 + 2NaCl + 2NaClO_3.$$

According to the process of Best[3] it is manufactured also by acting with chlorine on a solution of sodium carbonate or bicarbonate at temperatures not exceeding 35°, the reaction being probably:

$$3Na_2CO_3 + 3Cl_2 = NaClO_3 + 5NaCl + 3CO_2.$$

It is also prepared by the electrolysis of the chloride in a similar manner to the potassium salt.

Sodium chlorate is dimorphous, crystallising in combinations of the cube and tetrahedron showing also tetartohedral faces,

[1] *Hypochlorite und elektrische Bleiche*, 1903. See also Allmand, *Applied Electrochemistry*, 1912, p. 318; and Kershaw, *J. Soc. Chem. Ind.*, 1912, **31**, 54.

[2] *Hypochlorite und elektrische Bleiche*, 1905.

[3] *J. Soc. Chem. Ind.*, 1895, **14**, 865. See also Grossmann, *J. Soc. Chem. Ind.*, 1896, **15**, 158.

or in rhombohedral forms of the hexagonal system. It has a sp. gr. of 2·29, and becomes damp when kept exposed to air. It is much more soluble in water than the potassium salt, 100 parts of water dissolving, according to Kremers:

At	0°	20°	40°	60°	80°	100°	120°
Parts of $NaClO_3$	81·9	99	123·5	147·1	175·6	232·6	333·3.

It dissolves readily also in warm alcohol.

Sodium chlorate melts at 302° (Carnelley), 248° (Retgers), and is then for the most part converted into sodium chloride and perchlorate, with evolution of only a small quantity of oxygen (Schlossing). It is used chiefly in the manufacture of aniline black, its greater solubility making it more suitable for this purpose than the potassium salt.

Sodium Perchlorate, $NaClO_4$, is prepared by heating the chlorate or by neutralising perchloric acid with soda, and is manufactured in quantity from sodium chloride by electrolysis. It is very soluble in water, from which it crystallises at the ordinary temperature in long pointed plates containing one molecule of water, and at 50° in anhydrous rectangular prisms.[1] It occurs in small quantities in Chili saltpetre.

Sodium and Sulphur.

140 *Sodium Sulphides.*—These compounds are prepared in a similar manner to the corresponding potassium salts (p. 351), which they closely resemble. The monosulphide, Na_2S, crystallises with $9H_2O$ at ordinary temperatures; hydrates with $6H_2O$ and with $5\frac{1}{2}H_2O$ are formed from solutions above 48°.[2] The hydrosulphide, NaHS, crystallises with $2H_2O$ and $3H_2O$, and is also obtained as an anhydrous powder by heating the sulphide at 310° in a current of hydrogen sulphide.[3] If pure anhydrous sodium hydrosulphide, prepared by the action of hydrogen sulphide on sodium ethoxide in absolute alcohol,[4] is heated slowly and the hydrogen sulphide removed as it is formed, a quantitative yield of pure sodium sulphide, Na_2S, results as a light buff powder.[5]

By the action of sulphur on sodium hydrosulphide in alcoholic

[1] Potilitzin, *J. Russ. Phys. Chem. Soc.*, 1889, i. 258.
[2] Parravano and Fornami, *Atti R. Accad. Lincei*, 1907 [5], **16**, ii. 464.
[3] German Patent, 194881.
[4] Rule, *Journ. Chem. Soc.*, 1911, **99**, 558.
[5] Thomas and Rule, *Journ. Chem. Soc.*, 1913, **103**, 871.

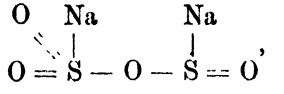
solution, *sodium tetrasulphide*, Na_2S_4, is obtained as a dark greenish-yellow crystalline powder. It reacts with metallic sodium in absolute alcohol to give the *disulphide*, Na_2S_2, as a bright yellow, microcrystalline powder, readily soluble in water to form a deep yellow solution.[1] Whilst these are the only anhydrous polysulphides isolated, there is evidence that Na_2S_3 and Na_2S_5 exist in aqueous solution, and a crystalline salt, $Na_2S_5,7H_2O$, has been obtained.[2] The disulphide is relatively stable, losing sulphur only at 700—800°.[3]

By the action of selenium or tellurium on a solution of sodium in liquid ammonia, the selenides, Na_2Se, Na_2Se_4, and tellurides, Na_2Te, Na_2Te_3, are formed.[4] Sodium sulphide is prepared on the large scale, and used in the manufacture of soluble soda-glass.

Sodium Hyposulphite, $Na_2S_2O_4$.—This salt, the formation and preparation of which have already been discussed (Vol. I., p. 451),[5] is used by the dyer and calico printer as a reducing agent for indigo, and is also employed in the laboratory for the purpose of estimating free oxygen or the quantity of that element contained in substances from which it is readily evolved. It has been obtained also by the direct action of sulphur dioxide on sodium hydride [6] according to the equation:

$$2NaH + 2SO_2 = Na_2S_2O_4 + H_2.$$

According to Binz [7] and to Reinking, Dehnel, and Labhardt,[8] this salt has the constitutional formula



which represents it as an anhydro-salt of sulphurous acid, $HSO_2.OH$, and of the hypothetical sulphoxylic acid, $HSO.OH$. This constitution is confirmed by its behaviour with organic reagents.[9]

Normal Sodium Sulphite, Na_2SO_3.—The anhydrous salt is

[1] Rule and Thomas, *Journ. Chem. Soc*, 1914, **105**, 177.

[2] See also, however, Yeoman, *Journ Chem. Soc.*, 1921, **119**, 38; Bloxam, *Journ. Chem. Soc.*, 1900, **67**, 761; Locke and Austell, *Amer. Chem. J.*, 1898, **20**, 592; Blanksma, *Proc. K. Akad. Wetensch. Amsterdam*, 1901, **3**, 457.

[3] Thomas and Rule, *Journ. Chem. Soc.*, 1917, **111**, 1063.

[4] Hugot, *Compt. rend.*, 1899, **129**, 299, 388.

[5] See also *Bull. Soc. Ind. Mulhouse*, 1904, **74**, 348; *Ber.*, 1905, **38**, 1048; Jellinek, *Zeit. anorg. Chem.*, 1911, **70**, 93.

[6] Moissan, *Compt. rend.*, 1902, **135**, 647.

[7] *Zeit. Fabr. u. Textil. Chem*, **4**, 161.

[8] *Ber.*, 1905, **38**, 1075.

[9] *Ber.*, 1906, **39**, 3317.

obtained as a crystalline precipitate by heating a cold saturated solution of the hydrated salt, and remains unaltered in the air. The hydrate $Na_2SO_3,7H_2O$ is prepared by saturating a solution of a known quantity of sodium carbonate with sulphur dioxide, and then adding the same quantity of sodium carbonate. The crystals which are deposited are transparent monoclinic prisms, which lose the whole of their water at 150°. The anhydrous salt crystallises in short hexagonal prisms.[1] The solution has an alkaline reaction and sharp taste. Crystals of the hydrate $Na_2SO_3,10H_2O$ are obtained, according to Muspratt, by allowing the aqueous solution to evaporate over sulphuric acid.

The solubility of the anhydrous salt is almost independent of the temperature; 100 parts of water dissolve 28·01 parts at 37° and 28·26 parts at 84°. The solubility of the hydrate $Na_2SO_3,7H_2O$ is as follows :—100 parts of water dissolve [1]

At	2°	10·6°	18·2°	29°	37·2°
Parts of Na_2SO_3	14·82	20·01	25·31	34·99	44·08

The transition temperature of the two modifications is about 22°.[1]

Sodium sulphite is used as an " antichlor " to remove any excess of chlorine from fabrics which have been bleached with chloride of lime, and sometimes also as an antiseptic.

Sodium Hydrogen Sulphite, $NaHSO_3$.—If a solution of sodium carbonate is saturated with sulphur dioxide whilst cold, this salt separates out in cloudy crystals, and alcohol precipitates it from aqueous solution as a white powder. It has an acid reaction, smells of sulphurous acid, and has an unpleasant sulphurous taste. A saturated solution of this salt is a commercial article, used by brewers for sterilising casks, etc.

Sodium Disulphite or *Sodium Metabisulphite*, $Na_2S_2O_5$, or $Na.SO_2.O.SO_2.Na$, is obtained by supersaturating a soda solution with sulphur dioxide, and may be prepared on the large scale by passing sulphur dioxide into dry monohydrated sodium carbonate, Na_2CO_3,H_2O.[2] It is a white crystalline soluble salt, which gradually evolves sulphur dioxide in the air and is converted into sodium sulphate.

Normal Sodium Sulphate, Na_2SO_4.—This compound is commonly known in the anhydrous state by the commercial name of *Salt-*

[1] Hartley and Barrett, *Journ. Chem. Soc.*, 1909, **95**, 1178.

[2] Carey and Hurter, Patent 4512, Nov. 1882; *J. Soc. Chem. Ind.*, 1883, **2**, 349.

cake, whilst the hydrate, $Na_2SO_4,10H_2O$, is called Glauber's salt. We find the first mention of this salt in Glauber's work, *De naturâ salium*, published in 1658. He obtained it as the residue left in the preparation of hydrochloric acid by the action of oil of vitriol upon common salt, and believed this simple aperient to be possessed of most valuable medicinal properties, whence it came to be known as *Sal mirabile Glauberi*.

The salt occurs native in the anhydrous condition as thénardite, and in solution in sea-water and in the water of salt-lakes, as well as in large quantities in certain mineral springs. Thus the water at Friedrichshall contains large quantities of the salt, which since 1767 has been obtained by evaporation and used in medicine as *Sal aperitivum Fridericianum*. A native compound of sodium sulphate with calcium sulphate, $Na_2SO_4,CaSO_4$, termed *glauberite*, is also found in several localities.

Sodium sulphate is prepared as salt-cake, the first step in the manufacture of carbonate of soda by the Leblanc process. The details of production are described under the head of the alkali manufacture.

Sodium sulphate is obtained as a residue in many chemical operations, especially in the preparation of nitric acid from Chili saltpetre in the sulphuric acid manufacture.

If ordinary Glauber's salt is allowed to remain exposed to the air, or more quickly if heated, the anhydrous salt is obtained; and if a solution of Glauber's salt saturated at about 35° is slightly heated, rhombic crystals of the anhydrous salt separate out. These are identical in form with crystals of thénardite, and isomorphous with those of silver sulphate, Ag_2SO_4. It has a specific gravity of 2·655, melts at 883°,[1] possesses a saline bitter taste, has a neutral reaction, and does not dissolve in alcohol. When heated on charcoal before the blowpipe in the reducing flame, sodium sulphide is formed.

One hundred parts of water dissolve the following quantities of the salt calculated as anhydrous sodium sulphate (Mulder [2]):

At	0°	10°	20°	30°	34°	40°
Na_2SO_4	5·02	9·00	19·40	40·00	55·00	48·8

At	50°	60°	70°	80°	90°	100°	103·5°
Na_2SO_4	46·7	45·3	44·4	43·7	43·1	42·5	42·2

The saturated solution boils at 103·5° (Mulder), 101·9° (Berkeley). Its abnormal solubility has already been discussed (p. 122).

[1] Nacken, *Chem. Centr.*, 1908, i. 1850.

[2] Compare Berkeley, *Phil. Trans.*, 1904, [*A*], **203**, 209.

Hydrated Sodium Sulphate.—The decahydrate, $Na_2SO_4,10H_2O$, commonly known as Glauber's salt, crystallises from aqueous solution at the ordinary temperature in large colourless monoclinic prisms, which are isomorphous with chromate and selenate of sodium. These crystals effloresce on exposure to dry air, melt in their water of crystallisation at 32·48°, and lose the whole of it below 100°.

The Hepta-hydrated Salt, $Na_2SO_4,7H_2O$, is deposited in hard, clear, rhombic crystals when a supersaturated solution of the decahydrate is allowed to cool below 12°, or when such a solution is covered with a layer of warm alcohol of specific gravity 0·835.[1]

Sodium Hydrogen Sulphate, $NaHSO_4$.—This salt, commonly known as bisulphate of soda, is obtained in large triclinic prisms when equivalent quantities of sodium sulphate and sulphuric acid are dissolved in water and the solution evaporated at a temperature above 50°. Unlike the corresponding potassium salt, it is decomposed by dry alcohol to form an intermediate sulphate, $Na_2SO_4,NaHSO_4$,[2] which crystallises in lustrous needles.[3] A hydrated salt, $NaHSO_4,H_2O$, is also known (D'Ans.). Ordinary "nitre cake" consists mainly of the intermediate sulphate, $Na_2SO_4.NaHSO_4$, mixed with either Na_2SO_4 or $NaHSO_4$ in excess, according as the "acidity" is below or above 18 per cent. H_2SO_4.[4] A complete investigation of the equilibrium between sodium sulphates and water with sulphuric acid, from −30° to 120°, has shown that $NaHSO_4,H_2SO_4$; $NaHSO_4,H_2SO_4,1{\cdot}5H_2O$; and $Na_2SO_4,2NaHSO_4$ also exist.[5]

Sodium Disulphate, $Na_2S_2O_7$, is formed by heating sulphur trioxide with common salt (Rosenstiel):

$$2NaCl + 3SO_3 = Na_2S_2O_7 + SO_2Cl_2.$$

The same compound is formed by the gentle ignition of sodium hydrogen sulphate. When more strongly heated, it yields sulphur trioxide and normal sulphate.

Sodium Thiosulphate, $Na_2S_2O_3$.—This salt, discovered in 1799 by Chaussier, and still commonly known by its old name of hyposulphite of soda, is prepared on the large scale for use as an antichlor in the paper manufacture, and as a solvent

[1] Compare Hartley, Jones, and Hutchinson, *Journ. Chem. Soc*, 1908, **93**, 825; Gernez, *Compt. rend*, 1909, **149**, 77; Smits and Wuite, *Proc. K Akad. Wetensch. Amsterdam*, 1909, **12**, 244.

[2] Butler and Dunnicliff, *Journ. Chem. Soc.*, 1920, **117**, 649.

[3] D'Ans, *Ber*, 1906, **39**, 1534.

[4] Butler and Dunnicliff, *loc. cit.*

[5] Pascal and Ero, *Bull. Soc. chim.*, 1919, [4], **25**, 35.

for the unaltered silver bromide in photography. It is obtained by boiling sulphur with soda-lye, and passing sulphur dioxide into the yellow solution until colourless, or by boiling sodium sulphite with sulphur. A cheaper process is to decompose the soluble calcium thiosulphate obtained by the oxidation of alkali waste, either by means of sodium carbonate or sulphate. The solution of sodium thiosulphate is drawn off from the carbonate or sulphate of calcium and evaporated down in iron pans. The anhydrous salt is obtained by passing oxygen or air over anhydrous sodium sulphide at 100—150°.[1]

Sodium thiosulphate forms large transparent prisms belonging to the monoclinic system which contain $5H_2O$. The salt is odourless, possesses a cooling taste, and does not exhibit an alkaline reaction, nor does it undergo alteration in the air. The crystals melt in their own water at 48·5°, and when heated to 215° all the water is driven off, whilst at 220° they decompose with separation of sulphur (Pape). The salt has a specific gravity of 1·672, is very soluble in water, in which it readily forms supersaturated solutions, but does not dissolve in alcohol.

Sodium thiosulphate forms a large number of hydrates, and the equilibrium curve of this substance and water is very complex.[2] The ordinary pentahydrate is stable in contact with water at all temperatures up to 48·2°; from this point to 65° the dihydrate is stable, and above 70° the anhydrous salt. Isomeric hydrates with $5H_2O$ and $2H_2O$ also exist as well as hydrates with $6H_2O$, $4H_2O$, $1\frac{1}{2}H_2O$, $4/3H_2O$, $1H_2O$ (3 isomerides), and $\frac{1}{2}H_2O$.

The aqueous solution cannot be preserved for any length of time without decomposition, as it very slowly deposits sulphur and is partially converted into sulphite: it is rapidly decomposed by ultra-violet light, with deposition of sulphur, and in dilute solution sodium hyposulphite can be detected as a primary product of this decomposition.[3] Sodium thiosulphate is represented by the formula[4] $SO_2\begin{cases}ONa\\SNa\end{cases}$. When treated with sodium

[1] German Patent, 194882.

[2] Taylor, *Proc. Roy. Soc., Edin.*, 1898, **22**, 248; Young and Mitchell, *J. Amer. Chem. Soc.*, 1904, **26**, 1389, 1413; Young and Burke, *J. Amer. Chem. Soc.*, 1906, **28**, 315; Dawson and Jackson, *Journ. Chem. Soc.*, 1907, **91**, 552; Jones, *ibid.*, 1909, **95**, 1672.

[3] Marmier, *Compt. rend.*, 1912, **154**, 32.

[4] Compare Vol. I. p. 458; also Price and Twiss, *Journ. Chem. Soc.*, 1907, **91**, 2024.

amalgam it yields sodium sulphite and sodium sulphide:

$$Na_2S_2O_3 + 2Na = Na_2SO_3 + Na_2S.$$

It is acted upon by iodine in aqueous solution at the ordinary temperature with formation of sodium tetrathionate:

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6,$$

and is largely employed in volumetric analysis in association with the estimation of iodine. Ferric salts also convert it into tetrathionate.[1]

Sodium and Nitrogen.

141 *Sodium Azoimide*, NaN_3, obtained by warming sodamide in a current of nitrous oxide, forms hexagonal crystals readily soluble in water. It can be kept molten for some hours without decomposition.[2]

Sodamide, $NaNH_2$.—This compound, discovered by Gay-Lussac and Thénard, is prepared by passing dry ammonia gas over sodium heated to 300—400° in an iron retort, and forms a waxy mass of crystalline structure, which is white when pure but frequently has a greenish or olive-brown colour.[3] It melts at 210°,[4] and at a temperature of 500—600° slowly decomposes into its elements, but does not, as stated by Gay-Lussac and Thénard,[5] yield a nitride of the formula Na_3N. When heated in a current of carbon dioxide sodamide glows with formation of caustic soda and cyanamide.

Sodium Nitrite, $NaNO_2$, is formed when the nitrate is heated, and is usually manufactured either by the electrical oxidation of atmospheric nitrogen (Vol. I., p. 551), or by heating sodium nitrate with lead, or with charcoal or sulphur in presence of caustic soda.[6] To obtain the pure salt, silver nitrite is treated with the equivalent amount of a solution of sodium chloride, or nitrous fumes from nitric acid and starch or arsenious acid are passed into a solution of caustic soda or sodium carbonate.[7] The salt is faintly yellow, melts at 271°, and yields a yellow solution

[1] Hewitt and Mann, *Journ. Chem. Soc*, 1913, **103**, 324.

[2] Curtius and Rissom, *J. pr. Chem.*, 1898 [2], **58**, 261; Dennis and Benedict, *Zeit. anorg. Chem.*, 1898, **17**, 18.

[3] Titherley, *Journ. Chem. Soc*, 1894, **65**, 504.

[4] Wohler and Stang-Lund, *Zeit. Elektrochem.*, 1918, **24**, 261.

[5] See, however, Zehnder, *Ann. Phys. Chem.*, 1894, **52**, 56.

[6] See Morgan, *J. Soc. Chem. Ind.*, 1908, **27**, 483.

[7] Divers, *Journ. Chem. Soc.*, 1899, **75**, 86.

in water faintly alkaline to litmus (Divers). According to Boguski, the pure dry salt is colourless.[1] It crystallises in oblique four-sided prisms or transparent rhombohedra, and is somewhat hygroscopic; at 15°, 100 parts of water dissolve 83·3 of the salt. It is largely used in making synthetic dyestuffs.

Sodium Nitrate, $NaNO_3$.—This salt, commonly known as cubic saltpetre or Chili saltpetre, is of special historical interest, as it was by the examination of differences in crystalline form exhibited by this compound and ordinary nitre that the distinction between the alkalis potash and soda was first observed by Bohn in 1683. Boyle, somewhat later, noticed that cubic saltpetre was formed in the preparation of aqua regia from common salt and nitric acid, and Stahl first pointed out the distinct character of the alkali-basis of common salt, and fully described the preparation of cubic saltpetre.

Sodium nitrate occurs in nature as a wide-spread deposit known as "Caliche" in the rainless districts of Tarapaca, Peru, Northern Chili, and Bolivia.[2] In these beds it is associated with common salt, gypsum, sodium sulphate, and smaller quantities of sodium iodate, chlorate, and perchlorate, the crude material containing from 27 to 65 per cent. of the pure salt. This is purified by solution and crystallisation. After refining, the salt contains about 97·7 per cent. of pure nitrate, 1·84 of sodium chloride. 0·35 of sodium sulphate, and 0·11 of water.[3]

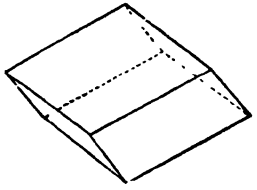


FIG. 95.

The best mode of separating the last 2 per cent. of sodium chloride is to add to the boiling and saturated solution one-tenth of its weight of nitric acid, stir it until cool, and collect the precipitated nitrate, which may then be washed by a dilute acid and afterwards dried.

Sodium nitrate crystallises in obtuse rhombohedra,[4] whose interfacial terminal edge angle is 106° 36′ (Fig. 95), and is therefore isogonous with calcspar.

The specific gravity of the salt is 2·26. It melts without decomposition at 316—318° (Carnelley), and when ignited undergoes decomposition with evolution of oxygen, nitrogen, and

[1] *J. Russ. Phys. Chem. Soc.*, 1899, **31**, 513.

[2] See Bryce's *South America*, pp. 42, 208.

[3] Compare Newton, *J. Soc. Chem. Ind.*, 1900, **19**, 408.

[4] Sénarmont, *Compt. rend.*, 1854, **38**, 105; Barlow and Pope, *Journ. Chem. Soc.*, 1908, **93**, 1538.

nitrous fumes. It is very soluble in water and deliquesces when exposed to moist air. One hundred parts of water dissolve :[1]

At	0°	10°	20°	40°	60°	80°	100°	119°
Parts	73	80·5	88	104·9	124·6	148	175·5	208·8

The solution containing 58·5 parts of the salt to 100 of water solidifies at —18·5°, and the saturated solution boils at 119°.

This salt dissolves also in dilute alcohol. One hundred parts of spirit, containing 61·4 per cent. of alcohol, dissolve at 26° 21·2 parts of sodium nitrate. It does not deflagrate so violently as nitre with charcoal or other inflammable bodies, but it has sometimes been used for making blasting and other powders which are not required to fire quickly.

Sodium nitrate is used in considerable quantities for the manufacture of nitric acid and also of sulphuric acid, but much the largest quantity is employed as a manure, since it readily yields up its nitrogen to plants growing in soil where it is present. This salt and ammonium sulphate are by far the most important sources of nitrogenous manure. In 1860 the output of the crude nitrate from South America was over 60,000 tons, and has greatly increased since that date, being about 761,000 tons in 1888, and 2,500,000 tons in 1912.

Sodium and Phosphorus.

142 *Sodium Phosphide*, Na_3P.—Sodium dissolved in liquid ammonia reacts with red phosphorus to form a red compound, $Na_3H_3P_2$, which loses phosphine when heated and is decomposed by water and acids with evolution of phosphine.[2] Phosphine also reacts with sodium in presence of liquid ammonia forming the compound, NaH_2P, which is converted by heat into the phosphide, Na_3P. This is decomposed by water, yielding phosphine.[3] An unstable phosphide, Na_2P_5, is formed when sodium and phosphorus are heated together in a vacuum at 450° for several days.[4]

Sodium Hypophosphite, $NaH_2PO_2.H_2O$.—This salt is obtained by adding sodium carbonate to a solution of calcium hypophos-

[1] Berkeley, *Phil. Trans.*, 1904, [A], **203**, 211; Miers and Isaac, *Journ. Chem. Soc.*, 1906, **89**, 428.

[2] Hugot, *Compt. rend.*, 1895, **121**, 206; 1898, **126**, 1719.

[3] Joannis, *Compt rend.*, 1894, **119**, 557.

[4] Hackspill and Bossuet, *Compt. rend.*, 1912, **154**, 209.

phite, and allowing the solution to evaporate in a vacuum. Pearly tabular crystals are deposited, which deliquesce on exposure to the air, and are readily soluble in absolute alcohol. It is now employed in medicine for the same purposes as phosphorus.

Sodium Trithiophosphite, $Na_3PS_3aq.$, prepared by heating phosphorus trisulphide with crystallised sodium sulphide in excess in concentrated aqueous solution, forms very soluble rectangular plates, stable in dry air.[1]

Normal Sodium Orthophosphate, Na_3PO_4.—This salt, first described by Thomson [2] as phospho-carbonate of soda, is prepared by adding in the form of caustic soda at least half as much sodium as it already contains to a solution of the next salt, common sodium phosphate, and evaporating to the point of crystallisation. The hydrated salt crystallises out, the mother-liquor retaining the excess of caustic soda. The crystals freed from the liquor are rapidly dissolved in twice their weight of hot water, the liquid filtered, and then left to crystallise (Graham). The anhydrous salt may be obtained by fusing common sodium phosphate or pyrophosphate with an excess of sodium carbonate. The pyrophosphate is not altered by boiling with caustic soda (Graham).

The crystals, containing $12H_2O$, form thin six-sided prisms, which do not change on exposure to air, and have a specific gravity of 1·618. They melt at 73·3°, and at 100° lose all but one molecule of water, which is given off at a red heat. 100 parts of water at 15·5° dissolve 19·6 parts of the hydrated salt (Graham), and the solution is strongly alkaline to litmus. A hydrate with $7H_2O$ has also been described.[3]

Di-sodium Hydrogen Orthophosphate, Na_2HPO_4.—This salt is the common phosphate of soda, which was first prepared from urine, and described in 1740 by Haupt under the name of *sal mirabile perlatum*. It was afterwards obtained by neutralising phosphoric acid with soda, and in 1787 was introduced as a medicine by Pearson. It occurs in the blood of animals, and especially in the urine of the carnivora. It is best prepared from bone phosphoric acid by adding sodium carbonate so long as effervescence occurs. The precipitated phosphates of calcium and magnesium are then filtered off, and the liquid is boiled down and allowed to crystallise. The large transparent crystals obtained

[1] Ephraim and Stein, *Ber.*, 1911, **44**, 3405. [2] *Ann. Phil.*, 1825, **26**, 381.
[3] Hall, *Journ. Chem. Soc.*, 1887, **51**, 97.

are monoclinic prisms containing $12H_2O$. They have a specific gravity of 1·525, melt at 35·0°, and are isomorphous with the corresponding sodium hydrogen arsenate, $Na_2HAsO_4,12H_2O$. Exposed to air, the crystals effloresce, but do not lose their form. They exist in two enantiomorphous forms, with a transition point at 29·6°.[1] The commercial salt usually contains about 2·5 per cent. of Na_3PO_4.[2]

The following is the solubility of the anhydrous salt in 100 parts of water:

At	10 26°	25 15°	40 29°	60 23°	99 77°
Na_2HPO_4	3·55	12·02	54·88	83·00	102·15

There are three breaks in the solubility curve, at 36·45°, 48°, and 95·2° respectively; the first corresponds with the transition from the hydrate with $12H_2O$ to one with $7H_2O$, the second with that from the latter to a hydrate with $2H_2O$, and the third with the change from the dihydrate to the anhydrous salt. The dihydrate is obtained by fusing the dodecahydrate in its water of crystallisation and evaporating the resulting solution at 70·75°; the anhydrous salt is similarly obtained at a temperature of about 99·5°.[3] The saturated solution boils at 105°.

This salt is insoluble in alcohol; it possesses a cooling saline taste, and turns red litmus solution blue. The solution is usually faintly alkaline to phenolphthalein; this alkalinity is ascribed by Geissler[4] to the presence of sodium carbonate, whereas according to Brunner[5] it is a property of the pure salt.

Common sodium phosphate is used as a mild purgative. The commercial salt frequently contains sodium sulphate, which can be removed by recrystallising from hot water.

Di-hydrogen Sodium Phosphate, NaH_2PO_4.—To prepare this salt phosphoric acid is added to a solution of common sodium phosphate until the mixture no longer precipitates barium chloride. It is then evaporated to a small bulk, and allowed to stand for some days to crystallise (Mitscherlich). This salt is dimorphous, two kinds of large transparent crystals separating out, containing one molecule of water; according to Mitscherlich, both are forms of the rhombic system, but according to Joly and

[1] Hammick, Goadby, and Booth, *Journ. Chem. Soc.*, 1920, **117**, 1589.

[2] Smith, *J. Soc. Chem. Ind.*, 1917, **36**, 415.

[3] Shiomi, *Mem. Koll. Sci. Eng. Kyōto*, 1908, **1**, 406; Kitawaki, *ibid.*, 1909–10, **2**, 237.

[4] *Zeit. anal. Chem.*, 1898, **37**, 323.

[5] *Ibid.*, 1898, **37**, 740.

Dufet, one of the varieties is monoclinic.[1] Hydrates with $2H_2O$ and $4H_2O$ are also known.[2]

The crystals have an acid reaction, and a specific gravity of 2·04. They lose all their water of crystallisation at 100°, and at 204° lose the elements of water (Graham) with formation of acid pyrophosphate:

$$2NaH_2PO_4 = Na_2H_2P_2O_7 + H_2O.$$

At 210° they give off the whole of their water and form mono-metaphosphate:

$$NaH_2PO_4 = NaPO_3 + H_2O.$$

Di-hydrogen sodium phosphate is very soluble in water, but not in alcohol. The solution is acid to litmus and phenolphthalein but neutral to methyl-orange.

Various double salts, such as $NaH_5(PO_4)_2$[3] and $Na_3H_3(PO_4)_2$,[4] are also known, and a *sodium polyphosphate*, $Na_4P_6O_{17}$, has been described which at high temperatures has a very corrosive action on glass, silica, and even platinum.[5]

Sodium Pyrophosphates.—These salts are tetrabasic, and give with silver nitrate a white precipitate of silver pyrophosphate, $Ag_4P_2O_7$; they do not coagulate albumen; their solutions when boiled with an acid yield the salts of the tribasic ortho-acid.

Normal Sodium Pyrophosphate, $Na_4P_2O_7,10H_2O$.—This salt is obtained in the anhydrous state as a colourless glassy mass by igniting common sodium phosphate. When it is dissolved in water, and the solution evaporated, crystals of the decahydrate are deposited in monoclinic prisms. The solution has an alkaline reaction. It is not converted into the ortho-salt by boiling alone, but this conversion takes place rapidly on addition of an acid, even acetic, to the boiling solution (Stromeyer). When gently heated, or exposed over sulphuric acid in a vacuum, it loses all its water. The solubility in 100 parts of water is:

At 0°	10°	20°	30°	40°	50°	60°	80°	100°
5·41	6·81	10·92	18·11	24·97	33·25	44·07	63·40	93·11

Di-hydrogen Sodium Pyrophosphate, $Na_2H_2P_2O_7$.—This salt is prepared by heating common sodium phosphate to 150° with

[1] *Compt. rend.*, 1886, **102**, 1391.
[2] Imadsu, *Mem. Koll. Sci. Eng. Kyōto*, 1912, **3**, 257.
[3] Giran, *Compt. rend.*, 1902, **134**, 711.
[4] Senderens, *Compt. rend.*, 1902, **134**, 713.
[5] Smith, *J. Soc. Chem. Ind.*, 1917, **36**, 415.

strong hydrochloric acid, or by heating sodium di-hydrogen phosphate to a temperature of 190—204°, as already explained. It may be prepared also by dissolving the normal pyrophosphate in acetic acid, and precipitating the solution with alcohol; it is thus obtained as a white crystalline powder, readily soluble in water, the solution having an acid reaction.

Sodium Metaphosphates.—These salts, which were first discovered by Graham (Vol. I., p. 670), exist in a large number of modifications, which all have the empirical formula $NaPO_3$, but their molecular formula is probably in most cases some multiple of this. Great uncertainty exists as to the true molecular weights of the various salts.

Sodium Hexametaphosphate, $(NaPO_3)_6$, the most important of these salts, often called deliquescent, vitreous, or Graham's metaphosphate, is prepared by heating to complete fusion either sodium di-hydrogen phosphate, microcosmic salt,[1] or acid sodium pyrophosphate (v. Knorre), or, in a similar manner, from all the other metaphosphates. The melted mass must be quickly cooled, to avoid the formation of the trimetaphosphate. The product is a vitreous mass, soluble in water or alcohol, the solutions having a slightly acid reaction. The same salt appears to be formed by the action of sodium sulphide solution on the lead metaphosphate prepared by heating lead oxide with phosphoric acid and fusing the resulting salt at a temperature above 400° (Fleitmann's tetrametaphosphate).[2] The solution gradually decomposes with formation of acid sodium pyrophosphate. When treated with ammonium chloride it yields a salt having the formula $Na(NH_4)_5(PO_3)_6$, and hence is probably a hexametaphosphate. According to Tammann,[3] it is a mixture of at least two isomeric hexametaphosphates.

Insoluble Sodium Metaphosphate, $(NaPO_3)_x$.—This salt, whose molecular weight is unknown, but which is usually termed the *monometaphosphate*, is obtained by heating microsocmic salt at 335°, or sodium nitrate with a slight excess of syrupy phosphoric acid. It is a white powder almost insoluble in water, but soluble in dilute acids, which is converted by boiling caustic soda solution into sodium orthophosphate.[4]

Sodium Dimetaphosphate, $(NaPO_3)_2.2H_2O$ (Fleitmann).—This

[1] Graham, *Phil. Trans*, 1833.
[2] Warschauer, *Zeit. anorg Chem*, 1903, **36**, 188.
[3] *J. pr. Chem.*, 1892 [2], **45**, 467.
[4] Maddrell, *Journ. Chem. Soc.*, 1851, 373.

is prepared by the action of a boiling solution of sodium sulphide on copper dimetaphosphate, which is obtained by heating a mixture of phosphoric acid with a copper salt or copper oxide, at a temperature not exceeding 448°. It dissolves in 7·2 parts of water, and crystallises in slender needles. It has a strong tendency to form double salts.[1]

According to Tammann, it has the molecular formula $(NaPO_3)_3$, whereas Warschauer,[2] from the determination of the equivalent conductivity at different concentrations, concludes that this salt is in reality a tetrametaphosphate, the hydrated salt having the formula $(NaPO_3)_4,4H_2O$.

Sodium Trimetaphosphate, $(NaPO_3)_3,6H_2O$.—Some doubt also exists as to the true molecular formula of this salt. From a study of the normal salts which can be prepared from it, such as $NaCa(PO_3)_3$, Fleitmann attributed to it the formula given above, but Tammann [3] was led by the determination of the freezing point and electrical conductivity of a series of solutions to formulate it as the dimetaphosphate, Fleitmann's dimetaphosphate being considered on similar grounds as the trimetaphosphate. v. Knorre [4] and Wiesler,[5] on the other hand, decide for the original formula from the determination of the equivalent conductivity at various concentrations.

It is formed when microcosmic salt is exposed to a moderate heat (Graham), and when the fused hexametaphosphate is allowed to cool slowly.[6] It is best prepared pure by heating ordinary sodium phosphate with one-third of its weight of ammonium nitrate for six hours at 300° and recrystallising the product (v. Knorre).

The cold solution in water is permanent, and neutral both to methyl-orange and phenolphthalein; when boiled it becomes acid with formation of sodium di-hydrogen phosphate.

In addition to these a large number of other metaphosphates have been described, namely, tetra-, penta-, octo-, deca-, and tetrakaideca-metaphosphates, having the general formulæ:

$$(M'PO_3)_4,\ (M'PO_3)_5,\ (M'PO_3)_8,\ (M'PO_3)_{10},\ \text{and}\ (M'PO_3)_{11}.$$

[1] *Pogg. Ann.*, 1849, **78**, 246, Glatzel, *Diss. Wurzburg*, 1880; quoted by v. Knorre, *Zeit. anorg. Chem.*, 1900, **24**, 369.

[2] *Zeit. anorg. Chem.*, 1903, **36**, 165.

[3] *Zeit. physikal. Chem.*, 1890, **6**, 122; *J. pr. Chem.*, 1892, [2], **45**, 417.

[4] *Zeit. anorg. Chem.*, 1900, **24**, 369. [5] *Ibid.*, 1901, **28**, 177.

[6] Fleitmann and Henneberg, *Annalen*, 1848, **65**, 307; Tanatar, *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 99.

Sodium and Arsenic.

143 *Sodium Arsenide*, $AsNa_3$, is prepared by heating arsenic with excess of sodium and removing the latter by liquid ammonia. It forms small black crystals.[1] *Sodium bismuthide*, Na_3Bi, is similarly prepared, and forms dark-grey crystalline laminæ, m. p. 776°, readily attacked by air or water.[2] The compound $AsNa_3,NH_3$, which forms brick-red crystals, is also known.[3]

Sodium arsenates.—These salts closely resemble the corresponding phosphates, with which they are isomorphous. The normal arsenate, $Na_3AsO_4,12H_2O$, is soluble to the extent of 26·7 parts in 100 of water at 17°, and melts at 85·5°; $Na_2HAsO_4,12H_2O$, is efflorescent, crystallises from solutions below 8°, melts at 28°, and has a solubility of 56 parts in 100 of water at 14°. A second, well-defined hydrate, $Na_2HAsO_4,7H_2O$, which crystallises from solutions at 15—20°, is quite stable under normal conditions; the crystals begin to lose water at 30°, melt at 57°, and are completely dehydrated at 120°. The anhydrous salt is readily soluble in water, 100 parts of water dissolving 61 parts at 15°; at 180°, it is rapidly converted into the pyroarsenate, $Na_4As_2O_7$.[4] The dihydrogen arsenate, NaH_2AsO_4,H_2O, is also readily soluble. An impure arsenate of sodium is prepared on the large scale by dissolving arsenious oxide in caustic soda, and adding sodium nitrate; the solution is boiled down, and the residual mass heated in a furnace until it appears to be perfectly dry. This product is largely used in calico-printing as a substitute for cow-dung, which was formerly employed in clearing the cloth after mordanting. The mordant consists of a solution of acetate of either aluminium or iron, and the cloth, after having been printed with these mordants, is hung up and exposed to air. In this, which is termed the *ageing process*, a portion of the acetic acid evaporates, leaving basic acetates of iron and aluminium firmly attached to the fibre of the cloth. A portion of these salts is, however, mixed up with the thickening or starch which must be added to the mordant in order that the impression shall be sharp. To remove this excess of unfixed mordant, the cloth is subjected to a peculiar treatment termed the *dunging process*. For this purpose it will

[1] Lebeau, *Compt. rend.*, 1900, **130**, 502.
[2] Vournasos, *Ber.*, 1911, **44**, 3266.
[3] Hugot, *Compt. rend.*, 1898, **127**, 553.
[4] Wulff, *Apoth. Zeit.*, 1906, **20**, 1025.

not answer merely to wash the cloth in pure water, because the soluble portion of the mordant is then removed from the printed pattern, but attaches itself again to the unmordanted cloth, which it is intended should remain white. Long ago it was observed by the native dyers and calico-printers in India that if cow-dung be added to the wash water the excess of mordant can be removed without any staining of the cloth occurring. The action of the cow-dung in this process has not yet been satisfactorily explained, but experience has shown that sodium arsenate solution acts in a similar way, and at the present time the old process is generally superseded by the use of what is known in the trade as " dung substitute."

Sodium and Boron.

144 *Sodium Orthoborate*, Na_3BO_3.—When boron trioxide is fused with excess of caustic soda, three molecules of water are expelled and the ortho-salt remains :[1]

$$B_2O_3 + 6NaOH = 2Na_3BO_3 + 3H_2O.$$

This salt is very unstable; when dissolved in water, indeed, it is transformed into a hydrated metaborate.

Sodium Pyroborate, or Borax, $Na_2B_4O_7$.—The history of this the most important of the borates is lost in obscurity. It has already been stated under boron (Vol. I., p. 720) that in the works of the Latin Geber the word borax or baurach occurs, but whether or not this indicated the substance which we now call by that name is a mere matter of speculation. Even up to the end of the seventeenth century nothing certain was known either as to the source or the composition of borax, which was used as a flux, and which was early brought into European markets by the Venetians. It was not until 1747 that an exact knowledge of its composition was arrived at, when Baron pointed out that borax consists of a compound of boric acid (then called sedative salt) and soda.

Before the discovery of the boric acid lagoons (Vol. I., p. 731) the boric acid of commerce was obtained from Asiatic tincal, which is a crude decahydrate of borax, $Na_2B_4O_7,10H_2O$, and occurs native in Tibet. Since then tincal has been found in immense deposits in North America, these being generally the bottoms of lakes which have dried up more or less completely,

[1] Bloxam, *Journ. Chem. Soc.*, 1862, 143.

and large quantities are now put on the market from this source, the crude product simply requiring recrystallisation.

A large proportion of the borax used in Europe is still made from Tuscan boric acid, which is fused with half its weight of soda-ash in a reverberatory furnace, the product being lixiviated with hot water, and the borax allowed to crystallise. In France the two substances are boiled together and the product allowed to crystallise. A further source of borax is the mineral *boronatrocalcite*, $Na_2B_4O_7,2CaB_4O_7,18H_2O$, termed in commerce borate of lime or " tiza," and found in the nitrate beds of South America, and in the massive condition in Nevada; the mineral is finely divided and fused with the requisite proportion of soda-ash and sodium bicarbonate, the product being lixiviated and recrystallised.

Anhydrous Borax or Borax Glass is best obtained on the small scale by fusing 124 parts of crystallised boric acid with 53 parts of dry sodium carbonate. A transparent glass is thus obtained having a specific gravity of 2·367, which becomes opaque on exposure to air from absorption of water.

Fused borax glass dissolves many metallic oxides, which impart their peculiar colours to the glass, and it is therefore largely used in blowpipe analysis. The constitution of this glass appears to be very complex.[1] It is readily soluble in water, but insoluble in alcohol. Ordinary borax melts at 730°, but two other borates containing a higher proportion of boron trioxide, $Na_2O,3B_2O_3$ and $Na_2O,4B_2O_3$, melting at 694° and 783° respectively, have been described.[2]

Borax forms two important hydrates. *Octahedral Borax*, $Na_2B_4O_7,5H_2O$, is deposited when a supersaturated borax solution, prepared by dissolving three parts of the decahydrate in four parts of warm water, is allowed to evaporate spontaneously in a warm place. Another plan is to dissolve borax in boiling water until the specific gravity of the solution rises to 1·216, and then allow the solution to cool. The crystallisation of octahedral borax begins when the temperature reaches 79°, and continues until it sinks to 35·5°, after which common borax is deposited. The crystals are hard, transparent, regular octahedra, having a specific gravity of 1·815.

Common, or prismatic Borax, $Na_2B_4O_7,10H_2O$.—Anhydrous borax when exposed to moist air absorbs ten molecules of water

[1] Burgess and Holt, *Proc. Roy. Soc.*, 1904, **74**, 285.
[2] Bonomarev, *Zeit. anorg. Chem.*, 1914, **89**, 383.

and forms this salt. The decahydrate is deposited from solutions at all temperatures below 35·5° in the form of large transparent monoclinic prisms, which have a specific gravity of 1·71. When gently heated the crystals swell up, losing water and forming a spongy mass called *borax usta*, or burnt borax.

In contact with a saturated solution the decahydrate is stable up to 35·5°,[1] and above this temperature is converted into the pentahydrate. 100 parts of water dissolve :[2]

At	5°	10°	30°	45°	50°	55°	60°	70°
$Na_2B_4O_7$	1·3	1·6	3·9	8·1	10·5	14·2	20	24·4

80°	90°	100°
31·4	40·8	52·3

The aqueous solution has an alkaline reaction ;[3] hence borax is often used for purposes which require a weak alkali.

The impurities usually found in commercial borax are sodium carbonate, traces of the sulphates and chlorides of the alkali metals, and salts of magnesium and calcium. Sometimes it is adulterated with alum and common salt. Pure borax gives no effervescence with acids, and dissolves in two parts of hot water. The solution is not rendered turbid on addition of alkali, and does not give a precipitate either with barium chloride or silver nitrate.

Borax is largely used for a number of purposes, for glazing both earthenware and fabrics such as linen, as an antiseptic, and also in preparing clean surfaces of metals previous to soldering.

Sodium Metaborate, $NaBO_2.4H_2O$.—This salt is formed when borax is fused with the requisite quantity of sodium carbonate. It crystallises from water in monoclinic crystals having the above composition. A pentaborate, $Na_2B_{10}O_{16},10H_2O$, has also been described.[4]

Sodium Perborate, $Na_2B_4O_8,10H_2O$.[5]—When an intimate mixture of one molecular proportion of sodium peroxide and

[1] van't Hoff and Blasdale, *Sitzungsber. K. Akal. Wiss. Berlin*, 1905, 1086.

[2] Horn and van Wagener, *Amer. Chem. J.*, 1903, **30**, 344; compare Poggiale, *Ann. Chim. Phys.*, 1843, [3], **8**, 467.

[3] Shelton, *Proc. Chem. Soc.*, 1902, 169; Grünhut, *Zeit. physikal. Chem.*, 1904, **48**, 569; Lundberg, *Zeit. physikal. Chem.*, 1909, **69**, 442.

[4] Atterberg, *Zeit. anorg. Chem.*, 1906, **48**, 367; Dukelski, *Zeit. anorg. Chem.* 1906, **50**, 38.

[5] Jaubert, *Compt. rend.*, 1904, **139**, 796; *Rev. gen. Chim. pure appl.*, 1905, [vii], **8**, 163; Bosshard and Zwicky, *Zeit. angew. Chem.*, 1912, **25**, 938.

four molecular proportions of boric acid is added gradually to cold water a clear solution is first obtained from which a perborate of the above composition crystallises out; it cannot be recrystallised from water without decomposition. On the addition of a quantity of hydrochloric acid equivalent to one half of the sodium in this perborate to its aqueous solution, a perborate, $NaBO_3,4H_2O$, separates in the form of white crystals which are quite stable at ordinary temperatures. This salt is less soluble than the former. Its aqueous solution has an alkaline reaction and contains hydrogen peroxide; it begins to decompose slowly above 40° and evolves oxygen rapidly at 100°. By neutralising the solution with acids fairly concentrated solutions of hydrogen peroxide can be obtained. This compound appears to be a true per-salt as it does not contain hydrogen peroxide of crystallisation.[1]

Sodium perborate is used in laundry work and for hygienic purposes.

Sodium and Carbon.

145 *Sodium Carbide*, Na_2C_2.—When acetylene is passed over melted sodium at a temperature below 190°,[2] and when liquid acetylene is treated with sodium at the ordinary temperature,[3] a white solid known as *monosodacetylene*, C_2HNa or C_2H_2,C_2Na_2, is formed. This substance is produced also by mixing liquid acetylene with a solution of sodium in liquid ammonia and crystallises in microscopic, rhombohedral lamellæ. When this compound is heated, or treated with iodine in presence of benzene, the carbide, Na_2C_2, is left as a white solid, which is also formed when acetylene acts on sodium above 210°.

This substance has the sp. gr. 1·575 at 15°, is insoluble in all solvents, and when strongly heated in a vacuum, dissociates into its elements. It undergoes chemical change with great readiness and violence, free carbon being as a rule liberated. When gently heated in dry air or oxygen, it burns, forming sodium carbonate, and it is readily attacked by the halogen elements and by phosphorus. When it is carefully brought into water, acetylene is liberated and caustic soda produced. In hydrogen chloride it burns spontaneously, forming sodium chloride, hydrogen, and carbon.[4]

[1] Bosshard and Zwicky, *Zeit. angew. Chem.*, 1912, **25**, 993.
[2] Matignon, *Compt. rend.*, 1897, **124**, 775.
[3] Moissan, *Compt. rend.*, 1898, **126**, 302; **127**, 911.
[4] Matignon, *Compt. rend.*, 1897, **125**, 1033.

Sodium Carbonate, Na_2CO_3, commonly known as carbonate of soda or soda-ash, is prepared on an enormous scale, being one of the chief products of the alkali manufacture which is described in detail below (p. 296). The anhydrous salt is a white, opaque, porous mass or a white powder, which has a specific gravity of 2·5, melts at 852° without decomposition in absence of moisture, and possesses an alkaline taste and reaction, but less strongly marked than those of potassium carbonate. When the anhydrous salt is brought in contact with water, heat is evolved and an alkaline solution is formed. This alkalinity, as already explained (p. 111), is due to a partial hydrolysis of the salt into caustic soda and sodium bicarbonate, and it is found that a normal solution of the carbonate slowly loses carbon dioxide when it is boiled in a current of hydrogen.[1]

Owing to the existence of several different hydrates, the solubility of sodium carbonate shows an anomalous behaviour with rise of temperature, analogous to that of sodium sulphate (p. 122). The limits of stability of these hydrates in contact with a saturated solution are probably the following: $10H_2O$ from −2·1° to 31·8°; $7H_2O$ from 31·8° to 35·1°; $1H_2O$ from 35·1° to 104·7°, the boiling point of the saturated solution.[2] One hundred parts of water dissolve:

At	0°	10°	20°	30°	31·8°	35·1°	40°	50°	70°	104·7°
Na_2CO_3	7·1	12·6	21·4	40·9	46	51	49·7	47·5	45·8	45·1.

The *decahydrate* is obtained when a hot, fairly concentrated solution is allowed to cool, and forms large, transparent monoclinic crystals, which are known commercially as *soda-crystals* or *washing soda*, and are manufactured on the large scale. They readily effloresce on exposure to the air, yielding the monohydrate as a white powder, which is also formed by heating the decahydrate to 35·1°, at which temperature it melts and loses nine molecules of water. The *monohydrate* crystallises in rectangular rhombic plates, and is prepared commercially and sold under the name of *crystal carbonate*. Both these hydrates occur native, the former as *natron* and the latter as *thermonatrite*, in the soda

[1] Kuster and Grüters, *Ber.*, 1903, **36**, 748. See also McCoy, *Amer. Chem. J.*, 1903, **29**, 437.

[2] Ketner, *Zeit. physikal. Chem.*, 1902, **39**, 645; Epple, *Diss. Heidelberg*, 1899, p. 26, quoted in *Physikalisch-Chemische Tabellen*, Landolt-Bornstein, p. 555 (Berlin, Springer, 1905); Wells and McAdams, *J. Amer. Chem. Soc.*, 1907, **29**, 721; Jones, *Journ. Chem. Soc.*, 1909, **95**, 1672; Cumming, *ibid.*, 1910, **97**, 593.

lakes of Egypt [1] and Hungary, and also at Vesuvius and Etna, and in various parts of Asia, Africa, and America.

Of the remaining hydrates the *heptahydrate*, $Na_2CO_3,7H_2O$, is the most important, and is obtained by allowing a warm saturated solution to cool in absence of crystal nuclei; it appears to be dimorphous, crystallising both in rhombohedra and rectangular rhombic plates.

Sodium Hydrogen Carbonate, $NaHCO_3$.—This salt, commonly known as bicarbonate of soda, is likewise prepared on the large scale. It occurs in commerce in the form of a white, crystalline powder, or in crystalline crusts which consist of monoclinic tablets. It possesses a faint alkaline taste, and dissolves less readily in water than the normal salt. A solution of the bicarbonate is neutral to phenolphthalein, but alkaline to methyl-orange. One hundred parts of water dissolve : [2]

At	0°	10°	20°	30°	40°	50°	60°
$NaHCO_3$	6·90	8·15	9·60	11·10	12·70	14·45	16·40.

A solution of the bicarbonate gives off carbon dioxide on boiling, forming first the carbonate (trona) $Na_2CO_3,NaHCO_3,2H_2O$; [3] this carbonate is formed also when carbon dioxide is passed into a boiling solution of the normal carbonate and when solutions of the latter are exposed to the air for some time. The solid salt decomposes on gentle ignition into carbon dioxide, water, and the normal salt:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

Commercial bicarbonate of soda almost always contains some normal carbonate, and this may be removed by washing with small quantities of water; but, on drying, the residual salt is found again to contain some normal carbonate. A better method is to moisten the washed salt with alcohol, and then to dry it between folds of filter paper without application of heat. Even then it undergoes partial decomposition, and contains about one per cent. of the normal carbonate. In order to detect the presence of the latter salt in the bicarbonate a solution of mercuric chloride in two parts of water is added to a solution of the bicarbonate in fifteen parts of water, when a white cloudiness,

[1] *Jahrb. Min.*, 1900, i., 236.

[2] Dibbits, *J. pr. Chem.*, 1874, [2], **10**, 439.

[3] Soury, *Compt. rend.*, 1908, **147**, 1296; Habermann and Kurtenacker, *Zeit. anorg. Chem.*, 1909, **63**, 65.

which gradually becomes brown after several minutes, is produced in presence of the normal salt; the presence of the normal carbonate can be proved with certainty, however, only by a quantitative examination.

Trona, or Urao, is a carbonate of soda occurring native in Hungary, Egypt, British East Africa, Fezzan and Lake Chad in Africa, India, and America. It is a compound of the normal with the bicarbonate, and has the formula $Na_2CO_3,NaHCO_3,2H_2O$.[1] This is the substance to which the ancients gave the name *nitrum.* It occurs in small monoclinic crystals, and it can be prepared artificially as described above.

Sodium Percarbonate has already been described [2] (Vol. I., p. 835).

Sodium Cyanide, NaCN.—This salt is obtained by neutralising hydrocyanic acid with soda, and by heating sodium ferrocyanide either alone or with metallic sodium (see also potassium cyanide):

$$Na_4Fe(CN)_6 = 4NaCN + FeC_2 + N_2$$
$$Na_4Fe(CN)_6 + 2Na = 6NaCN + Fe.$$

When obtained by passing hydrocyanic acid into alcoholic soda it is a white, crystalline powder, which smells of hydrocyanic acid, and dissolves readily in water.

It is now manufactured on the large scale by Castner's method,[3] which consists in passing ammonia over metallic sodium heated in an iron retort to 300–400°, yielding sodamide according to the equation:

$$2Na + 2NH_3 = 2NaNH_2 + H_2.$$

This is then brought into contact with charcoal previously heated to dull redness, and thus converted into sodium cyanamide and hydrogen:

$$2NaNH_2 + C = CN.NNa_2 + 2H_2.$$

At a higher temperature, in presence of the excess of charcoal, the cyanamide is then converted into sodium cyanide:

$$CN.NNa_2 + C = 2NaCN.$$

The product is almost pure.

[1] Compare Lunge, *Sulphuric Acid and Alkali,* Vol. II., pp. 52 and 55, 3rd edition, 1909. Also "Egyptian Soda," Survey Department Paper No. 22, *Nature,* 1913, **90**, 527.

[2] Compare also:—Tanatar, *Ber.,* 1910, **43**, 127, 2149; Riesenfeld, *ibid.,* 1910, **43**, 566, 2594; 1911, **44**, 3589, 3595; Wolffenstein, *ibid.,* 1910, **43**, 639.

[3] Patent No. 21732 (1894).

Calcium cyanamide ("Nitrolim") also is used for the preparation of sodium cyanide (Vol. I., p. 864).

Sodium cyanide is very largely employed for the extraction of metallic gold.

Sodium and Silicon.

146 Silica acts on sodium carbonate at high temperatures with evolution of carbon dioxide and formation of silicates, different silicates being obtained according to the time of heating, the temperature, and the relative proportions of the two substances taken. Unlike potassium, however, sodium is capable of forming an *orthosilicate*, Na_4SiO_4, whilst the silicate richest in potassium is $K_8Si_3O_{10}$. If silica and sodium carbonate be fused together in equal molecular proportions, *sodium metasilicate*, Na_2SiO_3, is formed, and of this compound a number of definite crystalline hydrates have been obtained, crystallising with from 1 to 9 molecules of H_2O. The solution of this substance in water is strongly alkaline, and probably contains half the sodium as caustic soda, together with the silicate $Na_2Si_2O_5$.[1]

Sodium Disilicate, $Na_2Si_2O_5$, has been prepared as a crystalline product of the action of limited quantities of water at high temperatures upon specially prepared glasses.[2]

Soluble Soda Glass, which was discovered by Fuchs in 1818, is obtained by heating together 180 parts of white sand, 100 of calcined soda-ash, and 3 of charcoal in a reverberatory furnace, and also by dissolving powdered flint in hot aqueous caustic soda under pressure. Like the corresponding potash glass it consists of a mixture of several silicates, the melting point being higher the greater the proportion of silica present. Prepared by the first method, soluble soda glass forms a transparent glassy mass, sometimes colourless, but generally of a yellow, brown, or green colour, which, when powdered, readily dissolves in boiling water, forming a thick viscid liquid. Ultramicroscopic examination of sodium silicate solutions shows that they are two-phase systems in which the disperse phase is negatively charged.[3] When concentrated ammonia is added to the solution, a silicate having approximately the composition

[1] Kohlrausch, *Zeit. physikal. Chem.*, 1893, **12**, 773; Hantzsch, *Zeit. anorg. Chem.*, 1902, **30**, 295; Mylius and Groschuff, *Ber.*, 1906, **39**, 116.

[2] Morey, *J. Amer. Chem. Soc.*, 1914, **36**, 215.

[3] Stericker, *Chem. Met. Eng.*, 1921, **25**, 61.

$Na_2Si_4O_9$ separates out,[1] and a hydrate of this silicate, containing $12H_2O$, is formed when precipitated silica is dissolved in boiling caustic soda and the filtrate evaporated down.[2]

Silicate of soda is employed in fixing fresco colours by the process of stereochromy. It is employed also as a cement in the manufacture of artificial stone. This is made by mixing the solution with sand and lime; it is likewise used as a cement for joining the broken surfaces of porcelain, stone, etc. Another purpose for which soluble glass is employed is as an addition to cheap soap. The so-called silicated soap was patented early in the last century and was subsequently largely made by William Gossage, who also took out a patent for its manufacture; it is now prepared in large quantities by adding a solution of this compound to the soap whilst settling.

Sodium Silicofluoride, Na_2SiF_6, is prepared in a similar way to the potassium compound, and is very similar to this latter salt; 100 parts of water dissolve, at 17·5°, 0·652 part of the salt, and at 101°, 2·459 parts (Stolba).

Detection and Estimation of Sodium.

147 The presence of a sodium compound can be readily detected by the production of the yellow tint which it imparts to the non-luminous gas-flame. This reaction was first observed by Melville in 1752, and was made use of by Marggraf in 1759 to distinguish the base contained in common salt from that peculiar to the vegetable alkali, which imparted a violet tint to the flame.

The spectrum of the yellow sodium flame consists of two bright yellow lines coincident with the two dark solar lines known as Fraunhofer's D-lines. These lines have wave-lengths of 5896 and 5890 Å.U. and lie so close together that in an ordinary one-prism spectroscope they appear as one line.

The flame reaction of sodium is the most delicate known among spectrum reactions (p. 169).

The absorption spectrum of sodium vapour has been mapped by Roscoe and Schuster.[5] A series of bands in the blue makes its appearance at a low temperature, and as this is raised bands in the red and yellow stretching as far as the D-lines

[1] Heintz, *Jahresb.*, 1871, 276.
[2] Walker, *Quart. Journ. of Science*, 1866, **3**, 371.
[5] *Proc. Roy. Soc.*, 1874, **22**, 362.

come out. When the vapour of sodium is examined in a red-hot iron tube the colour of the limelight as seen through it is a dark blue.

In the processes of quantitative analysis sodium generally occurs together with potassium. The process for the separation of these two metals is described under that metal, as well as the indirect methods by which the quantity of each of the two metals can be ascertained. If it is desired to determine the sodium directly, the best process is the following one suggested by Bunsen. The alcoholic solution of the soluble double chloride of sodium and platinum is evaporated in a flask which is filled with hydrogen gas, and reduced by exposure to light, or by addition of a reducing agent such as aldehyde. Sodium chloride, hydrochloric acid, and metallic platinum are then formed: the solution of common salt is filtered from the platinum, evaporated to dryness, and the weight of the salt ascertained after gentle ignition. As sodium chloride is volatile at a red heat, it is advisable to transform the salt into sulphate before ignition.

Sodium, moreover, forms sparingly soluble salts of antimonic acid and of dihydroxytartaric acid,[1] and can be estimated in presence of potassium by precipitation with the potassium salt of either of these acids.[2]

The Atomic Weight of sodium was determined by Stas. He found as the result of ten experiments that 100 parts by weight of pure silver required from 54·206 to 54·2093 parts of sodium chloride for complete precipitation. This gives a mean of 54·208, and the atomic weight of sodium as 23·05.

This ratio has been redetermined by Richards and Wells,[3] who employed more perfectly purified silver, and estimated the end point of the reaction between silver nitrate and sodium chloride by means of a specially devised instrument, the nephelometer.[4] The ratio obtained was Ag : NaCl = 100 : 54·185, whilst that of AgCl : NaCl was 100 : 40·780. Hence, taking the accepted values for silver (Ag = 107·88) and for chlorine (Cl = 35·46), these results give 22·99. The value now adopted (1922) is 23·00.

[1] Fenton, *Journ. Chem. Soc.*, 1898, **73**, 167.
[2] Bulstern and Blaise, *Zeit. anal. Chem.*, 1897, **36**, 513.
[3] *J. Amer. Chem. Soc.*, 1905, **27**, 459.
[4] *Amer. Chem. J.*, 1904, **31**, 235.

THE ALKALI MANUFACTURE.

148 The history of the manufacture of the alkali, soda, is one of great and peculiar interest. The following is a description (1) of the oldest known sources and processes, (2) of the Leblanc process, (3) of the cryolite process, (4) of the ammonia process, and (5) of the electrolytic processes,[1] followed by a description of the several forms in which the alkali now appears in commerce. The manufacture of bleaching powder is described separately under calcium.

The Oldest Known Sources and Processes.

149 *Natural Soda.*—From time immemorial an alkali has been obtained as a saline efflorescence from the ground in parts of Egypt, and from certain alkali lakes in that country;[2] the substance is known as trona or latroni, and it contains 20 or more per cent. of "sodium sesquicarbonate" $Na_2CO_3,NaHCO_3,2H_2O$ (see pp. 292 and 331); it is still exported from Alexandria at the rate of about 2,500 tons per annum. Nearly every district of India produces alkaline earth, known as dhobi's earth, containing from 11–36 per cent. of the double carbonate, which has been used for ages for washing, dyeing, and in the manufacture of soap and glass bangles. Very many districts are so impregnated with alkali that they form wastes or alkali deserts, as in Tibet and Utah. At Owens Lake in California the water is so nearly saturated with alkali that shallow receptacles are filled with it; it is then allowed to evaporate spontaneously, after which the crystals receive a slight wash to purify them; it is computed that this lake contains 50,000,000 tons of soda, and that the annual increase is 200,000 tons; and it is expected that the American market may in time be supplied from this source. In 1910 a great deposit of soda was found and explored in Lake Magadi, East African Protectorate. The lake covers an area of 30 square miles; the reddish water is only a few inches deep, and under this is a deep layer of natural soda in large, radiating crystals looking like pink marble, which is estimated to weigh 200,000,000 tons, and which might supply the world for one hundred years.

[1] For details of other suggested methods, see Lunge, *Sulphuric Acid and Alkali Manufacture* (London, Gurney and Jackson), and Partington, *The Alkali Industry* (Baillière, Tindall and Cox, 1918).

[2] Pliny, *Hist. Nat.*, Lib. 31, cap. 10.

This has been developed by the Magadi Soda Company, who have built 100 miles of railway to connect with the Uganda Railway, while the Government are prepared to deal with the transport on the Uganda Railway and to give loading facilities for ocean shipping at Kilindini. This soda is now supplied to Eastern markets.

Soda from Plant Ashes.—From very ancient times it has been known that the ashes of plants contained alkali, and they were used for cleansing, and for making soap and glass. Whereas almost all land plants yield an alkali that is mostly potash, certain land plants growing near the sea shores yield an alkali that is mostly, but not entirely, soda; such plants are grown on the Spanish coasts, and they have been cut and burned for centuries to prepare the ash barilla, which never contains more than 30 per cent. of sodium carbonate and often only 3 per cent.; as late as 1834 the import of Spanish soda into this country was 12,000 tons, and it realised £11 to £45 per ton. Sea plants yield an ash that is still poorer in potash and richer in soda, and these were cut or collected on the north-west coasts of France, Ireland, and Scotland, and burned to prepare an ash containing only 2½ to 5 per cent. of soda, known as "kelp." In the Orkney Islands a large number of persons used to be engaged in this work. Kelp is now used as a source of potassium chloride and of iodine. Land plants contain portions of soda which are not inconsiderable, and in the manufacture of beet-root sugar the residual molasses finally yield a charcoal from which soda is extracted in France, Germany, Austria and Belgium, on a limited scale.

Oldest known chemical processes of preparing soda.—In 1768 Hagen described the double decomposition between sodium sulphate and potassium carbonate; the less soluble potassium sulphate crystallises first from the solution, and soda crystals were then obtained from the mother-liquor. This process was also described by Accum as being carried out in a soda works in London prior to 1808. A similar double decomposition due to Bergman was carried out with sodium chloride and potassium carbonate; and some years later, in 1795, Lord Dundonald obtained a patent connected with the process, and from 1802–1815, Losh, at Walker-on-Tyne, made soda called "British Ash" which sold for £16 to £20 per ton.

In 1773 Scheele acted on sodium chloride solution with oxide of lead, obtaining an insoluble oxychloride of lead and a solution

of caustic soda; in 1782 soda was being made in England by this process, and in 1787 Turner patented a yellow lead oxychloride, a pigment known as "Turner's yellow."

But the most important process for subsequent developments was that of Malherbe in 1778. He heated sodium sulphate with carbon, obtaining sodium sulphide, and to the molten mass added iron scrap to combine with the sulphur. After due manipulation in the furnace the melt was withdrawn and the blocks were allowed to stand in the air until they fell to powder, which, when lixiviated, gave a solution from which soda crystals were at once obtained. The similarity of this process to that next described, in all particulars except the use of iron, may be noted.

The Leblanc Process.

150 One of the effects of the French revolutionary wars was the stoppage of the supply of potash to France and therefore the diminution of the important manufactures dependent upon its use. Under these circumstances the French Government issued an appeal to chemists urging the importance of utilising all the materials natural to their own country, "so as to render vain the efforts and hatred of despots," and commanded all citizens who "have commenced establishments or who have obtained patents for the manufacture of soda from common salt to make known to the Convention the locality of these establishments, the quantity of soda supplied by them, and the quantity they can hereafter supply." A Commission was appointed to investigate this subject, and in 1794 it reported on thirteen different processes, the particulars of which had been submitted. The preference was given to the operations devised by an apothecary of the name of Leblanc, who had erected a soda manufactory at St. Denis, near Paris; this had been at work for about three years. The process which constituted Leblanc's invention consisted of the conversion of common salt by oil of vitriol into Glauber's salt, whilst the evolved hydrochloric acid was converted into sal-ammoniac. The sulphate of soda was mixed, according to Leblanc's first description in 1790, with half its weight of chalk and a quarter of its weight of charcoal, but, according to his patent of 1791, with an equal weight of chalk and half its weight of charcoal, which proportions had yielded the best

results. From the surface of the fluxing mass a large number of flames broke forth similar to the flame of a candle; as soon as this phenomenon ceased the operation was finished. The batch was drawn out of the furnace with iron rakes, and collected in any kind of moulds to give it the shape of the commercial blocks of soda of that time. The fluxed mass was purified by powdering and boiling with water, or else it was allowed to fall to powder in the air and then washed. The calcareous substance and unburnt charcoal were removed by settling and filtering. From the solution the soda was separated on boiling down, and dried in a warm place.

Why Leblanc should have reacted with calcium carbonate on his fused sodium sulphide is not clear, because the first explanation of Leblanc's process was given in 1830 by Dumas, who, believing that calcium sulphide was soluble in water, supposed the existence of insoluble oxysulphide, 2CaS,CaO. The existence of this hypothetical compound was first doubted in 1858 by Kynaston, and disproved by Scheurer-Kestner in 1862; and in 1861 Gossage proved that calcium sulphide was insoluble in water. The Commissioners of 1794 say in their report:— "Citizens Leblanc, Dizé, and Shée were the first who submitted to us particulars of their process, and this was done with a noble devotion to the public good." The consequences of the French Revolution and subsequent war deprived Leblanc of funds; the works were suspended from 1794 to 1801, and he was unable to work his process. It is sad that the man who thus originated a world-wide industry, and to whom we owe cheap soap and cheap glass, did not benefit from his discoveries, and, not receiving the reward promised by his Government, died in 1806 by his own hand in poverty and despair.[1]

Other alkali works in France were more successful than Leblanc's original manufactory. Several of these were situated at Marseilles, the seat of the French soap trade, and conveniently placed for obtaining three of the necessary raw materials; (1) sulphur, from Sicily; (2) salt, by the evaporation of salt-water by the sun's heat; (3) limestone. They were, however, at a disadvantage in being at a distance from coal.

Although the process for making alkali was published in the *Annales de Chimie* for the year 1797, it is remarkable that not till 1814 was this process taken up in England by Losh, on the Tyne, on an exceedingly small scale. In 1823 the salt

[1] "Nicolas Leblanc: sa vie et ses travaux," by Aug. Anastasi, Paris, 1884.

duty of £30 per ton was abolished, and the way being thus opened for the use of salt as a raw material for the production of an artificial soda, which could compete with the natural sodas and the various soda ashes from plants, the same year saw the erection of an alkali works in Liverpool by James Muspratt. To prove the superiority of his product to the natural sodas and plant soda ashes Muspratt had at first to give his product away, but he soon established a growing industry. It must not be supposed, however, that Leblanc's process was complete in all its details, or was suited without alterations to English industrial requirements.

The hydrochloric acid evolved in the salt-cake process was not converted into sal-ammoniac as Leblanc had devised, but was allowed to escape into the air as a waste product, which destroyed vegetable life of all kinds for miles around, leading to complaints of nuisance and to frequent litigation. Hardly an assize passed without an action for nuisance or damage, and the present generation can scarcely form an idea of the prejudice aroused against alkali works for the first forty years of their existence. In 1836 Gossage introduced his plan of condensing hydrochloric acid, and though in the next ten years it was adopted by many works, yet many others, especially the smaller ones, continued to manufacture sulphate of soda without condensing the hydrochloric acid, and even those works which had condensers used them only in proportion as they found a sale for hydrochloric acid. The use of chlorine made from hydrochloric acid for manufacturing bleaching powder was extended from 1837 by the reduction of the excise duty on paper from 3*d.* to 1½*d.* per pound, which led to a greatly increased demand. In 1817 chlorine made from hydrochloric acid was first used on a large manufacturing scale for the preparation of potassium chlorate. In 1861 the paper duty was abolished, and with the consequent establishment of a vast number of daily and weekly newspapers and journals, and the reprinting of standard works in all parts of the kingdom, an enormously increased demand for paper materials was created. Straw, esparto grass, and wood fibres, which had hitherto been used only in very small quantities as compared with cotton and linen rags, were now used in rapidly increasing quantities, and as these require roughly three times as much bleaching powder per unit weight of raw material as do the rags, and as they produce much less

weight of paper, it is evident that the demand for hydrochloric acid was vastly increased. It was computed that in 1862 one-third of all the hydrochloric acid gas produced was still allowed to escape into the air, a fraction which amounted to about 1,000 tons per week; and this nuisance was only brought to an approximate end by the passing of the Alkali Act in 1863, which rendered compulsory the condensation of 95 per cent. of the hydrochloric acid gas produced. Thanks to the increased uses for and value of hydrochloric acid, the statutory condensation was rapidly obtained and exceeded. In 1874 another Act was passed requiring that the exit gases shall not contain more than 0·2 grain of hydrochloric acid per cubic foot of gas, and this limit is now fully observed. The means employed to condense the hydrochloric acid gas are described under the head of Hydrochloric Acid (Vol. I., p. 205). Where an acid was produced too weak to use or sell it was run away to waste, thereby often creating a fresh series of nuisances by reason of it finding its way into the drainage from the waste heaps of the lixiviation process—a liquor loaded with soluble sulphides.

The black-ash produced up to 1823 contained only 10 to 12 per cent. of alkali (Na_2O), and though Leblanc had shown how to prepare from this, as his final product, a nearly pure hydrated sodium carbonate, "soda crystals," $Na_2CO_3,10H_2O$, yet this was not done commercially, and the black-ash was sold as such and with all its impurities to soap-makers; in 1823 it realised £12 per ton. A black-ash containing 24 per cent. of alkali was first made by Muspratt in 1823, since when the strength has not been materially increased.

The details of the economical lixiviation of the black-ash, and the evaporation of the liquor by the waste heat from the black-ash furnaces, are due, not to Leblanc, but to English alkali-makers, who produced in quantity not only Leblanc's "soda crystals," but also a new and much stronger alkali, namely, the white-ash or soda-ash, selling at £22 per ton in 1833. It consisted of impure anhydrous sodium carbonate, and according to its impurities and methods of preparation contained from 48 to 52 per cent. of alkali (Na_2O). The impurity present in largest quantity in the alkaline liquor was sodium hydroxide, and this was carbonated either by calcining with a considerable quantity of sawdust, or by leading in waste furnace gases, or carbonic acid gas.

To the English alkali-makers also was due a further entirely

new development in the making of strong alkali. The first step was the introduction of "caustic ash" a mixture of anhydrous sodium carbonate and sodium hydroxide, obtained by using a larger proportion of lime than previously in the black-ash mixing, and by not adding sawdust or carbonic acid gases when evaporating the alkaline liquor to dryness. About 1850 this was followed by methods of separating the bulk of the sodium carbonate as the monohydrate, Na_2CO_3,H_2O, from the liquor, and evaporating the mother-liquor, now containing essentially sodium hydroxide, until it contained 60 per cent. of alkali and on cooling solidified into a crystalline mass known as "cream caustic." About 1857 the methods of removing the various impurities were improved, and the caustic liquor was evaporated at much higher final temperatures, so that anhydrous white caustic soda containing 70 per cent. of alkali was obtained. In 1861 Lancashire furnished 4,680 tons of caustic soda, but in 1862 methods had been found at St. Helens of so altering the charge in the black-ash furnace, and so working the liquor as to obtain stronger and whiter caustic soda, which at once found extended use in soap and paper manufactories. From 1873 the developments were stimulated by the success of Solvay's Ammonia Soda Process in making soda-ash of excellent quality and in a very economical manner; but he could not make caustic soda except by an additional operation. By 1878 the output of caustic soda by the modified Leblanc process reached 94,000 tons a year. In 1888 the methods of separating the impurities from the raw caustic soda solutions had been so improved by the Greenbank Alkali Company that the finished caustic soda contained 77 per cent. of alkali, a figure which is even now only slightly exceeded.[1]

Lastly, the process of Leblanc left the insoluble portion of the black-ash as great mounds of waste creating a general nuisance that led the manufacturers into great trouble for many years. The waste underwent oxidation, and rain and drainage waters dissolved from it soluble sulphides, polysulphides, and thiosulphates, which found their way into the drains and streams of the district, whither also was discharged the waste weak hydrochloric acid made in the early years of the process; and the resultant sulphuretted hydrogen was sufficient to be a nuisance

[1] In practice a product containing 98·1 per cent. NaOH is referred to as "78 per cent. alkali." Theoretically, 100 per cent. NaOH corresponds with 77·5 per cent. Na_2O.

to the inhabitants of districts lying even several miles away from the waste. With improvements in the construction of the salt-cake furnaces, and also in the condensing towers for the hydrochloric acid, the production of waste weak acid was stopped and with it the production of sulphuretted hydrogen. But the drainage of the sulphide liquors from the heaps continued to kill all life in the water-courses. Many processes have been tried to turn the waste calcium sulphide to useful account, but it was not till 1888 that in the Chance-Claus process a satisfactory method was discovered of ending the nuisance and recovering

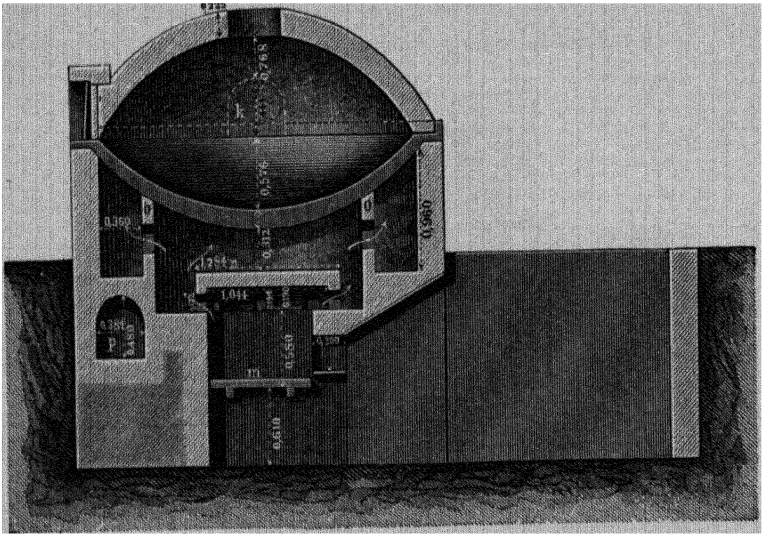


FIG. 96

the contained sulphur in a form of much greater value than that in which it was introduced; the process is described later (p. 315).

151 (1) *The Salt-cake Process.*—This process is usually commenced in large cast-iron pans nine feet in diameter but scarcely two feet deep. Through the doorway shown in the upper left hand corner of Fig. 96 is introduced the charge of 16 cwt. of common salt, and on to this is run the quantity of sulphuric acid necessary to decompose it completely. This amounts to 123·5 gallons, or 1,800 lbs. of chamber acid having a specific gravity of 1·42. Torrents of hydrochloric acid are given off, and the temperature of the mass rises to about 50°. All the strong hydrochloric acid gas which is thus evolved,

being confined by the brick covering of the pan, the closed charging door, and the closed discharging door indicated by *k* in Fig. 96, passes through the central opening in the cover, and is sucked through a set of attached earthenware pipes into the hydrochloric acid condensing towers, described under the heading of Hydrochloric Acid (Vol. I., p. 205). When the evolution of gas begins to slow down the pan is heated, with considerable precautions to avoid local overheating. After about one hour's heating the product is essentially a mixture of sodium hydrogen sulphate and common salt,

$$2NaCl + H_2SO_4 = NaHSO_4 + NaCl + HCl,$$

which will not react further unless the temperature is raised to a

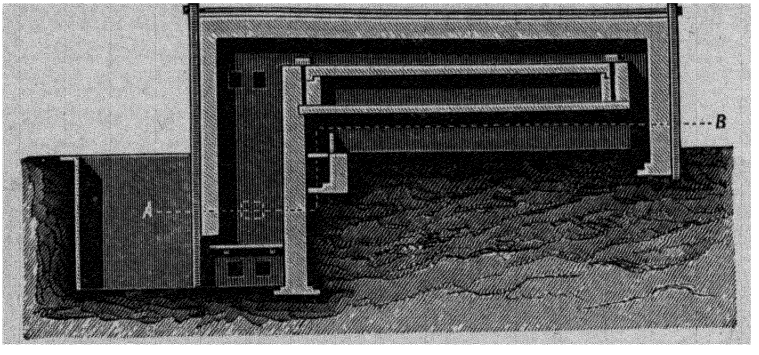


FIG. 97.

much higher degree than the cast-iron pot will stand. The mixture is therefore raked through the door indicated by *k*, Fig. 96, on to the firebrick hearth of an adjacent "roaster."

The roasters were at first simple reverberatory furnaces, which have since been modified mainly in order to obtain the strongest possible hydrochloric acid gas which is easy of condensation, but also to avoid contamination of the salt-cake with the ashes of the fuel. The older forms of roasters being no longer permitted to be erected, only the present form, due to Deacon of Widnes, is described; it is shown in Fig. 97. The fireplace is built contiguous to, but several feet below the brick chamber or muffle in which the salt-cake is roasted and the acid gas is evolved, and the exhaust flue is not above, but under the ground level.

With these modern furnaces it is comparatively easy so to regulate the draughts on the furnace and the draught on the

muffle and attached condensers that the pressure in the flue round the muffle is slightly greater than that in the interior of the muffle, thus preventing the passage of the acid gas from the muffle through the unavoidable cracks into the chimney, although allowing some of the fire-gases to pass into the muffle, but in such regulated quantity that they do not interfere with the successful working of the condensation.

Many attempts have been made to carry out the manufacture of salt-cake in mechanical furnaces, among which may be mentioned those of Jones and Walsh, Cammack and Walker, and Mactear.[1] The revolving furnace of the latter has been the most successful in practice, and consists (Fig. 98) of a circular revolving bed covered by a fixed arch, between which and the bed the furnace gases pass. The salt and acid are constantly fed into a large cup in the centre of the hearth, where they mix and overflow into the outer portion of the circle, and are subjected to the action of the hot gases; by means of fixed stirrers the mass is continuously mixed and gradually worked to the circumference, over which it then falls. The action is thus a continuous one, and the amount of hydrochloric acid evolved is therefore constant, so that in spite of the fact that the acid-gas is mixed with the whole of the furnace gases, the condensation is carried out more readily and a more concentrated acid is obtained than in the ordinary process. Other types of continuous salt-cake furnaces have been described.[2]

Another important process for making salt-cake is that of Hargreaves. The object of this is to dispense with the manufacture of sulphuric acid, and it depends upon the fact that, although sulphur dioxide cannot by itself decompose salt, it is able to do so in the presence of oxygen and water, if sufficient time be allowed for the reaction. In order to effect this decomposition, a series of large kilns or stoves, built of brick, is so arranged that each kiln can be put into communication with its neighbour, and each heated by a fire. Each kiln is then filled with specially prepared cakes of dried and porous salt, and the gases from the pyrites burners are led directly into these kilns arranged in series. By careful attention to temperature and to the quantity of air and steam admitted with the sulphur

[1] *Proc.* First General Meeting, Soc. Chem. Ind., 1881, **26**; *Proc. Roy. Soc. Arts*, 1880–1, **29**, 178.

[2] See Lunge, *Sulphuric Acid and Alkali*, Vol. II (1909), p. 282, and Ullmann, *Enzyclopädie der technischer chemie*, Vol. IX, p. 900.

dioxide, it is possible to decompose the salt as perfectly as by the old process with sulphuric acid :

$$4NaCl + 2SO_2 + 2H_2O + O_2 = 2Na_2SO_4 + 4HCl.$$

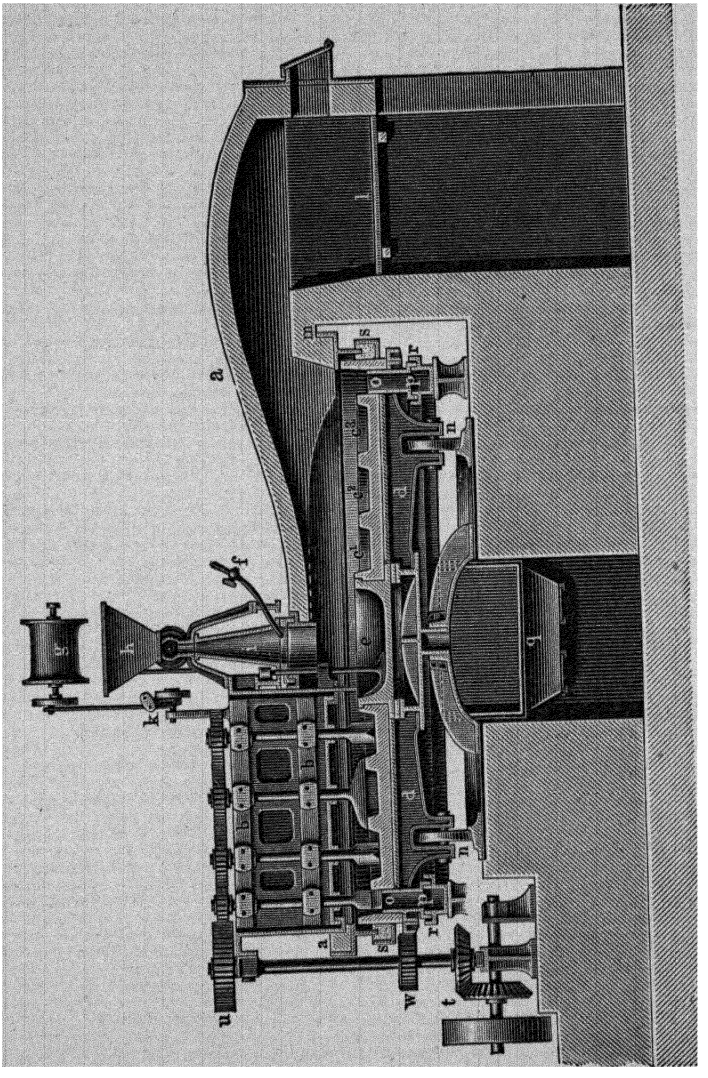


FIG. 98.—Mactear Furnace.

The hydrochloric acid gas is separated from the accompanying residual nitrogen in the hydrochloric acid condensing towers.

The following is an average analysis of salt-cake :

Na_2SO_4	$NaHSO_4$	NaCl	$CaSO_4$	Fe_2O_3 and insoluble	H_2O
95·27	1·48	1·35	0·92	0·32	0·18 = 99·52.

152 (2) *The Black-ash Process.*—The theory of this process, as given by Scheurer-Kestner and Pelouze, is a simple one, so far as the chief products are concerned, but it is complicated by many secondary reactions, and by the impurities in the raw materials.

When the salt-cake is heated with slack, or powdered coal, it behaves like all other fairly stable sulphates, being converted into the corresponding sulphide, thus :[1]

$$Na_2SO_4 + 2C = Na_2S + 2CO_2,$$

and the characteristic part of the Leblanc process is the heating of the sodium sulphide with chalk or limestone (calcium carbonate), whereby sodium carbonate and calcium sulphide are formed, of which the former is exceedingly soluble in water at 40°

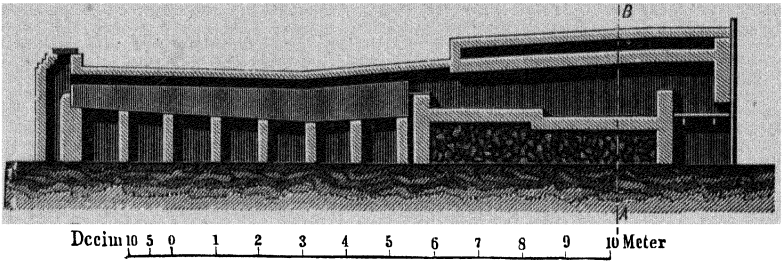


FIG. 99.—Longitudinal Section of Balling Furnace.

to 50°, whilst the latter is insoluble in water of the same temperature :

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

In practice these two reactions are made to take place simultaneously, by mixing about 10 parts by weight of salt-cake, 10 parts of limestone, and 5–7 parts of coal, and heating the same in a reverberatory furnace, termed a balling furnace. The right-hand half of Fig. 99 shows the longitudinal section of such a furnace.

After exposure to the reducing flames from the furnace for two hours, with frequent stirring, the end of the operation is indicated by the appearance of yellow flames or "candles" on the surface of the melt, due to the formation of carbon monoxide at the elevated temperature of the furnace by the action of carbon on calcium carbonate :

$$C + CaCO_3 = 2CO + CaO;$$

[1] Kolb, *Ann. Chim. Phys.*, 1866, [4], **7**, 118; Lunge and Fischer, see Lunge, *Sulphuric Acid and Alkali*, 1909, Vol. II., Part II., p. 521.

this evolution of gas is also of importance for the subsequent lixiviation of the black-ash, as it renders the mass porous. The liquid mass is scraped out into iron barrows or trucks and allowed to cool, and in this state is known, from the colour of the mass, as black-ash ball.

The old black-ash furnace or balling-furnace, in which the mixing of the materials is effected by hand labour, has been replaced by a furnace termed a revolving black-ash furnace, the general arrangement of which is shown by the left-hand side of Fig. 100 and in Fig. 101. In this furnace, first patented by Elliott and Russell in 1853, but first successfully operated by Williamson and Stevenson in 1855, the mixing of the materials is effected mechanically. The charge of about 4 tons is introduced by means of a hopper into a large horizonal cylinder (B), through which flames from a furnace (A) are allowed to pass; this cylinder, worked by an engine (C), revolves first at a slow rate, afterwards increasing to a maximum velocity of five or six revolutions per minute. The cylinder is from 10 to 12 feet in diameter and generally from 15 to 18 feet long, but they have also been made up to 30 feet long.[1] Each charge takes about two hours, and when completed the charging hole in the side of the cylinder is opened, and by slowly moving the cylinder to bring the hole lower and lower, the fused mass is forced to flow into a series of iron trucks placed beneath it. The advantages of the revolving black-ash furnace over the hand-worked ones consist chiefly in the saving of labour and the production of a material which possesses a more constant composition.

Péchiney (1877) showed that cyanides in the black-ash may be destroyed by adding a little fresh salt-cake just before the charge is finished. The addition of the salt-cake destroys the cyanides formed from the nitrogen of the coal by utilising their powerful reducing action:

$$2NaCN + Na_2SO_4 = Na_2CO_3 + Na_2S + CO + N_2.$$

Weldon (1878) added at the same time 6 parts of salt-cake and 7 of limestone. Mactear (1874) had previously added quicklime to the extent of 6 to 10 per cent of the weight of the original salt-cake and 14 to 16 per cent. of furnace cinders.

The addition of the limestone causes the evolution of carbon monoxide to make the candle flames, and produces a limited amount of quicklime, both of which aid the subsequent

[1] Smith, *Journ. Soc. Chem. Ind.*, 1887, **6**, 416.

lixiviation of the black-ash. Such processes appear to have gone out of use, and the materials are now always added in one batch.

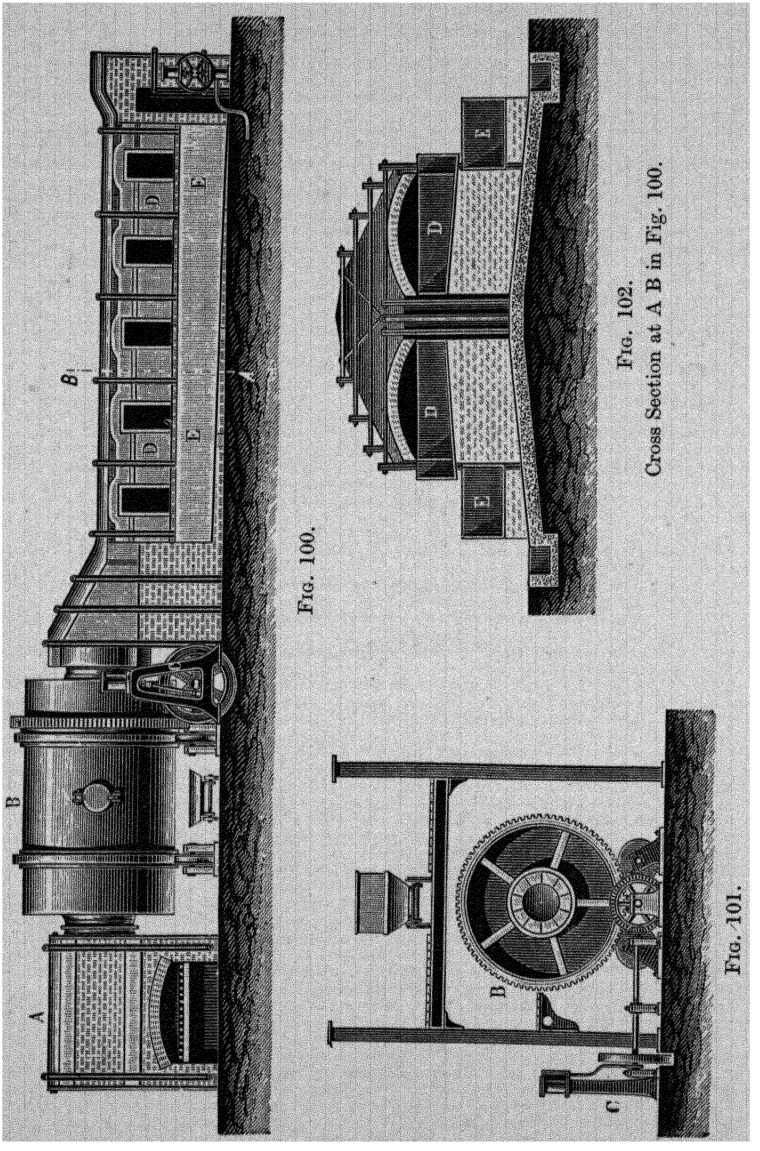


Fig. 100.

Fig. 102. Cross Section at A B in Fig. 100.

Fig. 101.

Black-ash contains as principal constituents 36 to 45 per cent. of sodium carbonate, and 28 to 31 per cent. of calcium sulphide; as remnants of the ingredients, 0·5 to 1·5 per cent. of sodium sulphate, 1 to 7 per cent. of coal, and 3 to 6 per cent.

of limestone; as unchanged impurities of the ingredients 1·5 to 2·5 per cent. of sodium chloride, 1 to 1·5 per cent. of iron as oxides, 1 to 2 per cent. of aluminium silicate, 1 to 2 per cent. of sand, and about 0·5 per cent. of magnesia; as intentional secondary product 8 to 10 per cent. of calcium oxide; as unintentional secondary products 1·5 to 2·5 per cent. of sodium silicate, 0·5 to 1·5 per cent. of sodium aluminate, 1 per cent. of sodium ferrous sulphide, and small quantities of sodium cyanide and sodium thiocyanate from the nitrogen of the coal, also ultramarine.

153 (3) *Lixiviating the Black-ash.*—The next operation consists in the treatment of the black-ash with water. The cakes are broken up, and to facilitate this they are first allowed to stand in the air for two or three days, when they absorb water and begin to split up spontaneously. The water must be at a temperature of about 40°, because if employed much hotter the reverse reaction,

$$Na_2CO_3 + CaS = Na_2S + CaCO_3,$$

begins, though very slowly. During lixiviation heat is evolved and the temperature rises to about 60°, and as local temperatures must be still higher, it can be understood why the black-ash liquors always contain appreciable amounts of sodium sulphide. The amount of water used must be limited in quantity so as to obtain sufficiently strong solutions; but in limiting the water the moistened black-ash must not be allowed to project through the liquor surface into the air, because it would then absorb oxygen with great rapidity; even the liquors absorb oxygen, and hence, and also because of the reversal of the reaction, the lixiviation has to be conducted as quickly as possible; the products of the oxidation are sodium polysulphides, thiosulphate, sulphite, and sulphate. The process used was invented by Buff and Dunlop. A series of vats is employed in which the broken black-ash is placed; water is allowed to flow on to that portion of the ash which by previous operations has already been nearly exhausted, and the liquor, slightly increased in specific gravity, falls to the bottom of the tank, whence it flows by a pipe to a slightly lower level in the second tank. Here and in the succeeding tanks the same actions occur, until in the last tank the strong liquor coming into contact with the fresh black-ash is brought up to full strength, and then flows from the bottom of that tank by a pipe which rises to a certain

height. The height is so adjusted that a steady flow of liquor passes through all the tanks continuously; owing to the increasing specific gravity of the liquor, the liquor level in each tank adjusts itself a little lower than in the preceding tank. The final liquor has a specific gravity of about 1·3 and is always coloured. The average time needed for the lixiviation of a charge is about forty-eight hours. The residue remaining in the vats is known as alkali waste, and is described on page 314. During the lixiviation the caustic lime transforms a considerable quantity of the sodium carbonate into caustic soda:

$$CaO + Na_2CO_3 + H_2O = 2NaOH + CaCO_3.$$

The liquor contains the following approximate quantities in grams per litre:

Na_2CO_3	NaOH	NaCl	Na_2SO_4	Na_2SiO_3	Na_2S	$NaAlO_2$
225–275	50	20	13	4·8	4	3·8

$Na_2S_2O_3$	Na_4FeCy_6	NaSCN	$Na_2S{\cdot}FeS$
1·6	0·3	0·2	0·1.

The ratio of caustic soda to carbonate may be larger than this, say 1 to 3, on account of the reaction just described.

154 (4) *Purifying the Black-ash Liquor.*—The black-ash liquor may be made to yield directly a deposit of soda crystals, but its many impurities cause the crystals to be discoloured and impure; hence many, and very various, methods have been adopted to purify the crude liquor.

(*a*) Keeping the liquor warm and allowing it to settle causes a deposit of undissolved fragments from the black-ash, also of ferrous sulphide and sodium aluminium silicate.

(*b*) Acting on the liquor with carbon dioxide, for the purpose (1) of converting the caustic soda into sodium carbonate, (2) of converting sodium sulphide into sodium carbonate with evolution of sulphuretted hydrogen gas, (3) of decomposing the sodium ferrous sulphide into sodium carbonate and insoluble sulphide of iron, (4) of decomposing sodium silicate and sodium aluminate into sodium carbonate and insoluble silica and alumina, or compounds of the same. The sodium ferrous sulphide on calcination gives ferric oxide, which discolours the soda-ash.

(*c*) Acting on the liquor with air, for the purpose of converting the sodium sulphide and sodium ferrous sulphide ultimately into sodium sulphate and oxide of iron. According to Lunge the oxidation stops at thiosulphate. This method was

used in 1853 by Gossage. The action of the air was sometimes aided by adding precipitated manganese dioxide (Weldon Mud).

(*d*) Addition of zinc or zinc oxide, both of which are soluble in caustic soda solutions, to decompose the sodium sulphide, sodium ferrous sulphide, and sodium ferrocyanide, with formation of insoluble zinc sulphide, iron sulphide, and zinc ferrocyanide.

(*e*) Heating the liquor to 180° under pressure (after it has been carbonated as above), whereby the ferrocyanides are destroyed by very complicated reactions.

After any of these treatments the liquor is allowed to settle, when the still warm and clarified liquor may be drawn off and crystallised by cooling.

Finishing the Black-ash Liquor.—The course adopted has varied much at different times and at different works, and it is regulated more by trade than by scientific requirements.

The purified liquors may be allowed to cool, and deposit washing soda crystals, $Na_2CO_3,10H_2O$, which with draining and slight washing are then ready for the market. The mother-liquors, being then much more impure, are worked up by one of the following methods.

The liquors are more frequently evaporated to deposit crystals of the monohydrate, Na_2CO_3,H_2O, from the liquor while it is still boiling, and for this purpose the waste heat of the black-ash furnace is employed. Large iron pans, shown in Fig. 99 on the left side, and at DD in Figs. 100 and 102, are kept filled with the liquor, and as the temperature rises and the water steams off, minute crystals of sodium carbonate monohydrate, Na_2CO_3,H_2O, deposit until the pan is filled with a thick magma of these and the mother-liquor. It is on account of this thick magma of crystals that the English arrangement of setting the evaporating pans is adopted, that is, the pan is not heated from below, but the liquor is heated from above, the fire gases coming into actual contact with the liquor. The doors in the pan sides shown in the several figures are then opened, and the contents are raked out into the drainer (E in Figs. 101 and 102), and there allowed to drain; the mother-liquor from the crystals contains largely increased amounts of caustic soda and of salt compared with the sodium carbonate, and it is either mixed with sawdust, evaporated to dryness, and calcined for the purpose of ultimately making a low grade ash, or else it is evaporated to dryness without any such addition to obtain

ultimately a product known as "caustic ash." By special attention the monohydrate crystals may be obtained in a condition of great purity, and after well draining and slight washing they are sent into the market under the name of "crystal carbonate." Evaporation is also effected in Thélen pans, semi-cylindrical iron pans heated below by hot furnace gases, and provided with scrapers attached loosely to the arms of a revolving horizontal shaft.

By heating the monohydrate in a reverberatory furnace it is converted into the anhydrous sodium carbonate, Na_2CO_3, commercially known as "soda-ash." Monohydrate containing sodium ferrous sulphide or sodium ferrocyanide always gives an ash coloured yellow by ferric oxide.

When soda-ash is to be used for cleaning wool it must be particularly free from caustic soda, but if it is to be used for soap or paper-pulp making, the presence of even a considerable amount of caustic soda is an advantage.

155 *Production of Caustic Soda from Black-ash Liquor.*— A totally different method of dealing with the caustic soda found in black-ash liquor was initiated by Gossage in 1853. Taking the mother-liquor from the monohydrate crystals with its high accumulated contents of caustic soda already referred to, he continued the evaporation, but as any "salt" was deposited, whatever its nature, it was fished out with perforated ladles and so removed, until the residual caustic soda, which is the most soluble of all the constituents of the liquor, became so concentrated that on cooling the whole set into a solid mass, still containing 10 to 15 per cent. of water. This was the first solid caustic soda made commercially, and was known as "cream caustic"; it did not contain more than 60 per cent. of alkali (Na_2O), and was blue, green, yellow, or red, but never white.

As the uses for solid caustic soda rapidly extended, the black-ash was so mixed as to yield more caustic soda in the liquor; and lastly, instead of evaporating the black-ash liquor to recover what sodium carbonate it contained, it was diluted considerably till only of about 1·09 specific gravity, and the sodium carbonate present was then causticised by adding the necessary amount of lime and heating:

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3.$$

After this the mixture was blown with air to oxidise the sulphides of sodium and iron, allowed to settle, and the liquors were

evaporated. During the evaporation some of the impurities, consisting of sodium sulphate and chloride, and also the small amount of sodium carbonate always remaining unacted on by the lime, crystallise and are fished out or allowed to settle; the purer liquid in the last stages of the evaporation is oxidised by a current of air or by nitre, whereby sulphides are converted into sulphate, whilst ferrocyanide is destroyed with separation of graphite, and a red precipitate of ferric oxide is thrown down. When the caustic has become anhydrous the separation of the iron is complete, as was first pointed out by Ralston in 1860, and the addition of less than a handful of nitre or of sulphur will cause a large pot holding 16 tons of molten caustic to change from yellow through white to green or *vice versa*. After partial cooling, during which the ferric oxide settles, the still molten caustic, colourless as water, is ladled into thin sheet-iron drums. White caustic soda was first manufactured largely in 1862. By great attention to the methods of purification the caustic soda now manufactured is made to contain as much as 76 per cent. of alkali, but various other strengths are made, down to 60 per cent. of alkali. Sodium carbonate is no longer the principal product of the Leblanc process, but sodium hydroxide.

Alder Wright has made a series of experiments on the loss of sodium occurring in the Leblanc processes. He believes it to be as follows:

Sodium compounds vaporised . .	1·14 per cent.
Sodium sulphate undecomposed . .	3·49 ,,
Sodium compounds rendered insoluble .	5·44 ,,
	10·07 ,,

156 *Alkali Waste and its Utilisation.*—The insoluble waste remaining from the lixiviation of the black-ash has a variable composition, but its nature may be seen from the following analyses, the first from a black-ash charge made for carbonate, and the second from a charge made for mixed caustic and carbonate:

CaS.	$CaCO_3$.	Moisture.	Coke.	$Ca(OH)_2$.	$Na_2CO_3,CaCO_3,5H_2O$	Sundries.
30·17	18·53	33·79	8·46	1·22	4·01	4·51
26·46	22·26	32·98	3·84	6·33	5·63	3·31

The double carbonate of sodium and calcium occurs native as gay-lussite in certain Salt Lake deposits, and this compound

is the cause of the loss from sodium compounds rendered insoluble. To avoid its formation the amount of lime in the black-ash charge is reduced to a minimum.

For every ton of soda-ash there are one and a half to two tons of waste produced, and this accumulates in enormous quantities.

The present method of utilising alkali waste is due to Chance, who after years of experimental work at Oldbury, near Birmingham, devised a process that has been adopted by many large English and French works. The waste gas from lime-kilns, containing about 28 per cent. of carbon dioxide and 72 per cent. of nitrogen, is forced by powerful pumps through a series of from four to six tall closed cylinders containing a thin creamy mixture of alkali waste and water. The first action of the gas is to convert the calcium sulphide into hydrosulphide and carbonate:

$$2CaS + H_2O + CO_2 = Ca(SH)_2 + CaCO_3.$$

The nitrogen, the only gas remaining at this stage, is sometimes allowed to escape, so as to increase the strength of the sulphuretted hydrogen ultimately obtained, 40 per cent. of the nitrogen otherwise necessarily present being thus actually eliminated. The second action of the carbon dioxide is to convert the calcium hydrosulphide into calcium carbonate and sulphuretted hydrogen, which necessarily is admixed with the nitrogen that accompanied the carbon dioxide:

$$Ca(SH)_2 + CO_2 + H_2O = CaCO_3 + 2H_2S.$$

As it is not possible to separate these two processes completely, the strongest gas obtainable contains:

H_2S.	CO_2.	N_2.
33·5	1·7	64·8

but if no attempt is made to separate the two processes, the resultant gas contains only 25 per cent. of sulphuretted hydrogen. The residual "cream" from the carbonating towers is entirely free from sulphides, and is filtered in presses so as to obtain: (1) a clear liquid containing about 2 per cent. of sodium bicarbonate, which is used to dissolve fresh charges of black-ash, and (2) cakes of innocuous calcium carbonate. This material is usually stacked in waste heaps, though some has been used in the making up of the black-ash charge, and some for making Portland cement.

The second part of the Chance process consists in so burning the sulphuretted hydrogen as to produce sulphur and water:

$$2H_2S + O_2 = 2S + 2H_2O.$$

Since the air used in burning the sulphuretted hydrogen contains about four-fifths its volume of nitrogen, it is clear that, starting even with the strongest gas obtainable (see above), the proportion of nitrogen to sulphuretted hydrogen in the mixture submitted to combustion will be at least 4 : 1 by volume. The combustion is carried on continuously in a kiln, called the Claus kiln, lined with fire bricks, and provided with a false bottom, on which rests a layer of broken brick, and then a thinner layer of oxide of iron, which acts as a catalytic agent. and enables the reaction to proceed. The gas and air are led, each in carefully regulated quantity, under the false bottom, where they are kindled; the heat evolved by the reaction maintains the necessary temperature of the kiln. A portion of the sulphur runs molten from the kiln, the rest distils off with the water, and by passing the vapours through cooling chambers the sulphur is condensed, partly in the molten form, and partly in the form of "flowers." If the kiln is made to do too large an amount of work, its temperature rises higher, and a new reaction sets in:

$$3S + 2H_2O = SO_2 + 2H_2S,$$

which leads to a loss of 12 to 20 per cent. of the sulphur in the exit gases.

In practice not only do the exit gases from the Claus kiln always contain small but appreciable quantities of sulphuretted hydrogen and sulphur dioxide, but the waste nitrogen from the carbonating towers is liable to contain sufficient sulphuretted hydrogen to create a nuisance, if the carbonators are worked so as to produce a strong sulphuretted hydrogen. These drawbacks have been overcome by burning the small amount of sulphuretted hydrogen to sulphur dioxide, absorbing this and the sulphur dioxide originally present in a tower containing limestone and water, and running the resultant weak acid calcium sulphite to waste.

Cryolite Process.

157 Cryolite, or sodium aluminium fluoride, $3NaF,AlF_3$, a mineral mined only in Greenland to the extent of 6,000 to

7,000 tons per annum, is used as the raw material for the manufacture of a limited amount of sodium carbonate.[1] The process, devised by Thomsen of Copenhagen in 1849, and first utilised on a large scale in 1854, is founded on the fact that when this mineral is heated with chalk, carbon dioxide escapes, leaving behind a mixture of calcium fluoride and sodium aluminate :

$$2(3NaF,AlF_3) + 6CaCO_3 = (3Na_2O,Al_2O_3) + 6CaF_2 + 6CO_2.$$

The sodium aluminate is separated from the calcium fluoride by lixiviation and the solution carbonated with carbon dioxide. There is thus obtained a solution of sodium carbonate ready for evaporation to the crystallising point, and a granular precipitate containing 45 per cent, of alumina, 20 per cent. of sodium carbonate, and 35 per cent. of water, from which the sodium carbonate is extracted by long-continued washing with hot water.

In 1865 the monopoly for the cryolite was obtained by a firm near Pittsburg, and hardly any soda is made from it elsewhere.

Ammonia-Soda Process.

158 This process consists in passing carbon dioxide into a solution of sodium chloride containing ammonia; ammonium carbonate and ultimately ammonium bicarbonate is formed, which then enters into reversible double decomposition with the sodium chloride to form sodium bicarbonate :

$$NH_4HCO_3 + NaCl \rightleftarrows NaHCO_3 + NH_4Cl.$$

Sodium bicarbonate being very slightly soluble in a solution of either ammonium chloride or sodium chloride separates out, and after mechanical removal of the mother-liquor may be converted by calcining into the normal carbonate and carbon dioxide, which last is used again in the first part of the process. The mother-liquors, containing ammonium chloride and a considerable proportion of unaltered sodium chloride, are heated with lime, and the ammonia thus recovered is used again in the first part of the process. The only essential waste product is therefore a solution of calcium and sodium chlorides, but in practice a considerable amount of lime sludge is produced.

The reaction is incomplete, only two-thirds of the common

[1] Thomsen, *Dingl. Polyt. Journal*, 1862, **166**, 441.

salt being decomposed under working conditions. The remaining third is wasted. The equilibrium has been investigated by Fedotieff.[1]

Simple as the process is from a chemical point of view, the practical difficulties, of mechanical nature, were so great that, although the process was patented in England in 1838 by Dyar and Hemming, it was not until 1855 that it was first practically carried out by Schlösing and Rolland near Paris. They did not, however, succeed in overcoming all the numerous practical difficulties surrounding the subject, and discontinued the process in 1857. The credit of having brought the process to an economical issue belongs to Solvay, who in 1861 took out his first patent, in 1863 erected his first factory near Brussels, and in 1872 made the process really successful, so that he was enabled to build a very large factory near Nancy. In 1872 Solvay's output was only 10 tons of soda per day, but in 1888 the Solvay Syndicate Works in England were reported to make 125,000 tons, while those on the Continent made 245,000 tons, and those in America 60,000 tons, a total of 430,000 tons out of the world's total production of 900,000 tons by all processes; in 1900 the production of ammonia-soda amounted to 900,000 tons, while the total by all processes was 1,500,000 tons. It probably now exceeds 3,000,000 tons per annum. The works started in England under Solvay's patents were those of Brunner Mond & Co., at Northwich; they commenced operations in 1874 and were the first works to use natural brine direct; various improvements introduced by L. Mond enabled their output to be increased from 2,500 tons in 1875 to 169,000 tons in 1892. Owing to the erection of other ammonia-soda works in this country the output of ammonia-soda steadily rose until in 1895 it reached 428,614 tons, thus exceeding the 408,173 tons produced by the Leblanc process. In 1904 the British ammonia-soda works consumed 1,703,805 tons of salt as such or in the form of brine. Many minor modifications have been introduced by numerous manufacturers, and the processes conducted in the ammonia-soda works of to-day contain many details differing from Solvay's original proposals.

The advantages of the process over the Leblanc process are: (1) that the cost of manufacture is less, chiefly because of the use of the brine pumped directly from the salt beds and because of the smaller amount of fuel required; (2) that it gives rise to

[1] *Zeit. physikal. Chem.*, **1904, 55, 2.**

no noxious by-products, although the disposal of the waste-liquors containing calcium chloride and lime sludge is a difficulty, and (3) that it yields a purer product. The disadvantages of the process are: (1) great care has to be exercised to avoid any considerable loss of ammonia, the cost of which is relatively very high; (2) the whole of the chlorine of the sodium chloride is lost, as no simple and economical process has yet been devised for recovering it from the calcium chloride on a very large scale, notwithstanding numerous attempts; (3) the proportion of salt used per ton of sodium carbonate made is much greater than in the Leblanc process.

Brine, pumped direct from the mine, always contains minor constituents that cause considerable trouble. The constituents (grams per litre) contained in a typical sample are:

$NaCl$	$CaSO_4$	$CaCl_2$	$MgCl_2$
290	4·5	2·1	0·6.

By treatment with milk of lime and subsequent settling, the magnesium chloride may be converted into calcium chloride and a precipitate of magnesium hydroxide, and the latter removed. By the subsequent addition of either sodium carbonate, or of liquors containing ammonium carbonate, the bulk of the calcium salts is precipitated as calcium carbonate and this also is removed by settling. The purified brine must not be too strong, because otherwise the addition of ammonia gas would so reduce the solubility of the sodium chloride as to cause some of it to crystallise out. Ammonium chloride may also be precipitated if the brine is fully saturated. Whether water requires to be added or not depends upon the manner of preparing the ammonia gas, because this may bring with it larger or smaller proportions of water vapour. In practice no initial purification of the brine, except that involved in the saturation with ammonia, is usual, although troublesome scale-formation in the apparatus may occur with unpurified brine.

The apparatus for saturating the brine with ammonia is sometimes a simple vertical tank containing the purified brine, into the bottom of which the moist ammonia gas is forced by pressure generated in the still where the gas is made. Sometimes it is a tower subdivided by many partitions over which the liquor flows gradually downwards, while the ammonia gas at almost atmospheric pressure passes up the tower. Whatever the form of the apparatus the solution becomes warm, and by

various cooling devices is partially cooled. Owing to the residual lime and magnesia salts in the brine, a precipitate of the carbonates of these metals is formed, which is prevented from becoming admixed with the sodium bicarbonate subsequently formed by passing the ammoniacal brine continuously through a series of large settling tanks, from the conical bottoms of which the mud may be drawn off. The resulting liquor, containing an average of 60–75 grams NH_3 and 270 grams NaCl per litre, is run into a montejus, whence it is forced by gas pressure from the carbon dioxide mains into the carbonating tower.

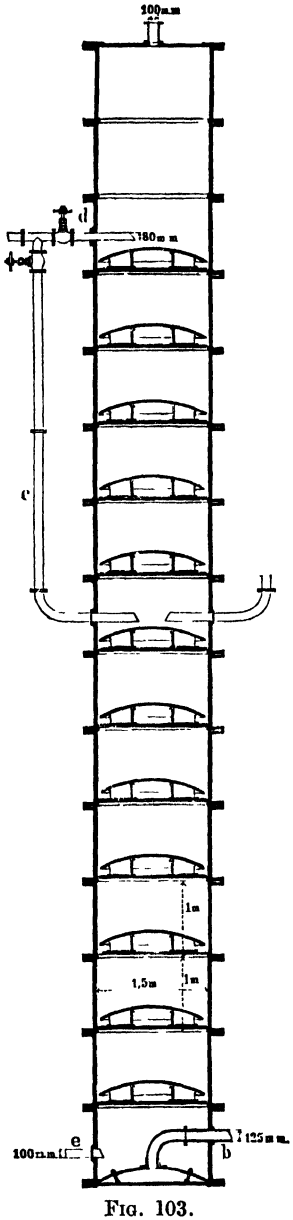


FIG. 103.

The form of carbonating tower introduced by Solvay is shown in Fig. 103, and consists of a large number of superposed cylindrical compartments or drums, one of which is shown on a larger scale in Fig. 104. The bottom of each compartment has a large circular opening in the centre, over which is a perforated sieve having the shape of a spherical segment, which is supported by light stays and does not quite reach the inner wall of the drum. The cooled ammoniacal brine enters some distance below the top of the tower by the pipe *c*, and fills the tower nearly to the top. The carbon dioxide, forced in through *b* under a pressure of 1·5–2·5 atmospheres, is divided by the sieve holes into numerous small streams, which pass through the brine and reunite in the large central opening of the next compartment; this subdivision of the gas is repeated in each compartment. But as the holes in the Solvay tower after about a fortnight's work get plugged up with a scale of sodium bicarbonate, the

process has to be stopped and the towers washed out with boiling water, and then allowed to cool.

To obviate this difficulty other forms of carbonator are used, amongst which may be mentioned that of Honigmann, viz., a set of three cylinders, through which the carbon dioxide is passed in succession at a much lower pressure than that employed by Solvay. When the contents of the first vessel are carbonated, it is discharged, refilled with fresh ammoniacal brine, and replaced in the series, but as the last vessel; the vessels are 10 feet in diameter and 10 feet high only. The utilisation of carbon dioxide is less complete in this apparatus than in the Solvay tower, and the latter is now almost the only form of apparatus used. In

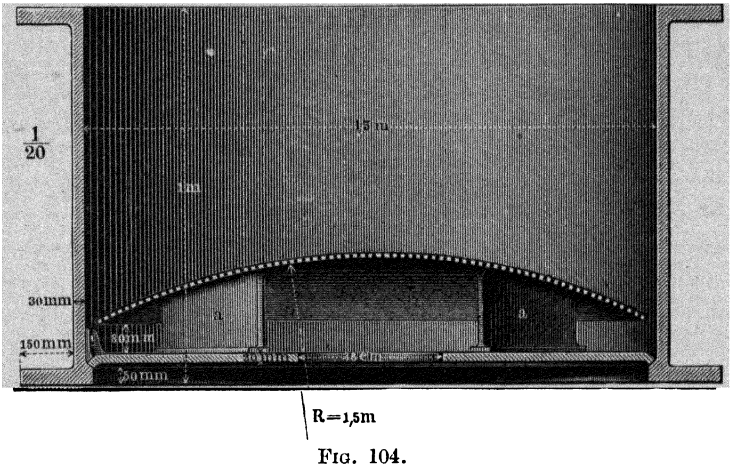


FIG. 104.

France the Boulovard process is used, in which carbonisation is effected in a battery of iron cylinders with horizontal agitators.

The carbon dioxide is obtained partly from the continuous shaft lime-kilns required to prepare the lime subsequently used to recover the ammonia, and in that case contains about 30 per cent. of carbon dioxide, and requires cooling and freeing from accompanying dust and sulphur dioxide; this is effected by making it bubble several times through shallow layers of flowing water. Carbon dioxide is also obtained from the calcination in closed pans of the sodium bicarbonate, and is then much purer than the above (p. 323). The gas is drawn by a powerful pump, and delivered at a pressure of about 45 lb. per square inch for the Solvay towers, or 10 lb. for the Honigmann apparatus, cooled to about 30°.

The absorption of the carbon dioxide to form first normal ammonium carbonate, $(NH_4)_2CO_3$, and then the bicarbonate, $(NH_4)HCO_3$, is accompanied by the evolution of a considerable amount of heat which is removed by a series of horizontal water-cooling tubes (Cogswell tubes) passing through the Solvay tower, or by flowing cooling water over the exterior of the Honigmann carbonators. In no case may the temperature exceed 70°, or the ammonium carbonates begin to decompose; neither may the temperature be lowered too much, because then the sodium bicarbonate comes down so finely divided that it is most difficult to filter and wash, and at 10° ammonium chloride begins to crystallise out. During the reaction the temperature should be kept at 30–40°, but just at the last it may be reduced to 15°, to render the separation of the sodium bicarbonate more complete.

The inert gases escaping from the carbonating apparatus always carry away about 3–4 per cent. of carbon dioxide and about 8 per cent. of the total ammonia originally present in the ammoniacal brine; to recover the latter the gases are passed through a series of scrubbers, some containing brine, others water, and others dilute sulphuric acid. Two towers in series may also be used; the first is worked to the normal ammonium carbonate stage, and the process finished in the second by a stronger current of carbon dioxide.

Every half-hour a portion of the contents of a Solvay tower is drawn off from the bottom of the tower, or at suitable intervals one of the Honigmann carbonators is blown empty by compressed gas. The pasty liquid runs on to rotary vacuum filters, consisting of hollow perforated drums covered with flannel, inside which a reduced pressure is maintained. The drum dips into a trough containing the magma and the flannel retains the crystals of sodium bicarbonate; the latter is washed very carefully with water to remove the ammoniacal mother-liquor as completely as possible, and scraped off continuously by a knife. In washing approximately 10 per cent. of the bicarbonate is lost.

The washed bicarbonate is dried and calcined, by which treatment the small quantity of accompanying ammonium salts is decomposed with liberation of free ammonia, and about three-quarters of the bicarbonate is converted into sodium carbonate, carbon dioxide, and steam. The bicarbonate must be freed as completely as possible from mother-liquor, since the ammonium chloride in the latter forms sodium chloride on

calcination: $2NH_4Cl + Na_2CO_3 = 2NaCl + 2NH_3 + CO_2 + H_2O$. Many different forms of apparatus have been patented for conducting this operation; that known as a Thélen pan is largely used. It consists of a semi-cylindrical cast-iron pan heated externally from below, and provided with a central shaft having an oscillating or rotary motion; to the shaft are fixed arms carrying pivoted shovels, which push the encrusted carbonate off the pan sides and gradually move it from end to end, so that it is discharged of uniform quality. The pan is suitably covered, so that the evolved gases may be sucked away; they are cooled, then passed through a scrubber to recover the ammonia, and are lastly forced by a special pump into the carbonating apparatus; if due care is taken in working the apparatus, the gases may contain 60–80 per cent. of carbon dioxide.

The resulting sodium carbonate may for some purposes be used as it is, but for others it is necessary to heat it more strongly, to decompose all the bicarbonate and to make it less voluminous for packing and shipping. This second heating is done in reverberatory Mactear furnaces fired by coke, and no use is made of the carbon dioxide in the resulting gases. The hot product is cooled on iron plates, and then packed in casks or bags. It usually contains a little sodium chloride (see above).

The mother-liquor from the sodium bicarbonate contains approximately one-third of the original salt unaltered; and in place of the salt actually decomposed it contains the corresponding amount of ammonium chloride, and in addition an excess of ammonium bicarbonate equal to about one-fifth of the ammonium chloride present. The treatment of the mother-liquor consists first in simple heating, which decomposes almost all the ammonium bicarbonate. The resultant gases, carbon dioxide and ammonia, are separated from the bulk of the accompanying steam by the use of a distilling column, and are then both utilised by being absorbed by fresh brine in the ammonia apparatus. To the residual hot liquid containing the sodium and ammonium chlorides a sufficiency of lime is added, and the treatment with steam continued in a column still until the gases evolved, which are cooled to condense part of the moisture and drawn off by an air pump, are practically free from ammonia. The efficient recovery of the ammonia at this stage, and also at the minor stages previously described, is the criterion for the commercial success of the whole manufacture, for the preparation in one operation of one ton of "ammonia

ash," valued at £4, requires the assistance of the ammonia obtained from no less than two and a half tons of ammonium sulphate, valued at £32. The efficiency of the recovery has been constantly improved, until now in well-conducted works it is well over 99 per cent.

The waste liquor from the ammonia stills, with considerable quantities of suspended calcium carbonate and hydroxide, is run into settling tanks to deposit the solids, which are waste, and the clear liquor, containing the undecomposed salt, and calcium chloride corresponding to the decomposed salt, is run into the water-courses also to waste. Schreib proposed to separate ammonium chloride from the bicarbonate mother-liquors by saturation with salt and ammonium carbonate. The ammonium chloride is filtered off and the liquid sent to the carbonators. It is proposed to utilise some such process in connexion with the synthetic production of ammonia by the Haber process. A certain amount of ammonium chloride is made from the mother-liquors by Brunner Mond & Co. by saturation with salt at 0°.

In recent years the ammonia-soda works have not been content to send out their alkali in the form of soda-ash only, for they now convert the same into soda crystals, by solution in warm water and crystallisation by cooling, or into caustic soda, by the ferric oxide process (see p. 332) or by the old method of dissolving in boiling water and agitating with lime. The liquor produced in either of these ways being quite free from sulphides is not so corrosive towards iron, and therefore it is no longer necessary to adhere to the simple forms of evaporators—thick cast iron pans—which are so usual in alkali works. In 1902, an improved form of vacuum evaporator was introduced by Kestner which has been successfully applied very widely to ammonia soda-ash liquors on the Continent, and a little later to Leblanc caustic liquors in this country. The economy in fuel effected by this apparatus is very considerable; the apparatus is termed a climbing film one, because the liquor while undergoing evaporation exists only as a very thin film on the sides of the long vertical heating tubes up which it is driven by the violent rush of the steam evolved from itself. The tubes are enclosed in a steam jacket. The liquor contains 77 per cent. of caustic soda; it is evaporated further in iron pots over a fire until fused caustic soda remains.

Electrolytic Processes.[1]

159 Although the electrolytic decomposition of common salt solution with the production of caustic soda was noticed by Cruickshank in 1800, and although the quantitative relations of such electrolysis were made known by Faraday, who also showed how to convert mechanical into electrical energy, yet it was not until 1872, after Gramme in Belgium had built the first useful dynamo, that electrochemical processes other than the deposition of thin coatings of copper, silver, gold, and nickel became commercially possible. A British patent was granted to Charles Watt in 1851 for the electrolysis of common salt.

The first electrochemical process on a large scale was that of copper refining, started in 1876; this was followed in 1883 by the work of Höpfner in Duisberg on the electrolysis of molten sodium chloride.

In 1885 as the result of work by Breuer at Duisberg on the electrolysis of aqueous solutions of alkali-chlorides an experimental works was erected in Griesheim. The separation of the products of the electrolysis was here effected by a porous diaphragm made from Portland cement mixed with acidified brine; the shape of the diaphragm was that of a box, through the lid of which the carbon anode passed. After the complete setting of the cement, a soaking in water removed the crystallised salt and the lime salts produced by the added acid, and the diaphragm was thus made very porous so as to permit an easy passage of the electric current. In the present type of cell twelve such porous vessels with anodes are placed in an outer iron vessel, serving as a cathode, with an additional iron cathode between evey pair of anodes. The vessels are filled with potassium chloride solution, and the same solid salt is fed into the anode vessel to keep that liquor saturated. The temperature is maintained at about 80° by means of heating pipes in the bath. On passing the electric current, chlorine is evolved at the carbon anodes and thence passes away by suitable pipes, while the potassium is liberated at the cathodes and reacts there with the water to form caustic potash and hydrogen, which may be utilised. When the caustic has increased to 40–80 grams per litre of the cathode liquor, the liquor is removed and evaporated in multiple-effect vacuum evaporators so arranged as to allow of the removal of

[1] Foerster, *Elektrochemie wässeriger Lösungen*, 1915; Askenasy, *Technische Elektrochemie*, 1916; Thompson, *Applied Electrochemistry*, 1911.

the large quantity of undecomposed potassium chloride which separates; the concentrated mother-liquor is then further evaporated in nickel pans to produce the solid alkali. The current efficiency is only 70–80 per cent. The carbons are quickly attacked, and the escaping chlorine contains 8–10 per cent. of carbon dioxide. The porous diaphragms do not completely prevent the cathode liquor from obtaining access to the anode, hence hypochlorites and chlorates are formed in the anode liquor and oxygen is evolved at the anode, so that the escaping chlorine may contain 10 per cent. of electrolytic oxygen.

More resistant anodes are now made of cast magnetite prepared thus: burnt pyrites, from the manufacture of sulphuric acid, is heated in an electric furnace to fusion; the Fe_2O_3 is thus converted into FeO, and therefore, further quantities of Fe_2O_3 are added just before casting into the anode forms, so as to bring the melt to the composition Fe_3O_4. With these anodes a current efficiency of 80 to 84 per cent. is reached.

This Griesheim process, in spite of its many imperfections, is so successful that in 1912, at works in Griesheim, Bitterfeld, Westeregeln, Ludwigshafen, and Rheinfelden in Germany, at Lamotte in France, at Flix in Spain, and at works in South Russia, no less than 33,000 horse power were being employed.

In England there is no native potassium chloride to convert into caustic potash, and the pecuniary inducements to electrolyse sodium chloride were not nearly so great. The first serious attempts were not made till 1888, when at the Snodland Paper Works in Kent the process of Greenwood was tried. In this a diaphragm built up of alternate layers of porcelain rings and asbestos was utilised. The caustic liquid produced contained but 2·2 per cent. of caustic soda and this was accompanied by 10·7 per cent. of sodium chloride.

In 1892 Hargreaves and Bird introduced a novelty in that the cathode, instead of being separate from the diaphragm, is so completely adjacent to it that the two are built up together, and the liquor which percolates from the anode compartment through the diaphragm hangs upon the iron wire gauze forming the cathode by capillary attraction only, and the cathode compartment contains no other liquor. From the cathode the alkali is washed away by passing steam into the cathode compartment. The anodes consist of blocks of carbon, and the chlorine evolved is used in the manufacture of bleaching-powder. Two-thirds of the salt is decomposed. The efficiency of the cell is increased

by bringing into the cathode compartment kiln gases containing carbon dioxide, but the product is thereby changed from caustic soda to sodium carbonate, which is obtained as crystals $Na_2CO_3,10H_2O$. The cell is worked at 85°, the current density being 0·028 amp. per sq. cm., and the voltage 3·6 to 4·5, usually 4 volts. The current efficiency is 92 per cent. The chlorine gas is 97 to 98 per cent. pure and a 10 to 15 per cent. solution of sodium carbonate is obtained. Each cell takes 2000 to 3000 ampères. This process is worked with the Cheshire brine at Middlewich.

In 1905 Townsend[1] introduced at Niagara Falls and at Sault St.-Marie in the United States a cell very similar to that of Hargreaves and Bird with a more complete counterflow movement. The improvement is made by filling with high boiling mineral oil that part of the cathode chamber which in the Hargreaves-Bird cell is full only of steam and waste combustion gases. The hydrostatic heads of the brine and of the oil may be made nearly to balance, and by regulating the outlet level of the brine the percolation of the brine through the diaphragm to the cathode can be controlled and the percentages of caustic and salt in the product kept at any desired figures. The hydrogen bubbles and the alkaline liquor are constantly thrown off from the cathode into the body of the oil; the hydrogen rises to the surface of the oil, whilst the liquor sinks to the bottom and is then drawn off by an inverted syphon. The Townsend cell is used by the Hooker Electrochemical Co. at Niagara Falls. The capacity is 2000 to 2200 amperes. The cell is 2·4 m. long and 0·9 m. high, and 30 cm. thick. The mean voltage is 4·5. The anode current density is 0·13–0·16 amp. per sq. cm., the current efficiency is 95 to 96 per cent. The caustic liquor contains 150–200 grams NaOH and about an equal weight of NaCl per. litre. The chlorine contains only about 2 per cent. of CO_2. Larger cells, with capacities up to 16,500 amps., are in use.[2]

In 1892 Castner in Oldbury, near Birmingham, and Kellner in Vienna began to electrolyse brine in a fundamentally different manner. In all the foregoing and also in all the subsequent processes it is to be noted that great difficulties are encountered in the endeavour to separate completely the products of two reactions:

$$2NaCl = 2Na + Cl_2, \text{ and } 2Na + 2H_2O = 2NaOH + H_2.$$

[1] *J. Soc. Chem. Ind.*, 1907, **26**, 746.

[2] Palmaer, *Elektrolyse von Kochsalzlösungen in Verbindung mit der Zellulose-industrie*, Stuttgart, 1916, p. 42.

In none of the electrolytic processes above-mentioned is this complete separation obtained; by that next described the separation is obtained. In 1807 Davy discovered sodium amalgam; in 1882 and succeeding years proposals were made to use it in the electrolysis of brine. Of these, the processes of Castner and of Kellner in 1892 have proved successful.

The anodes are arranged in the upper part of the brine, and at the bottom of the latter is a moving layer of mercury which forms the cathode. When the electric current is made to pass, chlorine gas is evolved at the anodes and rising through the brine passes out from the apparatus by a suitable pipe. The sodium liberated at the cathode unites there with the mercury to form sodium amalgam, which rapidly diffuses from the surface into the mass of the mercury below. Whilst sodium is acted upon with great rapidity by water, with sodium amalgam the reaction takes place much more slowly, and therefore it is easily possible to remove the sodium amalgam from the apparatus. The sodium amalgam passes into an adjacent cell or compartment which is fed with water and contains also an iron electrode; these three items form the elements of a galvanic battery and as soon as the circuit is closed the water or the dilute caustic soda solution is electrolysed, hydrogen being evolved on the iron electrode and oxygen being evolved on the amalgam, which thus loses its sodium, and the strength of the caustic soda solution is increased. Finally the mercury is returned to the first compartment or cell and the operations are repeated. The two essential reactions are thus absolutely separated, and the caustic soda solution obtained is very much stronger and purer than can be obtained by any of the preceding or succeeding processes. Mercury processes are used at Weston Point and Oldbury in England, at Mannheim, Mülheim, Osternienburg, and Rheinfelden in Germany, at Jemeppe in Belgium, and at Niagara Falls in the United States. The cells at Niagara take 630 amps. at 4·3 volts; the temperature is 40° C. The current densities on the graphite and mercury electrodes are 0·16 and 0·12 amp. per sq. cm., respectively. The current efficiency is 90 per cent. The chlorine is 97 per cent. pure.

In 1898 a modified form of a process originally devised by Richardson and Holland in 1890 was worked out at Aussig in Bohemia with certain modifications. Into the upper part of a bell-shaped vessel is fixed an anode, and also an inlet for a constant small supply of brine; twenty-five of these bells stand in a

large bath that contains the cathodes. The caustic soda solution formed is denser than the surrounding brine, and sinks down into the tank in which the bells are immersed. By very careful attention to the various dimensions, the current density, and above all to the feed of the fresh brine into the upper part of the bell, and the removal of the caustic liquors from the outer cell, this process with its simple apparatus has been made to yield good results. A large portion of the improvement over the original process of Richardson and Holland is attributed to the counterflow movement between the constant brine feed and the electrolytic migration of the hydroxyl ions from the cathode to the anode. In 1913, works in Austria and in Germany were utilising 12,000 horse power.

In 1906 the principle of the counterflow of an electrolyte and the migration of an ion was embodied in a cell designed by Billiter.[1] In this cell (made by Siemens, and hence known as the Billiter-Siemens cell), a horizontal diaphragm of asbestos covered loosely with a mixture of barium sulphate and asbestos wool is supported on an iron gauze which constitutes the cathode. Below this is an empty compartment. The anode consists of graphite plates supported over the diaphragm. Brine is run continuously into the anode chamber, avoiding disturbance of the liquid present which, owing to the migration of the sodium and chlorine ions, separates into three layers. The bottom layer, on, and in, the diaphragm is a dense solution of caustic soda; above this is a neutral brine layer, and at the top a slightly acid layer. The caustic soda solution drains through the diaphragm into the space below, from whence it is removed immediately by a pipe. Hydrogen is evolved from the cathode into this space and passes out by another pipe. In 1917 the process had been installed in sixteen works, using a total of 28,000 horse-power.

Billiter has also designed another cell (known as the Billiter-Leykam cell) using the same principle of the counterflow of an electrolyte and the migration of an ion, in which the diaphragm is dispensed with, the cathode consisting of a grid of iron bars each surrounded by asbestos hose through which the hydrogen travels out of the cell without disturbing the body of the liquid. The liquid, fed in regularly and carefully at the top, flows through the grid, the caustic soda solution produced finding

[1] Billiter, *Die elektrische Alkalichloridgewinnung*, 1913, Vol II; *Zeit. Elektrochem*, 1917, **23**, 327–334.

its way out at the bottom through a pipe. In 1912, at Gratwein, 1000 horse-power was used for this process.

In 1906 the same principle was carried to its limit by Finlay, who adopted the principle for both the anion and the cation. He divided a cell by two diaphragms into three compartments; into the middle or second of these he fed brine, which then passed in two opposite directions through the diaphragms, to the anode in the first compartment, and to the cathode in the third compartment. When making a liquor containing 8 per cent. of caustic soda, the current efficiency is said to be as high as 98 to 99 per cent., but no particulars of the use of the cell are available.

Other types of cell, *e.g.* the Nelson and the Moore cells, have been largely used in America.

In 1912, a total of 70,000 horse power was expended on alkali chloride electrolytic processes.[1]

The following table summarises the main features of commercial cells which have been published:

	Castner.	Griesheim.	Hargreaves-Bird.	Townsend.	Aussig.	Billiter.
Normality NaOH obtained	7·5	1 to 2	15% Na_2CO_3	3·75-5	3·0	3·5-4·5
Cathodic current efficiency	90	82	92	95	90	95
Terminal voltage	4·3	3·6	4·2	4·5	4·0	3·5
K.W.H. per kg NaOH ..	3·2	2·9	—	3·2	3·0	2·5

Commercial Forms of Alkali.

160 *Soda Crystals.*—For household use, there is a considerable demand for the soda in the crystalline form containing 10 molecules of water. This is prepared by the direct Leblanc method (p. 312), or by dissolving calcined soda-ash in hot water, allowing the impurities to settle, and then running the clear liquor into crystallising tanks (p. 313).

Crystal Carbonate.—The monohydrated carbonate, Na_2CO_3,H_2O,

[1] Foerster, *Elektrochemie;* Allmand, *Applied Electrochemistry;* Ullman, *Enzyklopädie der technischen Chemie,* Vol. 3; details of apparatus and patents in the several volumes of *Monographien über angewandte Elektrochemie,* Vol. 41. The electrolytic decomposition of alkali chlorides with solid metal cathodes, by Billiter (1912); Vol. 23:—The same with liquid metallic cathodes, by Lucion (1906); Vols. 24, 29, 32 and 33:—The electro-chemical patents of Germany (1906), of England (1908), and of America (1910), by Ferchand; Vol. 12:—The electro-chemical industries of Germany, by Ferchand (1904); and Vol. 28:—The electro-chemical and electro-metallurgical industries of Great Britain by Korshaw (1907).

known as "crystal carbonate," has the advantage over soda crystals that it contains a larger percentage of alkali, and dissolves much more readily in water, and that with a slight evolution of heat.

Sodium Bicarbonate, $NaHCO_3$, is used in medicine, and for preparing aerated waters, and for baking powders. It was formerly manufactured on a large scale by exposing soda crystals enclosed in large chambers to carbon dioxide generated by the action on limestone of the dilute and otherwise waste hydrochloric acid obtained in the Leblanc soda process. The gas was slowly absorbed by the crystals, which lost their transparency, and then their water of crystallisation :

$$Na_2CO_3,10H_2O + CO_2 = 2NaHCO_3 + 9H_2O.$$

The large quantity of water liberated dissolved and washed away the greater part of the impurities present in the soda crystals, and when the flow of liquor ceased the reaction was complete; the wet bicarbonate was dried at a very gentle heat.

In 1882 Carey, Gaskell, and Hurter introduced a cheaper method of manufacture by treating crystal carbonate, Na_2CO_3,H_2O, with pure carbon dioxide in a revolving cylinder, and so obtaining a bicarbonate of greater purity, corresponding to the greater purity of the raw material. A still cheaper process is now used, the bicarbonate produced as first product in the ammonia-soda process being purified from the accompanying ammonium chloride by recrystallisation from warm water (Mond, 1884), or by heating in an atmosphere of carbon dioxide to drive off the ammonia. Usually, the crude salt is boiled with water, the escaping ammonia being recovered, and the solution recarbonated.

Sodium Sesquicarbonate.—This form of alkali was first manufactured in 1886 by Watts and Richards. The salt has the composition $Na_2CO_3,NaHCO_3,2H_2O$, and is obtained by mixing the ingredients in aqueous solution and allowing them to crystallise above 35°. The salt is permanent in the air, is readily soluble in water, and finds application in wool washing.

Caustic Soda.—The methods employed by the Leblanc Alkali Works for the manufacture of caustic soda have already been described. The ammonia-soda works also manufacture caustic soda, and the quality obtained is better; it tests 77 per cent. alkali (Na_2O).

Another method of converting sodium carbonate into caustic

soda was introduced by Löwig in 1882. The carbonate mixed with ferric oxide is heated in a revolving furnace to bright redness, when carbon dioxide is evolved, and a compound of Na_2O and Fe_2O_3 is formed, called sodium ferrite; this is cooled, crushed, and decomposed by treatment with a small quantity of nearly boiling water, when the ferric oxide is regenerated ready for the next operation, and a very strong solution, viz., about 30 per cent. of caustic soda, is formed.

The Castner electrolytic process produces a strong solution of caustic soda directly as already described, and by evaporation and fusion it yields at once caustic soda of the highest purity attainable.

Caustic soda, besides being manufactured in the solid form of various grades of purity so as to test 60, 70, 74, 76, 78 per cent. alkali (Na_2O), is also made in the form of a strong solution of 1·45 specific gravity, containing 41 per cent. of caustic soda.

Caustic soda is used for making hard soap, for disintegrating vegetable materials to obtain the fibre for paper-making, for bleaching cotton, for extracting creosote oils, purifying paraffin oils, manufacturing oxalic acid, alizarin, and sodium, and for many other purposes.

POTASSIUM. K = 39·10. At. No. 19.

161 The discovery of this metal is described as follows by Davy.[1] "A small piece of pure potash which had been exposed for a few seconds to the atmosphere, so as to give conducting power to the surface, was placed upon an insulated disc of platina, connected with the negative side of the battery of the power of 250 of 6 and 4, in a state of intense activity; and a platina wire, communicating with the positive side, was brought in contact with the upper surface of the alkali. The whole apparatus was in the open atmosphere.

"Under these circumstances a vivid action was soon observed to take place. The potash began to fuse at both its points of electrisation. There was a violent effervescence at the upper surface; at the lower, or negative surface, there was no liberation of elastic fluid, but small globules having a high metallic lustre, and being precisely similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright

[1] *Phil. Trans.*, 1808, **98**, 4.

flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered by a white film which formed on their surfaces. These globules numerous experiments soon showed to be the substance I was in search of, and a peculiar inflammable principle the basis of potash. I found that the platina was in no way connected with the result, except as the medium for exhibiting the electrical powers of decomposition, and a substance of the same kind was produced when pieces of copper, silver, gold, plumbago, or even charcoal were employed for completing the circuit.

"The phenomenon was independent of the presence of air, I found that it took place when the alkali was in the vacuum of an exhausted receiver."

To this metal Davy gave the name of potassium. Soon after Davy's discovery, Gay-Lussac and Thénard[1] showed that the metal might be obtained in greater quantity by decomposing potash by means of metallic iron at a white heat. For this purpose iron turnings or wire were heated to whiteness in a gun-barrel covered with clay, and melted potash was allowed to pass slowly over the ignited iron. The iron took up the oxygen of the hydroxide, whilst potassium and hydrogen were set free. The potassium passed over in the state of vapour, and was condensed in a copper vessel containing naphtha. A better method was suggested by Curadau,[2] consisting in the decomposition of the potash by means of charcoal at a white heat.

Davy's discovery of the compound nature of the alkalis attracted universal attention, and chemists throughout Europe were occupied with a repetition of his experiments and an examination of the remarkable properties of the singular metals which can thus be obtained. So singular indeed were these properties that many chemists denied to these substances the name of metal, and by some they were considered to be compounds of hydrogen, this view being apparently borne out by the evolution of hydrogen when these metals were thrown into water. But further examination of these substances proved them to be of a truly metallic nature.

Sources of Potassium.—Potassium is found in nature, in a state of combination, widely distributed. It occurs as a constituent of many silicates, forming from 1·7 to 3·1 per cent. of the granite composing the earth's solid crust. Amongst the silicates which contain potash as an essential constituent may

[1] *Ann. Chim.*, 1808, **65**, 325. [2] *Ibid.*, 1808, **66**, 97.

be mentioned potash felspar or orthoclase, leucite, and analcite. Pure chloride of potassium or *sylvine*, KCl, is found in considerable deposits, together with *carnallite*, $KCl,MgCl_2,6H_2O$, in the neighbourhood of Stassfurt in Germany; it is found also in considerable quantities in Searles Lake, California. This same salt and other potash compounds occur in small quantity in the water of the ocean, and in that of many lakes such as the Dead Sea, as well as in mineral waters and in ordinary spring water. Chloride of potassium is found also in cubic crystals surrounding the fumeroles of Vesuvius. All fruitful soil contains potassium compounds, derived from the gradual disintegration of the above-mentioned silicates. These are taken up by the rootlets of the plant, as no vegetable growth can flourish without this substance. It has been shown by Way that soil possesses the power of absorbing potash salts, whilst soda salts pass through it unabsorbed. The form in which the potash is contained in most soils is that of a salt of an organic acid, and this becomes converted into carbonate by ignition.

The potash which sheep draw from the land is excreted in large quantities from the skin in the sweat, termed by the French *suint*. No less than one-third of the weight of raw merino wool consists of this material.

During the war of 1914–1918, when Continental supplies of potash were cut off from this country, considerable quantities of potash were recovered from the waste gases of Portland cement kilns and of iron blast furnaces. In the latter case, it was found that additions of common salt to the furnace charges displaced the potash present, which was recovered in the flue dust and from the gases.

162 *Preparation of Metallic Potassium.*—The method first proposed by Curadau, and brought into a practical form by Brunner, was much improved by Wöhler, and especially by Donny and Mareska.[1] This process depends upon the fact that at a white heat carbon reduces potassium carbonate, as follows:

$$K_2CO_3 + 2C = 2K + 3CO.$$

An intimate mixture of charcoal and potassium carbonate is obtained by igniting crude tartar (acid potassium tartrate) in a covered iron crucible; the porous mass is rapidly cooled by dipping the crucible into cold water, and the charred mass introduced into an iron bottle. It has been usual to place the

[1] *Ann. Chim. Phys.*, 1852, [3], **35**, 147.

mixture in a wrought-iron mercury bottle, connected with a copper receiver by a short iron tube.

In the preparation of the metal potassium, according to Brunner's original method, serious explosions sometimes occurred, owing to the fact that at a very high temperature the metallic potassium unites with the carbon monoxide generated at the same time to form a black compound, $K_6C_6O_6$, which is excessively explosive. The formation of this compound may be prevented and danger of explosion avoided if the potassium vapour is rapidly cooled by using a form of condenser, first suggested by Mareska and Donny. It consists (Fig. 105) of two pieces

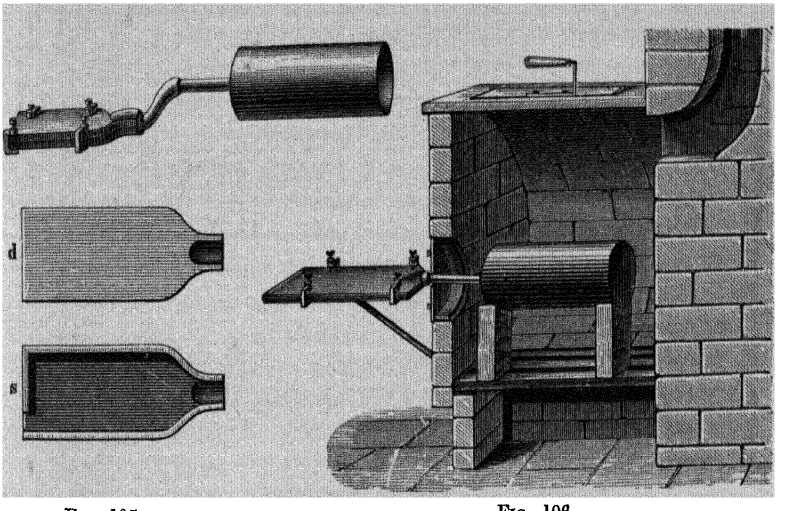


FIG. 105. FIG. 106.

of cast iron, *d s*, which can be clamped together so as to form a shallow box about a quarter of an inch deep, ten to twelve inches long, and four to five inches in width. The socket at the one end fits on to the short tube placed in the neck of the bottle, or at the closed end of the retort, whilst the open end permits a free passage to the gases or vapours given off in the reaction. It is necessary to prevent the oxidation of the iron of the retort by covering it with a coating of fire-clay. As soon as a white heat is reached the vapour of the metal begins to appear at the open end of the tube. The receiver is then adjusted to the end of the tube as shown in Fig. 106, and the metal begins to condense and drops out in the liquid state into a vessel filled with rock-oil placed beneath the receiver, which does not require

to be artificially cooled. Should any deposit or obstruction occur in the tube, this must at once be removed by a red-hot rod thrust into it. It is found in practice that about half the theoretical quantity of metal is obtained.

A process has been described in which caustic potash and metallic sodium, in exactly equivalent proportions, are heated together at 670°, air being excluded. Hydrogen is formed and potassium volatilises, and may be condensed.[1]

Potassium can be prepared on the small scale by the electrolysis of potassium cyanide. This salt is melted and then allowed to cool, so that a solid crust is formed; a current from three or four accumulators is then allowed to pass through the molten salt using electrodes made of gas carbon.[2]

A better method of obtaining potassium on the small scale by electrolysis is that proposed by Matthiessen.[3] For this purpose a mixture of potassium chloride and calcium chloride in molecular proportions, which melts at a much lower temperature than potassium chloride alone, is fused in a small porcelain crucible over a lamp, two carbon poles connected with six to eight Bunsen's elements being dipped into the fused salt. The flame of the lamp is then so adjusted that the portion of salt around the negative pole becomes solid, whilst around the positive pole the mixture is liquid, thus allowing the free escape of the chlorine. After the current has passed through for about twenty minutes in this way the crucible is allowed to cool, and opened under rock-oil, when a considerable quantity of pure potassium is found around the negative pole, no calcium being deposited.

A modification of the Castner process for the manufacture of sodium (p. 255) can be employed. On electrolysing fused potassium hydroxide the metal spreads throughout the electrolyte as a mist and becomes oxidised at the anode. If, however, the cathode is protected by a closed inverted cylinder of magnesite, the metal can be readily collected and when prepared by this method is particularly pure.[4] There is at present no great demand for metallic potassium; the cheaper sodium is equally applicable for almost all purposes, and, moreover, 23 parts of sodium are equivalent to 39 parts of potassium.

[1] Wickel and Loebel, D.R.-P., 307175.
[2] Linnemann, *J. pr. Chem.*, 1858, **73**, 413.
[3] *Journ. Chem. Soc.*, 1856, 30.
[4] Lorenz and Clark, *Zeit. Elektrochem.*, 1903, **9**, 269.

Chemically pure potassium is obtained by distilling pure potassium chloride with metallic calcium in a vacuum.[1]

163 *Properties.*—Potassium is a silvery-white, lustrous metal with a bluish tinge, having a density of 0·859 at 0°,[1] and it is therefore lighter than all other metals, with the single exception of lithium. It is brittle at 0° and possesses a crystalline fracture; at 15° it becomes soft like wax, and may be easily cut with a knife, and the two clean surfaces of the metal may be welded together like red-hot iron. It melts at 62·04°,[2] forming a liquid closely resembling mercury in its appearance. Potassium may be easily obtained in the crystalline form. For this purpose some of the metal is melted in a glass tube filled with coal-gas; as soon as the mass begins to solidify the tube is quickly turned round and the portion of metal still remaining liquid is poured off from the crystals; these form tetragonal octahedra having a greenish-blue colour.[3] Ordinary potassium is a metastable mixture of two modifications having a transition temperature at 59·6°.[4] It has been obtained in the form of a bluish-violet colloidal solution in ether by the electrical method (p. 82).[5]

Potassium boils at 757·5°,[6] 762·2°[7] and emits a beautiful green-coloured vapour exhibiting a characteristic channelled-space absorption spectrum (Roscoe and Schuster). The ratio of the specific heats of the vapour at constant pressure and constant volume is 1·64 at 700–1000°: hence the vapour is monatomic.[8] The green colour of potassium vapour can be readily shown by evaporating a small portion of the metal contained in a wide glass tube 30 cm. in length through which a current of dry hydrogen gas is passed. On heating the metal, the tube becomes filled with splendid green-coloured vapour, condensing on the cooler parts of the tube in the form of a bright metallic mirror. When the hydrogen which issues from the end of the tube is lighted, the flame is tinged with the violet colour characteristic of potassium. Next to cæsium and rubidium, potassium is the most electro-positive metal, and it is a good conductor of

[1] Hackspill, *Ann. Chim. Phys.*, 1913, [8], **28**, 613.
[2] Bernini and Cantoni, *Nuovo Cim.*, 1914, [6], **8**, ii, 241.
[3] Long, *Journ. Chem. Soc.*, 1861, **13**, 122.
[4] Cohen and Wolff, *Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 926.
[5] Svedberg, *Ber.*, 1905, **38**, 3616.
[6] Ruff and Johannsen, *Ber.*, 1905, **38**, 3601; compare Perman, *Journ. Chem. Soc.*, 1889, **55**, 326.
[7] Heycock and Lamplough, *Proc. Chem. Soc.*, 1912, **28**, 3.
[8] Robitzsch, *Ann. Physik*, 1912, [4], **38**, 1027.

electricity. In perfectly dry and pure air it does not undergo any change, but in ordinary air the clean surface of the metal soon becomes converted into caustic potash and potassium carbonate. The oxidation of a newly-cut surface of potassium in the dark is attended with luminosity (Baumhauer). Oxidation takes place so quickly when the metal is exposed to the air in thin layers that sometimes ignition occurs and the metal burns with its characteristic violet flame. When heated in the air to its point of volatilisation, it at once bursts into flame, but if the burning metal is plunged into perfectly dry air or oxygen the flame is immediately extinguished.

When thrown upon water, potassium decomposes the water with great vigour, sufficient heat being generated to ignite the evolved hydrogen which burns with the violet potassium flame. The molten globule swims about, being separated by a layer of steam from the surface of the water, and becomes gradually smaller, leaving at last a globule of fused potash, which causes an explosive burst as soon as its temperature sinks low enough to allow it to come actually in contact with the water.

Potassium acts as a powerful reducing agent, and hence it has been employed for the preparation of such substances as boron and silicon from their oxides, and magnesium, aluminium, and other metals from their chlorides. Potassium also decomposes nearly all gases which contain oxygen, and hence it is used in some cases to ascertain the composition of gases.

Sodium forms with potassium an alloy which is liquid at the ordinary temperature, and looks like mercury. The eutectic point lies at $-12{\cdot}6°$ and 66·6 atomic percentage of potassium. One compound only is formed, Na_2K, which decomposes at $+ 6{\cdot}9°$ into sodium and liquid, and is only reformed therefrom after some days at 0°.[1] The alloy is obtained, not only by melting the two metals together under rock-oil, but also by adding sodium to fused acetate of potassium, when gases are rapidly evolved and the alloy formed (Wanklyn). It is also formed when caustic potash is heated with sodium, and burns in the air, forming a mixture of the peroxides of sodium and potassium; this is used under the name of "pneumatogen" for the regeneration of expired air in life-saving apparatus.[2]

The electrical conductivity of potassium is little greater than

[1] Van Bleiswyk, *Zeit. anorg. Chem.*, 1912, **74**, 152.

[2] For other alloys of potassium, consult Smith, *Zeit. anorg. Chem.*, 1907, **56**, 109.

half that of sodium and exhibits a similar sharp increase at the melting point: the conductivity of the liquid alloy of both metals is less than one-fourth that of potassium itself.[1]

COMPOUNDS OF POTASSIUM.

Potassium and Oxygen.

164 Potassium forms two well-defined oxides only, namely, potassium monoxide, K_2O, and potassium peroxide, K_2O_4. The first of these corresponds to the stable monovalent potassium salts, and combines with water to form the hydroxide. The higher oxide does not yield corresponding salts, but behaves as a peroxide. In addition to these, oxides of the formulæ K_4O, K_8O_5, K_6O_4, K_4O_3, and K_2O_2 have been described, but their existence is doubtful.

Potassium Monoxide, K_2O.—When the mixture of oxides obtained by burning potassium in slightly moist air is strongly heated, it loses oxygen and leaves a residue of the monoxide, which may also be prepared by heating caustic potash with potassium:

$$2KOH + 2K = 2K_2O + H_2.$$

It is usually prepared by melting potassium and, without further application of heat, leading the requisite volume of pure and almost dry air over it.[2] According to Holt and Sims,[3] the product always contains metallic potassium, but it has been prepared pure by Rengade by distilling off the metal in a vacuum.[4]

The pure oxide is white at ordinary temperatures, but clear yellow at 200°. It decomposes at 400° into the dioxide and metal. It reacts violently with water to form the hydroxide.

165 *Potassium Hydroxide, or Caustic Potash*, KOH.—This compound, generally known by its old name of caustic potash, was considered to be an oxide of potassium, but Darcet,[5] in the beginning of 1808, showed that ignited caustic alkali contains some other ingredient in addition to oxygen and the metal. He believed that this ingredient was in all probability water, inasmuch as the calculated quantity of alkali contained in the carbonate neutralised more acid than the same quantity of the ignited

[1] Northrup, *Trans. Amer. Electrochem. Soc.*, 1911, **20**, 185.
[2] Kühnemann, *Chem. Centr.*, 1863, 491. [3] *Journ. Chem. Soc.*, 1894, **65**, 438.
[4] *Compt. rend.*, 1907, **144**, 753. [5] *Ann. Chim.*, 1808, **68**, 175.

caustic alkali. From this time forward caustic potash was considered to be a compound of potassium oxide and water, and it was not until a much later period that it was recognised to be a *hydroxide*, or a compound which is derived from water by the replacement of a portion of the hydrogen by a metal.

In order to obtain caustic potash, the metal may be allowed to act on water, but it is generally prepared by decomposing a dilute solution of potassium carbonate with slaked lime. For this purpose one part by weight of potassium carbonate is dissolved in twelve parts of water, the solution placed in an iron or silver vessel provided with a lid, heated to the boiling point, and then milk of lime gradually added until a portion of the filtered liquid evolves no carbon dioxide when treated with an acid. The solution is allowed to settle, and the clear liquid drawn off into a well-stoppered vessel. This is then evaporated in a silver basin until the hydroxide begins to volatilise. In order to ensure the complete separation of the carbonic acid from the potash, not less water than that mentioned must be used, and the water which evaporates from time to time must be renewed, for when only four parts of water are present to one part of potassium carbonate no decomposition takes place. A concentrated solution of caustic potash is found to decompose carbonate of calcium (Liebig [1]). A certain amount of the caustic potash of commerce is prepared in this way. It is usually cast in the form of sticks which contain more or less water as well as all the impurities of the original potassium carbonate, especially alumina, potassium chloride, potassium sulphate, and potassium silicate. It may be purified by dissolving in alcohol in the manner already described for caustic soda (p. 260).

A large amount of caustic potash is now made in Germany by the electrolysis of solutions of potassium chloride, the process being similar to that employed for the production of caustic soda from salt (p. 325).

Pure caustic potash may also be obtained by adding powdered potassium sulphate to a hot concentrated solution of barium hydroxide (baryta water) until a small quantity of sulphate of potassium remains in excess; this is then removed by a careful addition of baryta water. The clear solution poured off from the barium sulphate is evaporated in a silver basin, any baryta which remains in solution being deposited as carbonate by combination with the carbonic acid of the air.[2]

[1] See also Bodländer and Lucas, *Zeit. angew. Chem.*, 1905, **18**, 1137.

[2] Schubert, *J. pr. Chem.*, 1842, **26**, 117.

Attempts have been made to manufacture potash from the sulphate by the action of lime, but hitherto without success.[1]

Wöhler's process for obtaining pure caustic potash is to decompose pure potassium nitrate by metallic copper at a red heat.[2]

Properties.—Pure caustic potash is a hard, white, brittle substance, often exhibiting a fibrous structure, melting below a red heat to a clear oily liquid, and volatilising in the form of white vapours when more strongly ignited. The vapour of this substance decomposes, at a white heat, into potassium, hydrogen, and oxygen, and this decomposition explains, according to Deville, the formation of potassium by Gay-Lussac's method.

Caustic potash rapidly absorbs carbonic acid and moisture from the air, and dissolves in water with evolution of heat. According to Ferchland, one part of water dissolves 1·07 parts of caustic potash at 15°.[3] When the concentrated aqueous solution is cooled, the hydrate, $KOH,2H_2O$, crystallises in transparent, colourless, acute rhombohedra which melt at 35·5°. Crystalline hydrates, $2KOH,9H_2O$ and $2KOH,5H_2O$, have also been described,[4] and Pickering [5] has obtained evidence of the existence of KOH,H_2O, melting at 143°, and of $KOH,4H_2O$, melting at −32·7°. According to a German Patent, when solutions containing over 85 per cent. of hydroxide are cooled, anhydrous KOH crystallises out.[6]

The aqueous solution of caustic potash, sometimes known as *potash lye*, possesses an acrid taste and a peculiar nauseous odour: it acts as a powerful cautery, quickly destroying both animal and vegetable substances. For this reason its solution cannot be filtered except through glass or sand, and it is best clarified by subsidence. The following table gives the specific gravity at 15°/4° of solutions of potash of varying strength according to the experiments of Pickering.[7]

Per cent of KOH.	Specific gravity.	Per cent of KOH.	Specific gravity.
1 . . .	1·0083	30 . . .	1·2905
5 . . .	1·0452	35 . . .	1·3440
10 . . .	1·0918	40 . . .	1·3991
15 . .	1·1396	45 . . .	1·4558
20 . . .	1·1884	50 . . .	1·5143.
25 . . .	1·2387		

[1] Harold, *Zeit. Elektrochem.*, 1905, **11**, 417.
[2] *Annalen*, 1853, **87**, 373.
[3] *Zeit. anorg. Chem.*, 1902, **30**, 130.
[4] Gottig, *Ber.*, 1887, **20**, 1094.
[5] *Journ. Chem. Soc.*, 1893, **63**, 898.
[6] D.R.P., 189835 (1906).
[7] *Phil. Mag.*, 1894 [5], **37**, 359.

The solution saturated at 15° has the sp. gr. 1·5355 and the concentration of 51·7 per cent. Caustic potash also readily dissolves in alcohol.

The *liquor potassæ* of the Pharmacopœia contains about 5 per cent. of the hydroxide KOH, and has a specific gravity of 1·058. Caustic potash is largely used in the form of a lye for absorbing carbon dioxide in both organic and inorganic analysis. It absorbs moisture very rapidly from the air, and may therefore be employed for drying certain gases and liquids, especially organic substances which do not dissolve it and are not acted upon by it. The chief commercial use, however, of caustic potash is for the manufacture of soft soap. The soap-maker formerly prepared his lye by lixiviation of wood-ashes, the solution thus obtained being causticised by boiling with milk of lime. At the present day the commercial carbonate is employed for this purpose, or caustic potash is bought ready for use.

Potassium Peroxide, K_2O_4.—This oxide was discovered by Gay-Lussac and Thénard. It is best obtained by heating potassium in excess of slightly moist air or oxygen. The metal takes fire at a temperature of from 60° to 80°, and when the surface is kept clean, burns to peroxide. In order to obtain the oxide in the pure state, clean potassium must be moderately heated, first in a current of dry air, and then in dry oxygen. If the metal is at once exposed to oxygen, great heat is evolved and the glass is attacked. According to Vernon Harcourt,[1] it is best to bring clean dry potassium into a flask containing dry nitrogen, in which it is melted. The nitrogen gas is then gradually displaced by air; the grey film which covers the molten metal is seen to change to a deep blue; then a point is reached at which the rapid absorption of oxygen begins. Gradually, as the oxidation proceeds, the metallic coating of the inner surface of the bulb changes to a dead white; this, however, after a while assumes a yellow colour, due to the formation of the tetroxide. By the action of ozone on dry caustic potash an orange-yellow substance is formed, which is possibly identical with potassium peroxide.[2]

Potassium tetroxide is a dark chrome-yellow coloured powder, which fuses at a higher temperature than caustic potash, forming a black liquid, which, when the temperature falls, solidifies in lustrous tabular crystals; at a white heat, or when kept at a

[1] *Journ. Chem. Soc.*, 1862, **14**, 267.

[2] Baeyer and Villiger, *Ber.*, 1902, **35**, 3038.

red heat for some time, it is decomposed into potassium monoxide and oxygen. When exposed to moist air it loses oxygen, forming possibly potassium dioxide : [1]

$$K_2O_4 = K_2O_2 + O_2.$$

Thrown on to water it dissolves with considerable evolution of heat, forming caustic potash, hydrogen peroxide, and free oxygen. Carbon monoxide acts upon the peroxide at a temperature somewhat below 100° with the formation of potassium carbonate, a volume of oxygen equal to that of the carbon monoxide employed being liberated thus :

$$K_2O_4 + CO = K_2CO_3 + O_2.$$

The heated oxide is also decomposed by carbon dioxide with liberation of oxygen, and by hydrogen.[2]

Phosphorus and sulphur act violently upon the peroxide with formation of potassium phosphate and sulphate. When metals such as potassium, arsenic, antimony, and zinc are heated with this compound, they are oxidised with evolution of light and heat, whilst several metals such as bismuth, lead, iron, and silver undergo oxidation without the phenomenon of incandescence.

Potassium and Hydrogen.

166 *Potassium Hydride*, KH.—Potassium, when heated to 360° in hydrogen, yields the hydride KH, which crystallises in slender, white needles, and closely resembles the sodium compound (p. 264) in its properties.[3] It ignites spontaneously in fluorine, chlorine, or oxygen. When treated with moist carbon dioxide at the ordinary temperature, it is converted into potassium formate : [4]

$$KH + CO_2 = KHCO_2.$$

The absorption of hydrogen by potassium was previously observed by Gay-Lussac and Thénard, and by Troost and Hautefeuille,[5] who, however, did not obtain the crystalline hydride.

[1] Holt and Sims, *Journ. Chem. Soc.*, 1894, **65**, 437.
[2] *Ber.*, 1897, **30**, 2515.
[3] Moissan, *Compt. rend.*, 1902, **134**, 18.
[4] *Ibid.*, 1902, **134**, 261.
[5] *Ann. Chim. Phys.*, 1874 [5], **2**, 273.

Potassium and the Halogens.

167 *Potassium Fluoride*, KF.—This is formed when aqueous hydrofluoric acid is neutralised in a platinum vessel with caustic potash or potassium carbonate, and the solution evaporated down. This salt crystallises from solutions above 40° in anhydrous cubes, below that temperature in prisms of the hydrate, $KF,2H_2O$. The saturated solution of this hydrate at 18° contains 48 per cent. of the anhydrous salt.[1] It is very deliquescent, has a sharp saline taste, and melts at 885°.[2] When it is dissolved in aqueous hydrofluoric acid it forms an acid fluoride, KF,HF, crystallising in tetragonal tablets. These melt when heated, and at a dark red heat decompose into potassium fluoride and hydrofluoric acid, this decomposition being employed for the preparation of anhydrous hydrofluoric acid. Crystalline compounds, KF,2HF and KF,3HF, have also been obtained by Moissan.[3] Potassium fluoride forms a large number of double salts.

Potassium Chloride, KCl, is a substance closely resembling rock-salt. Indeed in earlier times no distinction was drawn between these two compounds, but it was later known as *sal digestivum Sylvii* or *digestive salt*. It occurs in sea-water as well as in that of many mineral springs, and forms the chief portion of the Stassfurt potash-salt. This salt exists in a bed 20 to 30 metres in thickness, lying above the deposit of rock-salt, and consisting chiefly of polyhalite, $2CaSO_4,MgSO_4,K_2SO_4,2H_2O$; carnallite, $KCl,MgCl_2,6H_2O$; and kieserite, $MgSO_4,H_2O$, interspersed with layers or veins of tachydrite, $CaCl_2,2MgCl_2,12H_2O$; boracite, $2Mg_3B_8O_{15},MgCl_2$; kainite, $K_2SO_4,MgSO_4,MgCl_2,6H_2O$, and sylvine, KCl. These last two appear to be formed by the action of water upon the preceding compounds. In these minerals a small quantity of the potassium chloride is replaced by potassium bromide, and crystals of anhydrite, $CaSO_4$, are found in the kieserite beds. The minerals composing this bed are all of them very deliquescent, and their position leads to the inference that the saline deposits at Stassfurt have been formed by the gradual evaporation of an inland sea- or salt-water lake. This is rendered more probable by the fact that in the manufacture of sea-salt in the so-called salterns on the Mediterranean

[1] Mylius and Funk, *Ber.*, 1897, **30**, 1716.
[2] Ruff and Plato, *Ber.*, 1903, **36**, 2357.
[3] *Compt. rend.*, 1888, **106**, 547.

coasts similar salts are deposited from the mother-liquors. A very elaborate investigation into the conditions of formation of these minerals has been made by van't Hoff.[1] In addition to the deposits at Stassfurt, similar beds have been found at Kulusz, in the East Carpathians. These potash salts do not occur in the majority of saliferous beds, and this is probably due to the fact that the upper saline strata have in most cases been washed away, whereas in the Stassfurt deposit they have been protected by a water-tight stratum of clay.[2] The mode of manufacture of potassium chloride from these potash salts is almost identical with that proposed by Balard [3] and Merle [4] for the preparation of the chloride from sea-water, and by Hermann [5] for preparing it from certain mineral springs.

The method depends on the fact that carnallite is easily soluble in a hot solution of magnesium chloride, whereas sodium chloride and magnesium sulphate are only slightly soluble in this liquid, and that when the hot liquor is allowed to cool the double salt does not separate out, but the more soluble magnesium chloride remains in solution whilst a part of the chloride of potassium crystallises out. The crude carnallite is crushed and treated with a mixture of the mother-liquors resulting from later processes of the manufacture, and steam is passed in. After separation of the suspended insoluble matter and the sodium chloride and kieserite, the liquor is run into crystallising vessels and allowed to cool gradually, a large proportion of crude potassium chloride separating out. The mother-liquor is then concentrated, and on cooling yields a further deposit of the crude chloride. The crude potassium chloride is purified by washing first with washing liquor from a former operation, and finally with water, the impurities removed being sodium chloride and magnesium chloride and sulphate. The quantity of potassium chloride in the various commercial products is from 75 to 98 per cent.[6]

In the salines on the west and south coasts of France the mother-liquors remaining after the common salt has been deposited, having a specific gravity of 1·22, are preserved in reservoirs during the summer, when a mixture of magnesium

[1] *Zur Bildung der ozeanischen Salzablagerungen* (Braunschweig, 1905).
[2] For a full account of these deposits, see Thorpe's *Dict. of Appl. Chem.*
[3] *Jahresb. Chem. Technol.*, 1865, 296.
[4] *Bull. Soc. Chim.*, 1868, [2], **10**, 63.
[5] *J. pr. Chem.*, 1853, **60**, 284.
[6] See *Ber. über Entwickl. Chem. Industrie*, **1**, 351.

sulphate and common salt (*sel mixte*) separates out. The mother-liquor from this is evaporated in flat pans and thus converted into carnallite, which is worked up as described.

Potassium chloride crystallises, like sodium chloride, in cubes. It has a cooling saline taste and a specific gravity of 1·995 : it melts at 790° (Ruff and Plato), and readily volatilises at a bright red heat. One hundred parts of water dissolve 28 parts of potassium chloride at 0°, 32·7 parts at 15°, and 56·5 parts at 100°.

When potassium chloride is melted in a current of hydrogen gas, or when the fused salt is subjected to electrolysis, a dark blue mass is formed.

Potassium chloride is used for the preparation of other potassium compounds such as the chlorate, the carbonate, the chromate, the hydroxide, the nitrate, and potash alum, but by far the greatest quantity is used for the preparation of artificial manures, for which purpose the crude salt is employed.

Potassium Bromide, KBr.—When bromine is dissolved in caustic potash a mixture of bromide and bromate of potassium is formed. If this mixture be evaporated and gently ignited. the bromate is decomposed, and pure potassium bromide is left, The usual method of preparing the salt on the large scale is by the action of bromine and water on iron filings; the iron bromide formed is then decomposed by potassium carbonate.

Potassium bromide crystallises in cubes possessing a sharp saline taste, melts at 750°, and volatilises at a high temperature; 100 parts of water at 15° dissolve 62 parts of the salt. It serves as a valuable medicine, especially in cases of nervous diseases. It unites with bromine,[1] forming a very unstable tribromide, KBr_3.

Potassium Iodide, KI.—This salt is prepared in a similar way to the bromide. It crystallises, like the two former salts, in cubes, which possess a sharp taste. Potassium iodide melts at 685° (Meyer, Riddle, and Lamb), 705° (Ruff and Plato), and can be easily vaporised at a higher temperature, the vapour having a normal density. One hundred parts of water dissolve at 0°. 127·9, and at 118·4°, the boiling point of the saturated solution, 222·6 parts of the salt, whilst at intermediate temperatures the solubility increases proportionally to the rise of temperature (Mulder). Potassium iodide is sparingly soluble in absolute alcohol, and is soluble also in acetone and glycerol. The commercial iodide of potassium generally possesses an alkaline

[1] See Worley, *Journ. Chem. Soc.*, 1905, **87**, 1107; Jakowkin, *Zeit. physikal. Chem.*, 1896, **20**, 719.

reaction; in order to obtain it perfectly neutral it must be dissolved in the smallest quantity of water, neutralised with dilute sulphuric acid, the potassium sulphate precipitated by the addition of pure alcohol, and the solution allowed to crystallise (Groves). Potassium iodide is largely used in medicine both for internal and for external application, especially in scrofulous and syphilitic diseases.

Potassium Tri-iodide, KI_3.—This compound is formed by saturating a concentrated solution of potassium iodide with iodine. A brown liquid having a metallic lustre is obtained, and this on evaporation over sulphuric acid yields needle-shaped almost black crystals with a metallic lustre. They are very deliquescent and readily lose iodine on warming (Johnson).[1]

Experiments on the distribution of iodine between carbon disulphide and potassium iodide solution show that this salt is dissociated in solution into the ions $K^{\cdot}$ and I_3', and is to be regarded as the salt of an acid, HI_3, which belongs to the class of strong acids.[2] There is, moreover, some evidence that the compound KI_9 exists in solution in nitrobenzene and other similar solvents.[3] According to Abegg, the only solid polyiodide of potassium which can exist at 25° is KI_7, but this salt has not been isolated.[4]

Potassium Iodotetrachloride, $KICl_4$, was prepared by Filhol in 1839, by the action of chlorine on a solution of potassium chloride containing iodine, in lustrous, golden-yellow crystals.

168 *Potassium Hypochlorite*, KClO.—When chlorine is passed into a dilute cold solution of caustic potash or potassium carbonate, a mixture of potassium chloride and potassium hypochlorite is obtained. This liquid was first prepared by Berthollet, and the solution, known by the name "Eau de Javel," was formerly largely used for bleaching purposes (see Vol. I., p. 346). It can also be prepared by electrolysis of potassium chloride solutions. Pure potassium hypochlorite has not yet been prepared.

Potassium Chlorate, $KClO_3$.—It appears likely that this salt was known to Glauber. In one of his works he mentions that he is acquainted with a means of converting muriatic acid into

[1] *Journ. Chem. Soc.*, 1877, 249.

[2] Jakowkin, *Zeit. physikal. Chem.*, 1896, **20**, 19; Dawson, *Journ. Chem. Soc.*, 1901, **79**, 238.

[3] Dawson and Gawler, *Journ. Chem. Soc.*, 1902, **81**, 524; Dawson, *ibid.*, 1904, **85**, 467.

[4] *Zeit. anorg. Chem.*, 1906, **50**, 414.

nitric acid, and in his "Continuatio Miraculi Mundi" he mentions a peculiar kind of saltpetre which he had prepared by means of common salt. This was probably potassium chlorate. In like manner Winterl, in 1789, believed that he had converted muriatic acid into nitric acid by strongly heating muriate of lime (calcium chloride) in a retort with black oxide of manganese and leading the product into a receiver containing a small quantity of caustic potash. Higgins also stated in 1786 that by the action of dephlogisticated muriatic acid (chlorine) on the alkalis a peculiar kind of saltpetre is formed. Potassium chlorate was afterwards prepared by Berthollet in his classical investigation of the action of chlorine on the alkalis in 1786.

This salt was formerly produced on the large scale by passing chlorine into a concentrated solution of caustic potash or potassium carbonate; being only slightly soluble in water it crystallises out when the solution is cooled. The product of these and any similar reactions is a hypochlorite so long as the alkali remains in excess:

$$2KOH + Cl_2 = KOCl + KCl + H_2O,$$

but directly the alkali is exhausted and the chlorine is present in excess the hypochlorite is suddenly converted with evolution of a considerable amount of heat into chlorate:

$$3KOCl = KClO_3 + 2KCl.$$

In order to use a less expensive potassium salt and also less of it, chlorine is passed into milk of lime until the chlorate is formed:

$$6Ca(OH)_2 + 6Cl_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O;$$

the clear settled liquor is concentrated by evaporation and a quantity of potassium chloride exactly equivalent to the calcium chlorate present is added; on cooling potassium chlorate crystallises out. From 1870 this process has been carried out on a very large scale in Widnes and St. Helens. Large quantities, however, are now made electrolytically elsewhere. A description of this industry has been given by Jurisch.[1]

The lime process is now being largely supplemented by a modification of Berthollet's original caustic potash method, in which the caustic potash and the chlorine are simultaneously formed by the electrolysis of a solution of potassium chloride

[1] *Die Fabrikation von chlorsaurem Kali*, 1888.

and immediately react upon each other; by repeating the operation upon the mother-liquors after cooling, the original solution is ultimately converted into potassium chlorate and hydrogen:

$$KCl + 3H_2O = KClO_3 + 3H_2.$$

The process was introduced in 1886 by Gall and Montlaur in Switzerland, and is now also in use in France, Germany, Austria, Sweden, and the United States, the necessary current being obtained in each case from water power. A description of the process has been published by Kershaw.[1] The yearly output of potassium chlorate is probably over 20,000 tons, the main portion of which is prepared electrolytically.

Potassium chlorate crystallises in large transparent monoclinic tablets having a glassy lustre; these when they are of certain dimensions, exhibit magnificent iridescent colours, and emit light when rubbed in the dark. The crystals of potassium chlorate have a feebly acid and cooling taste similar to that of nitre. They have the sp. gr. 2·35, melt without decomposition at 359° (Carnelley), and at 372° they begin to decompose with evolution of oxygen. The nature of the decomposition and the effect of the addition of certain oxides has already been discussed (Vol. I., p. 242). One hundred parts of water dissolve at 0°, 3·3 parts, at 20°, 7·1 parts, and at 104·2°, the boiling point of the saturated solution, 61·5 parts of the salt (Gay-Lussac, Legrand).

Potassium chlorate is largely used in the laboratory for the preparation of oxygen gas. It also acts as a powerful oxidising agent and is employed in the manufacture of lucifer matches and certain explosives, for pyrotechnic purposes, and in calico printing. In large doses it acts as an irritant poison, like nitre and other soluble potassium salts. It was formerly given in small doses in cases of scarlet fever, scurvy, and other diseases, as it was believed to act as an oxidising agent on the blood, but it has been shown that the whole of the salt passes out undecomposed in the urine. It is still employed as a gargle for the purpose of allaying inflammation of the throat.

The powerful oxidising properties of potassium chlorate can be readily exhibited. If a small quantity of the powdered salt be thrown on to glowing charcoal, a rapid combustion takes place. If a few grains of this salt, together with a few grains of flowers of sulphur, are rubbed together in a mortar, loud explosions

[1] *Die elektrolytische Chloratindustrie*, 1905.

occur, and if a grain of the mixture be struck with a hammer a loud detonation takes place. Only very small quantities of the mixture must be used, as otherwise the explosions may become dangerous. Further, if a small quantity of red phosphorus be carefully mixed by means of a feather with the same quantity of powdered potassium chlorate, the mixture will explode when struck even a slight blow with a glass rod. This may also be shown by allowing a few drops of a solution of phosphorus in carbon disulphide to fall on powdered potassium chlorate; after a few moments a violent explosion occurs.

Potassium Perchlorate, $KClO_4$.—The preparation of this salt by heating potassium chlorate has already been described and explained in Vol. I., p. 358. It is also prepared by the electrolytic oxidation of potassium chlorate in neutral or acid solution,[1] or more conveniently by submitting sodium chlorate to this treatment and then adding potassium chloride. It forms small rhombic crystals which possess a slightly saline taste and melt at about 610°; 100 parts of water dissolve at 0°, 0·71 part, at 50°, 5·34 parts, and at 100°, 18·7 parts of salt (Muir); it is almost insoluble in strong alcohol, and is therefore used for the quantitative estimation of potassium.

Potassium Bromate, $KBrO_3$, is obtained, according to Stas, by passing chlorine into a warm solution of potassium bromide and caustic potash:

$$KBr + 6KOH + 3Cl_2 = KBrO_3 + 6KCl + 3H_2O.$$

A portion of the salt crystallises out on cooling, and the remainder is precipitated on addition of alcohol, together with a little potassium chloride, from which it is easily separated by recrystallisation. According to Marignac, it forms hexagonal (ditrigonal pyramidal) crystals and separates out in six-sided tablets or prisms which have the appearance of cubes. One hundred parts of water dissolve 6·9 parts of the salt at 20°, and 49·8 parts at 100°. It melts at 434°, and is converted by ignition into potassium bromide and oxygen, bromine being also evolved when it is heated slowly.

Potassium Iodate, KIO_3, is formed together with the iodide by the action of iodine on caustic potash, but it is most readily obtained by heating potassium chlorate with iodine:

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2;$$

[1] Foerster, *Zeit. Elektrochem.*, 1898, **4**, 386.

the liberated chlorine combines with excess of iodine to form iodine mono- and tri-chloride.[1] Potassium iodate crystallises in small cubical crystals, melts at 560°, and begins to decompose at a much higher temperature than the chlorate. One hundred parts of water dissolve 8·1 parts of the salt at 20°, and 32·3 parts at 100°. It combines with iodic acid to form the compounds KIO_3,HIO_3 and $KIO_3,2HIO_3$ (see Vol. I., p. 370).

Potassium Periodate, KIO_4, is formed when chlorine is passed through a mixture of caustic potash and potassium iodate. It can also be obtained electrolytically by the anodic oxidation of potassium iodate. It separates out as shining crystals which are isomorphous with those of potassium perchlorate, and melt at 582°. When a hot concentrated solution of the salt is mixed with alcoholic potash, rhombohedra of *potassium meso-periodate*, $K_3IO_5,4H_2O$, are deposited. These have an alkaline reaction, and absorb carbon dioxide from the air. When the normal salt is evaporated together with caustic potash, triclinic prisms of *potassium di-periodate*, $K_4I_2O_9,9H_2O$, are deposited, which have an alkaline reaction (see also Vol. I., p. 371).

POTASSIUM AND SULPHUR.

169 *Potassium Monosulphide*, K_2S.—This substance is formed, according to Berzelius, by passing hydrogen over heated potassium sulphate. It forms a pale red crystalline mass, which becomes darker on heating, and melts to a black liquid below a red heat. Berthier obtained the same compound as a flesh-coloured mass by strongly heating the sulphate with carbon:

$$K_2SO_4 + 4C = K_2S + 4CO.$$

In order, however, to obtain this substance a larger amount of carbon is needed than that represented in the above equation; otherwise a mixture of higher sulphides with potassium carbonate is obtained (Wittstock). Indeed it appears impossible to obtain perfectly pure monosulphide in this way, as even the substance obtained by reduction with hydrogen contains higher sulphur compounds.[2] The mass deliquesces in moist air, and dissolves in water with evolution of heat.

If potash lye be saturated with sulphuretted hydrogen, and if then an equal quantity of alkali be added to the liquid, a solution

[1] Thorpe and Perry, *Journ. Chem. Soc.*, 1892, **61**, 925. See also Schlotter, *Zeit. anorg. Chem.*, 1905, **45**, 270.

[2] Bauer, *J. pr. Chem.*, 1858, **75**, 246.

of the monosulphide is obtained. This remains colourless if the air be excluded, possesses an alkaline taste, and acts on the skin as a strong caustic. When evaporated in a vacuum at a low temperature, four-sided prisms are deposited, having the formula $K_2S,5H_2O$.[1] Hydrates with $12H_2O$ and with $2H_2O$ have also been obtained (Bloxam). If this aqueous solution is boiled, only traces of sulphuretted hydrogen are given off, and when exposed to the air it becomes yellow from absorption of oxygen and carbon dioxide, and formation of potassium thiosulphate and potassium carbonate; the sulphuretted hydrogen which is liberated decomposes with formation of water and sulphur, and the latter substance unites with the monosulphide to form higher sulphides. On shaking the yellow solution with metallic copper it again becomes colourless. The main product of the action of air free from carbon dioxide on a solution of the monosulphide is sulphite, the liquid remaining colourless.

Potassium Hydrosulphide, KSH.—This substance was first prepared by Gay-Lussac by heating potassium in dry sulphuretted hydrogen. He then observed that the same quantity of potassium which was capable of evolving one volume of hydrogen from water was able to combine with all the sulphur in two volumes of sulphuretted hydrogen, liberating half the hydrogen:

$$2K + 2H_2S = H_2 + 2KSH.$$

Berzelius obtained the same compound by the action of sulphuretted hydrogen on carbonate of potassium heated to dull redness, but the product of this reaction is by no means pure (Bloxam):

$$K_2CO_3 + 2H_2S = 2KSH + H_2O + CO_2.$$

It can be obtained pure by passing sulphuretted hydrogen through anhydrous ether in which metallic potassium is placed.[2] This body forms a white or yellowish deliquescent mass, which when heated to 450–510° melts to a liquid, and at a higher temperature becomes of a dark red colour. It is very soluble in water, and the aqueous solution is very easily obtained by saturating caustic potash solution with sulphuretted hydrogen. This forms a colourless liquid which smells slightly of sulphuretted hydrogen, has an alkaline and bitter taste, decomposes

[1] Schone, *Pogg. Ann*, 1867, **131**, 380.
[2] Bloxam, *Journ. Chem. Soc*, 1900, **77**, 758.

very slowly when boiled, and on exposure to air containing carbon dioxide becomes yellow owing to the formation of higher sulphides. When exposed for a still longer time to the action of the air it becomes colourless, inasmuch as potassium thiosulphate is formed. If the concentrated solution is allowed to evaporate over caustic lime or caustic soda in a vacuum, colourless glittering rhombohedral crystals separate out, having the formula $2KSH,H_2O$.

A number of polysulphides have been described, having the formulæ K_2S_2, K_2S_3, K_2S_4, and K_2S_5, which are obtained by the action of sulphur, sulphuretted hydrogen, or carbon disulphide vapour on the monosulphide, or compounds which readily yield it. They are described as yellowish-red or dark red substances which dissolve readily in water.

From measurements of the rate of loss of sulphur by K_2S_5 when heated in a steady stream of hydrogen and from the freezing point curve for the system K_2S–S,[1] it appears that the sulphides of potassium form a complete series of the type K_2S_x, where x is any whole number from 1 to 6. The *disulphide*, K_2S_2, is the most stable, losing sulphur only at 700–800°.

Liver of Sulphur or Hepar Sulphuris.—This is an old name given to a mixture of potassium polysulphides with potassium sulphate, or potassium thiosulphate. It is obtained by gently heating sulphur with carbonate of potassium in a covered vessel. The composition of the liver-coloured mass thus obtained is variable, according to the proportions in which the bodies have been mixed and the temperature to which they have been heated. Liver of sulphur was well known to the alchemists of the middle ages. Stahl considered it to be a compound of the alkali with sulphur, and called it "sulphurised alkali." He also knew that it could be prepared by heating sulphate of potash with carbon, and used this fact to prove that only one kind of phlogiston exists (see Vol. I., p. 14). Liver of sulphur is used in medicine, and is termed in the Pharmacopœia *potassa sulphurata*. It is used also by gardeners to get rid of mildew and exterminate insect pests.

170 *Potassium Sulphite*, K_2SO_3, is prepared by dissolving 100 grams of caustic potash in 200 c.c. of water previously freed from dissolved air, and saturating with sulphur dioxide; a further quantity of 100 grams of caustic potash dissolved in a very

[1] Thomas and Rule, *Journ. Chem. Soc.*, 1917, **111**, 1063; compare Bloxam, *ibid.*, 1900, **77**, 767.

small volume of water is then added, and the solution allowed to evaporate *in vacuo*. Potassium sulphite separates in small deliquescent hexagonal crystals which are more soluble in cold than in hot water. The *monohydrated salt*, K_2SO_3,H_2O, is obtained by dissolving the metabisulphite in water, adding an equivalent quantity of caustic potash, evaporating and allowing to crystallise. The *dihydrated salt*, $K_2SO_3,2H_2O$, is obtained when the solution is allowed to evaporate over sulphuric acid, and forms oblique rhombic octahedra, which possess a bitter alkaline taste, and are also more soluble in cold than in hot water. The solutions readily undergo oxidation in the air.

Two isomeric potassium sodium sulphites, $Na{\cdot}SO_2{\cdot}OK$ and $K{\cdot}SO_2{\cdot}ONa$, are also known. These have already been described in Vol. I., p. 408.

Potassium Hydrogen Sulphite, $KHSO_3$, is produced when a solution of the normal salt or of caustic potash is saturated with sulphur dioxide. On addition of alcohol it separates out in needle-shaped crystals, which taste of sulphurous acid, and have a neutral reaction.

Potassium Metabisulphite, $K_2S_2O_5$, is formed when sulphur dioxide is passed into a hot saturated solution of potassium carbonate (Muspratt), or into a mixture of milk of lime and potassium sulphate (Boake and Roberts). It forms monoclinic crystals which are sparingly soluble in water and have an unpleasant acid taste. Potassium metabisulphite is employed in photography.

171 *Potassium Sulphate*, K_2SO_4.—The mode of preparing this salt was known as early as the fourteenth century. It was first obtained from the residues of the manufacture of *aqua fortis*, and afterwards by the action of sulphuric acid on crude potashes. Potassium sulphate is probably one of the salts whose constituents were first determined by analysis. Glauber, Boyle, and Tachenius were acquainted with its composition, and in the seventeenth century it was termed *arcanum* or *sal duplicatum*, because, according to the then prevalent ideas, it was made up of an acid salt and an alkaline salt. The decomposition of this salt into its constituent parts was at that time supposed to be a most difficult matter. Indeed, Stahl proposed the following question to the French Academy: How is it possible to decompose this salt instantly when held in the hand? Although none of the Academicians were able to answer this question, Stahl accomplished his purpose by adding nitrate of silver, which at once separated vitriolic acid from the alkali.

Potassium sulphate is found native in the lavas of Vesuvius. It is also obtained from the kainite, $K_2SO_4,MgSO_4,MgCl_2,6H_2O$, and schönite, $K_2SO_4,MgSO_4,6H_2O$, of the Stassfurt beds and of those of Kulusz, and as a by-product in several chemical manufactures, such as that of potassium dichromate, as well as in the lixiviation of kelp. It is now manufactured by the double decomposition of potassium chloride and magnesium sulphate in aqueous solution, and is also prepared to a small extent by the action of sulphuric acid on the chloride.[1]

Potassium sulphate crystallises in small, hard, rhombic pyramids, possessing a hexagonal or prismatic habit; it has a specific gravity of 2·6633 at 20°/4° (Tutton), and melts at 1050°. One hundred parts of water at 15° dissolve 10·3 parts of this salt, whilst 24·1 parts dissolve in the same quantity of water at 100°. Aqueous alcohol dissolves it in quantities proportional to the amount of water which the alcohol contains. It is insoluble in a solution of caustic potash of specific gravity 1·35 (Liebig), and in absolute alcohol. It has a bitter saline taste and can be volatilised only at a high temperature.

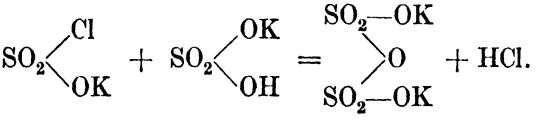
Potassium sulphate is used as a purgative, and is employed in large quantities for the manufacture of potash alum and potassium carbonate. Potassium sulphate itself as well as the mineral kainite and the double salt, $K_2SO_4,2MgSO_4,H_2O$, which is prepared from it, are also very largely used as fertilisers.

Potassium Hydrogen Sulphate, $KHSO_4$.—In 1751, Rouelle proved that in addition to the *arcanum duplicatum*, other salts exist containing an excess of acid chemically combined. Amongst these he mentions acid potassium sulphate, which he obtained in the crystalline state. The same salt is found native in the Grotto del Sofo, near Naples, in the form of long silky needles. It is frequently obtained in the laboratory as a by-product in the preparation of nitric acid from saltpetre and sulphuric acid. It crystallises in rhombic pyramids, according to Marignac, in rhombohedra according to Jacquelain, has a specific gravity of 2·163, melts at 197°, dissolves readily in water, and possesses an acid saline taste. When brought into contact with alcohol it is decomposed into sulphuric acid and the normal salt, which is insoluble in this liquid. When the acid sulphate is recrystallised from aqueous solution the normal salt is found to separate out first, then crystals of a salt having the composition

[1] Precht, *Zeit. angew. Chem.*, 1906, **19**, 1.

$K_2SO_4,KHSO_4$ are deposited, and at last the acid sulphate crystallises out. Salts of the formulæ $K_2SO_4,3KHSO_4$ and $K_2SO_4,6KHSO_4$ have also been described.[1]

Potassium Disulphate, $K_2S_2O_7$.—This salt is obtained by gently igniting the normal salt with sulphuric acid until the mass fuses quietly. It is also formed when the acid salt is heated with potassium chlorosulphonate, a compound obtained by the action of sulphur trioxide on potassium chloride:



The salt crystallises on cooling in long needles which decompose when brought into contact with water, evolving much heat and yielding the acid sulphate. When dissolved in fuming sulphuric acid this salt deposits transparent prismatic crystals of potassium hydrogen disulphate, KHS_2O_7.

Potassium thiosulphate, $K_2S_2O_3$, is prepared in a similar manner to, and closely resembles the corresponding sodium salt. Two isomeric sodium potassium thiosulphates are also known (Vol. I., p. 458).

Potassium Persulphate, $K_2S_2O_8$.—This salt is obtained by the electrolysis of a saturated solution of potassium hydrogen sulphate, and forms large tabular crystals which are sparingly soluble in water. Details of its preparation and properties have already been given in Vol. I., p. 455.

Potassium Selenate, K_2SeO_4, is isomorphous with potassium sulphate. It has the sp. gr. 3·0657 at 20°/4°, deliquesces in the air, and dissolves to the extent of 115 parts in 100 parts of water at 12°.[2] When a solution of this salt and selenic acid is electrolysed, a *perselenate* is formed,[3] which probably has the formula $K_2Se_2O_8$.

Potassium and Nitrogen.

172 *Potassium Azoimide*, N_3K, can be prepared by neutralising hydrazoic acid with potassium hydroxide, or by the action of nitrous oxide on potassamide,

$$2KNH_2 + N_2O = N_3K + NH_3 + NaOH.$$

[1] Stortenbeker, *Rec. trav. chim.*, 1902, **21**, 399.
[2] Tutton, *Journ. Chem. Soc.*, 1897, **71**, 846.
[3] Dennis and Brown, *J. Amer. Chem. Soc.*, 1901, **23**, 358.

Potassamide, NH_2K.—This compound was discovered by Gay-Lussac and Thénard in 1811. It is prepared by gently heating potassium in ammonia gas, and is usually obtained as an olive-green or brown mass, but when the potassium is heated in a silver boat, it forms a white waxy crystalline mass, which melts at 338° [1] and sublimes above 400°.[2] It quickly decomposes in moist air, yielding caustic potash and ammonia, and when water is added the same decomposition takes place with rapid liberation of heat, and frequently also of light. When strongly heated, it slowly undergoes decomposition into its elements, but does not, according to Titherley, leave a residue of the black potassium nitride described by Davy, which probably does not exist.

By the action of sodamide on potassamide [3] in liquid ammonia solution or of sodium iodide on excess of potassamide in this solvent, *dipotassium ammonosodiate*, $K_2[Na(NH_2)_3]$, is obtained: it crystallises well and does not lose ammonia at 100° *in vacuo*. *Dipotassium ammonolithiate*, $K_2[Li(NH_2)_3]$ may be similarly prepared.

Potassium Nitrite, KNO_2, is formed when saltpetre is heated until one-third of the oxygen is evolved (Mitscherlich). The residue invariably contains undecomposed nitrate, and also oxides of potassium. The above decomposition takes place more readily in the presence of metallic iron, copper, or lead (Stromeyer). In order to prepare it in this way two parts of lead may be employed to one part of saltpetre. The latter salt is fused, and the fused mass heated to dull redness, the lead then added little by little, and the cooled mass lixiviated with water. On evaporation, or on neutralising in the cold with dilute sulphuric acid and adding to the solution twice its weight of alcohol, crystals of the nitrite are precipitated.

Pure potassium nitrite is best prepared by decomposing silver nitrite with potassium chloride (Berzelius), by decomposing amyl nitrite with the exactly necessary quantity of alcoholic potash (Chapman), by passing nitrous fumes into caustic potash (Divers),[4] or by the electrolysis of a solution of potassium nitrate.[5] It forms small indistinct, yellowish, anhydrous crystals

[1] Wohler and Stang-Lund, *Zeit. Elektrochem.*, 1918, **24**, 261.
[2] Titherley, *Journ. Chem. Soc.*, 1894, **65**, 511.
[3] Franklin, *J. Physical Chem.*, 1919, **23**, 36.
[4] *Journ. Chem. Soc.*, 1899, **75**, 86.
[5] Dupare, Couchet, and Schlosser, *Zeit. Elektrochem*, 1906, **12**, 665.

which deliquesce in moist air, are soluble in one-third their weight of water, and are insoluble in alcohol. This salt is employed for the separation of cobalt and nickel, and also in organic chemistry.

173 *Potassium Nitrate, Saltpetre, or Nitre*, KNO_3.—This remarkable salt was known to the ancients, being termed *Sal petræ* by the Latin Geber. It was frequently called *Sal nitri* by the later alchemists, to distinguish it from *nitrum*, by which name the ancients signified the native carbonate of soda, a salt which was not unfrequently mistaken for nitre. When trade between the East and the West increased, the mineral alkali was imported under the special name of natron, and then the word nitrum was specially reserved to designate saltpetre.

Saltpetre occurs, together with other nitrates, as an efflorescence on the soil in various hot countries, especially in Bengal, but likewise in Egypt, Syria, Persia, and Hungary, as well as in America. In Ceylon[1] and India nitre is obtained by the lixiviation of certain porous rocks, whence the origin of the word sal-petræ. These yield from 2·5 to 8 per cent. of their weight of nitre. The formation of nitre, whether found in the soil or in porous felspathic rocks, is due to the gradual oxidation of nitrogenous organic matter in contact with an alkali in presence of a nitrifying organism. In the decay and putrefaction of such bodies ammonia is first formed and is then converted into nitrous and finally into nitric acid. Nitre is also found in the juices of certain plants. This fact was first pointed out by L. Lemery in 1717. Certain species of amaranthus, especially *A. atropurpureus*, contain no less than 22·7 per cent. of nitre in the dry plant (Boutin). Crude "Chile saltpetre" and the "caliche" from which it is obtained may contain considerable amounts of potassium nitrate: in certain *oficinas* this salt forms up to 30 per cent. of the total soluble nitrate in the raw material and quite commonly 5 per cent. or more occurs in the crude sodium nitrate of commerce.

In India, a caste of men termed Sorawallahs,[2] from *sora*, nitre, at one time made it the business of their lives to collect the raw material, and to manufacture and sell the salt, which, before the introduction of cheap artificial ice, was employed locally for producing frigorific mixtures and was also largely exported.

"The *Sorawallah* goes about the village, examining the small

[1] John Davy, *Quart. Journ. Sci.*, 1818, **5**, 233.
[2] Palmer, *Journ. Chem. Soc.*, 1868, **21**, 318.

surface drains which issue from holes in the mud-wall, usually found around native dwellings and their cow-houses; when he detects a faint white veil-like patch of crystalline formation, on or near the dark-coloured borders of these little drains, he knows that a considerable quantity of nitre exists, on or near the surface of all the surrounding earth; he accordingly proceeds to scrape off a very thin layer of the surface soil, which he carries away to his place of manufacture, as soon as his morning's collections are finished. On arriving there, the impregnated earth so collected is thrown into an earthen vessel containing either water or water which has been poured off from previous supplies of similarly impregnated earth." The liquid thus obtained was allowed to evaporate and the nitrate of potash recrystallised once or twice. "The *Sorawallah* makes fresh collections from precisely the same spots of ground from week to week, year to year, and from generation to generation after the manner of the Eastern world; the production of nitre is constant so long as the place continues to be inhabited; it even continues to appear in large, though gradually decreasing, quantities, for years after the village may have been deserted. The intervals at which fresh collections may be made from the same spot vary in different localities and in different seasons of the year, from one to seven, ten, or more days."

This production of nitre is doubtless preceded by the formation of nitrate of calcium, and this, by double decomposition with potassium carbonate, yields nitre and calcium carbonate. Indian saltpetre was introduced into Europe by the Italians,and first employed for medicinal and chemical purposes.

When the demand for gunpowder became great, nitre began to be manufactured in Europe. Agricola, in his celebrated treatise *De Re Metallica*, describes the process of refining saltpetre as follows:—"Saltpetre is obtained from a dry somewhat fatty earth, which is boiled with quick-lime and wood-ashes. The mass is then lixiviated and the solution evaporated."[1] During the blockade of the French ports, the artificial production of nitre was of necessity largely carried on in that country. For this purpose nitrogenous organic matter of animal or vegetable origin, after having been allowed to putrefy by exposure to air in a dark place was mixed with substances such as lime, mortar, or wood-ashes, containing the carbonates of potash, magnesia, or lime. The mixture was then heaped together in

[1] Berzelius, *Traité*, 3, 119.

ridges (saltpetre walls), or in low heaps (saltpetre mounds), which were then moistened from time to time by the drainage of dung heaps, or by urine, and exposed to the air. After standing for from two to three years the outer surface or saltpetre earth was removed and exhausted with water. This yielded the crude saltpetre ley which contained the nitrates of calcium and magnesium together with the chlorides of potassium and sodium. On boiling this liquor with potashes the calcium and magnesium salts were decomposed, and the clear solution was then crystallised. *Raw nitre* was thus obtained, and this by repeated solution and crystallisation was converted into *purified nitre*. In order still further to purify the salt, it was dissolved in boiling water, and the solution constantly agitated when cooling. The salt then separated out in small crystals termed *saltpetre-flour*, which enclosed much less of the mother-liquor, and therefore much less impurity than the large crystals. This finely-divided salt was then again purified by washing it with a saturated solution of pure nitre which dissolved out the last portions of foreign salts, thus rendering the saltpetre free from chlorides and fit to be employed in gunpowder-making.

Since the discovery of large quantities of potassium chloride at Stassfurt, this salt has been almost exclusively used for the artificial manufacture of saltpetre. This manufacture depends upon the fact that under certain conditions solutions of Chili saltpetre, $NaNO_3$, and of potassium chloride undergo, when mixed, a double decomposition, chloride of sodium being deposited and potassium nitrate remaining in solution. For this purpose equivalent quantities of sodium nitrate and potassium chloride are dissolved in the mother-liquor from a previous operation and heated by steam for about half an hour. The product is run into strainers, where it is kept hot, the greater part of the sodium chloride separating out under these conditions; the filtered liquor is then allowed to cool, and the resulting saltpetre meal, which contains 7 to 9 per cent. of sodium chloride and a little magnesium chloride, is purified by washing with mother-liquors resulting from subsequent washings, recrystallised, and finally washed with small quantities of pure water.

The equilibrium between the chlorides and nitrates of potassium and sodium in aqueous solution has been studied, and the data afford useful information as to the best method of preparing the so-called "conversion" saltpetre.[1]

[1] Reinders, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 1065.

Saltpetre occurs in commerce in the form of small well-formed crystals, and as "flour." The latter is much purer than the larger crystals, which are often hollow and contain chloride of potassium and other impurities. About 10,000 tons per annum are imported into the United Kingdom.

Potassium nitrate is dimorphous.[1] It usually crystallises in rhombic prisms, which often closely resemble regular six-sided prisms. If, however, a few drops of a solution of nitre be allowed slowly to evaporate, rhombohedral crystals are deposited, isomorphous with those of sodium nitrate, but these are very unstable and when touched are converted into an aggregate of small rhombic crystals. The rhombohedral form is stable above 129°, and a second rhombohedral form is known which is stable at a still higher temperature.[2]

Saltpetre has a specific gravity of 2·1; it melts at 339° (Person), and possesses a bitter cooling saline taste. It dissolves in water with absorption of much heat. This property of nitre was first pointed out by the Spanish physician Blasius Villafranca, in his tract published in 1550, entitled "Methodus refrigerandi ex vocato Sale-nitro vinum aquamque ac potus quodvis aliud genus." According to Rudorff, 16 parts of nitre when dissolved in 100 parts of water at 13·2° lower the temperature to + 3°.

One hundred parts by weight of water dissolve:

At	0°	10°	20°	40°	60°	80°	100°
KNO_3	13·3	20·9	31·6	63·9	109·9	169	246,

whilst at 114·1°, the boiling point of the saturated solution, 311 parts of the salt are dissolved.

Saltpetre is used in the laboratory, in medicine, for the salting or pickling of meat, to which it imparts a red colour, and for pyrotechnic purposes, but chiefly in the manufacture of gunpowder.

A salt of the composition $KNO_3,2HNO_3$, which is known as potassium trinitrate, crystallises out when a solution of potassium nitrate (1 mol.) in highly concentrated nitric acid (2 mols.) is cooled to −3°; the salt forms prisms which melt at 22°, and are decomposed by water. An unstable salt, KNO_3,HNO_3, is also known, which crystallises in plates.[3]

[1] Miller, *Phil. Mag*, 1840 [3], **17**, 38.
[2] Wallerant, *Compt. rend*, 1905, **140**, 264.
[3] Groschuff, *Zeit. anorg Chem.*, 1904, **40**, 1.

Nitre used in Explosives.[1]—The Chinese are said to have been acquainted with the mode of manufacturing gunpowder from early times, although employing it rather for making fireworks than for warlike purposes. It appears probable that the knowledge of this manufacture resulted from an improvement in the preparation of Greek fire, which was discovered in 673 A.D., and itself consisted of combustible and fusible substances such as pitch, resin, and sulphur, mingled with crude saltpetre. In the *Liber ignium* of Marcus Graecus, a work which dates from the early part of the thirteenth century, and bears many traces of Arabian influence, mention is made of the use of saltpetre, *sal petrosum*, as a constituent of gunpowder. None of the Arabian alchemists appear to have been aware of the property of saltpetre deflagrating when mixed with a combustible body, and not until the thirteenth century do we find this clearly pointed out by Roger Bacon as follows :—[2] "Talis natura est (sal nitrum), quod si immediate ignitos carbones tangat, statim accensum impetu evolat."

This fact is strikingly shown when a mixture of twenty parts of nitre and three parts of charcoal is thrown into a red-hot crucible, vivid incandescence and a violet combustion being noticed :

$$4KNO_3 + 5C = 2K_2CO_3 + 3CO_2 + 2N_2.$$

An intimate mixture of fifteen parts of saltpetre and five parts of sulphur also burns very brilliantly :

$$2KNO_3 + 2S = K_2SO_4 + SO_2 + N_2.$$

Detonating Powder, first described by Glauber, consists of a mixture of three parts of saltpetre, two parts of dry potassium carbonate, and one part of sulphur. When the mixture is heated in an iron spoon it first fuses and then explodes violently. In this reaction the sulphur forms potassium sulphide, which at the high temperature of the combustion is oxidised by the nitre, free nitrogen being evolved.

Powder of Fusion or *Baumé's Quick Flux*, also mentioned by Glauber, contains one part of nitre, one part of sulphur, and one of sawdust. This if set on fire burns with so much heat that a small silver coin exposed to it is rapidly melted.

174 *Gunpowder.*—Firearms appear to have been used in

[1] For much interesting information concerning the early history of gunpowder, see Guttmann, *Monumenta Pulveris Pyrii* (Printed for the Author at the Artist's Press, Balham, London, 1906).

[2] Breve breviarium de Dono Dei.

Florence in 1325, but field pieces were first employed by the English at the battle of Crécy in 1346.

Gunpowder consists of a mixture, in somewhat varying proportions, of charcoal, sulphur, and nitre. Its explosive power depends on the rapid combustion of the charcoal and sulphur at the expense of the oxygen of the nitre, and the sudden liberation of a large volume of gas, which occupies several hundred times the bulk of the solid powder. Hence gunpowder can burn in a closed space or under water, as it contains in itself the oxygen needed for the combustion. A singular fact which has been found to be true in practice is that the description of gunpowder which acts best is that which contains nearly two molecules of nitre to one atom of sulphur and three atoms of carbon. Hence it was formerly believed that the decomposition which took place when powder was fired was a very simple one, represented by the following equation:

$$2KNO_3 + S + 3C = K_2S + N_2 + 3CO_2.$$

If this equation represents the decomposition which actually occurs, it follows that the most effective powder must be composed of:

Nitre	74·9
Carbon	13·3
Sulphur	11·8
	100·0.

The compositions of the gunpowders employed by different nations approach closely to these theoretical numbers; but in no case, as will hereafter be seen, are these numbers exactly adhered to. Indeed, the fact that the charcoal employed in the manufacture of gunpowder does not consist of pure carbon, but contains considerable quantities of hydrogen and oxygen, is sufficient to show that the above simple reaction cannot represent the real decomposition which occurs when powder is fired. In addition to this, however, Gay-Lussac and Chevreul proved long ago that, in addition to nitrogen and carbon dioxide, carbon monoxide is evolved in the firing of gunpowder, whilst the residue does not merely consist of potassium sulphide, but contains the carbonate, sulphate, and other salts.

We owe the first careful experimental investigation concerning the nature of the decompositions which occur when powder is fired to Bunsen and Schischkoff.[1] They proved that

[1] *Phil. Mag.*, 1858 [4], **15**, 489.

a very large number of salts, such as sulphate, thiosulphate, sulphide, and carbonate of potassium, are contained in the smoke and solid residue remaining after the powder has been fired; whilst many other gases, especially carbon monoxide, hydrogen, and sulphuretted hydrogen, besides carbon dioxide and nitrogen, are formed. In these experiments the powder was fired into a vacuum, and consequently some conditions as regards temperature and pressure which are met with in the practical use of gunpowder were not maintained. Linck repeated these experiments with a different kind of powder, and Karolyi analysed the products obtained by exploding small charges in shells inclosed in a vacuous space.

Subsequently Abel and Noble[1] published the results of a very complete investigation on the products of combustion of powder fired under conditions similar to those which exist when it is fired in guns. The gunpowder operated upon included five kinds, viz., pebble powder, rifle large-grain (cannon powder), fine-grain powder, and rifle fine-grain powder, all English military powders, together with one spherical pellet powder of Spanish manufacture. The following table gives the complete analyses of the different powders employed:

	Pebble powder. Waltham Abbey	Rifle large-grain (cannon powder). Waltham Abbey.	Rifle fine-grain. Waltham Abbey.	Fine-grain Waltham Abbey.	Spanish spherical pebble powder.
Saltpetre	74 67	74 95	75 04	73 55	75 30
Potassium sulphate	0 09	0 15	0·14	0 36	0 27
Potassium chloride	—	—	—	—	0 02
Sulphur	10 07	10 27	9 93	10 02	12·42
Charcoal: Carbon	12 12	10 86	10 67	11 36	8 65
Charcoal: Hydrogen	0 42	0 42	0 52	0 49	0 38
Charcoal: Oxygen	1 45	1·99	2·66	2 57	1 68
Charcoal: Ash	0 23	0·25	0·24	0 17	0 63
Charcoal: total	14 22	13 52	14 09	14 59	11 34
Water	0 95	1 11	0 80	1·48	0·65

Quantities of gunpowder varying from 100 to 750 grams were exploded in a mild steel vessel of great strength, carefully tempered in oil. The main orifice of the vessel was closed by an accurately fitted screw firing-plug, in which was a second conical plug, carrying two insulated platinum wires, by means of which the charge could be fired by electricity. Two other apertures in the chamber communicated respectively with an arrangement for allowing the gases to escape and an apparatus

[1] *Phil. Trans.*, 1875, **165**, 49.

for determining the pressure of the gases at the moment of explosion. The pressures observed varied from 1 to 36 tons per square inch. The results of this investigation may be shortly stated as follows:

(1) The composition of the *gas* furnished by the explosion of all the English powders is remarkably uniform, but under high pressures the carbon dioxide increases and the carbon monoxide decreases.

(2) The composition of the *solid* products exhibits a much greater variation.

(3) The decomposition which an average gunpowder undergoes when fired in a closed space cannot be represented by even a comparatively complicated chemical equation.

(4) The volume of the permanent gases, measured at 0° and 760 mm., furnished by combustion of 1 gram of powder in a closed vessel is about 280 c.c., and is therefore about 280 times the volume of the powder.

(5) When 1 gram of powder is burnt the solid products of combustion amount to 0·57 gram, and the permanently gaseous products 0·43 gram.

(6) The pressure of the products of combustion when the powder entirely fills the space in which it is fired is about 6,400 atmospheres, or 42 tons per square inch.

(7) The heat developed by the burning of 1 gram of powder is about 705 thermal units.

(8) The temperature of explosion is about 2,200°.

The following tables give the analytical results obtained with three of the powders, including both the solid and gaseous products of combustion.

I. (*Pebble*); *II. R. L. G.* (*Rifle Large Grain*); *III. F. G.* (*Fine Grain*), *each under two different pressures.*

	Pebble. I.		R. L. G. II.		F. G. III.	
Pressure of explosion in tons per square inch . .	1·4	12·5	1·6	35·6	3·7	18·2
Percentage weight of solid products . . .	56·12	55·17	57·22	57·14	58·17	58·08
Percentage weight of gaseous products . . .	43·88	44·83	42·78	42·86	41·83	41·92

COMPOSITION BY WEIGHT (IN GRAMS) OF THE PRODUCTS OF EXPLOSION OF A GRAM OF POWDER AS FURNISHED BY THE ABOVE EXAMPLES.

	I.		II.		III.	
Potassium carbonate	0·3115	0·3098	0·3007	0·3755	0·3454	0·2499
thiosulphate .	0·1163	0·0338	0·1166	0·0491	0·0308	0·1863
sulphate . .	0·0843	0·0658	0·1171	0·0487	0·1409	0·1220
sulphide . .	0·0416	0·1055	0·0230	0·0413	0·0298	—
thiocyanate .	0·0005	0·0013	0·0000	0·0021	0·0001	0·0013
nitrate . . .	0·0027	0·0011	0·0032	0·0011	0·0005	0·0011
oxide . . .	—	—	—	—	—	0·0173
Ammonium sesqui-carbonate .	0·0009	0·0004	0·0003	0·0009	0·0009	0·0002
Carbon . .	—	—	0·0072	—	—	—
Sulphur . . .	0·0034	0·0340	0·0041	0·0527	0·0333	0·0027
Total solid .	0·5612	0·5517	0·5722	0·5714	0·5817	0·5808
Sulphuretted hydrogen . . .	0·0134	0·0084	0·0166	0·0077	0·0154	0·0081
Oxygen . . .	—	—	—	—	—	0·0006
Carbon monoxide .	0·0519	0·0473	0·0303	0·0356	0·0416	0·0258
Carbon dioxide . .	0·2577	0·2770	0·2597	0·2750	0·2512	0·2718
Methane	—	0·0012	0·0006	0·0015	—	0·0009
Hydrogen . . .	0·0007	0·0005	0·0005	0·0003	0·0010	0·0005
Nitrogen . . .	0·1151	0·1139	0·1201	0·1085	0·1091	0·1117
Total gaseous	0·4388	0·4483	0·4278	0·4286	0·4183	0·4192

The total theoretic work of gunpowder is about 332,000 gram-metres per gram, or 486 foot-tons per lb. of powder.

A difference between the products of powder of large and small grain can be observed. The very small grain powders furnish decidedly smaller proportions of gaseous products than a large-grain powder, and this again smaller than a pebble powder. The most important solid products are found to consist of the following potassium salts: carbonate, sulphate, thiosulphate, and sulphide. The proportion of carbonate is much larger, and that of sulphate very much smaller, than was formerly believed to be the case.

POTASSIUM AND PHOSPHORUS.

175 *Normal Potassium Orthophosphate*, K_3PO_4, is formed, according to Graham, when phosphoric acid is ignited with an excess of potassium carbonate. It is more general now to heat

a mixture of phosphatic slag or naturally occurring calcium phosphate with powdered coke and potassium sulphate. It is readily soluble in water, and crystallises in small needles. The mono-acid salt, K_2HPO_4, does not readily crystallise, and the di-acid salt, KH_2PO_4, is obtained by adding phosphoric acid to a solution of potassium carbonate until the liquid after boiling is neutral to phenolphthalein. The salt is deposited in deliquescent tetragonal crystals, easily soluble in water, but insoluble in alcohol. It is employed in the manufacture of artificial fertilisers.[1]

Potassium Tetrathiophosphate, K_3PS_4,H_2O, is obtained by the action of sodium sulphide in excess on phosphorus pentasulphide in concentrated aqueous solution, and forms crystals stable in air.[2]

Potassium Pyrophosphate, $K_4P_2O_7$.—When the mono-acid orthophosphate is ignited this salt is formed. It deliquesces on exposure, and is deposited in the form of fibrous crystals containing three molecules of water, when the solution is evaporated. The acid salt, $H_2K_2P_2O_7$, separates out as a white deliquescent mass when the normal pyro-salt is dissolved in acetic acid and alcohol added to the solution.

Potassium Metaphosphates.—These salts exist in a large number of polymeric modifications, which closely resemble the corresponding sodium salts (p. 283).

Potassium and Arsenic.

176 *Potassium Arsenide.*—Two arsenides of potassium, AsK_3 and As_4K_2, have been prepared by acting on a solution of potassium in liquid ammonia with arsenic, and heating the resulting compounds.[3]

Potassium Arsenite.—Arsenious oxide dissolves easily in an aqueous solution of potash, and if the minimum quantity of potash be employed, the compound $KAsO_2,H_3AsO_3$ may be obtained as a crystalline powder when the solution is mixed with alcohol. If this is warmed with a solution of potassium carbonate, potassium meta-arsenite, $KAsO_2$, is formed, and this when warmed with caustic potash yields potassium diarsenite, $K_4As_2O_5$, likewise precipitable by alcohol.

A solution of potassium arsenite is used in medicine under

[1] Meyer, *Zeit. angew. Chem.*, 1905, **18**, 1382.
[2] Ephraim and Stein, *Ber.*, 1911, **44**, 3405.
[3] Hugot, *Compt. rend.*, 1899, **129**, 603.

the name of Fowler's Solution. This solution is prepared by boiling one part of solid arsenious oxide with an equal weight of potassium carbonate in distilled water, and diluting the clear liquid so as to form 90 parts of solution.

Normal Potassium Arsenate, K_3AsO_4, is prepared by adding an excess of caustic potash to arsenic acid. On evaporation it is deposited in the crystalline form (Graham). Monohydrogen potassium arsenate, K_2HAsO_4, crystallises with difficulty, but the dihydrogen salt, KH_2AsO_4, can be obtained in large crystals. This last salt was known as *Macquer's arsenikalisches Mittelsalz*, and was formerly prepared by deflagrating equal parts of arsenious oxide and nitre, dissolving in water, and leaving the solution to crystallise. These crystals are isomorphous with dihydrogen potassium phosphate, and likewise turn blue litmus paper red.

Potassium and Boron.

177 *Potassium Metaborate*, KBO_2.—When boric acid and potassium carbonate (or any other potassium salt containing a volatile acid) are fused together in the proper proportions, the above salt is obtained. It is sparingly soluble in water, whence it is deposited in small monoclinic crystals, possesses an alkaline reaction, and absorbs carbonic acid from the air with formation of *potassium pyroborate* or *tetraborate*. This latter substance is obtained by adding caustic potash to a solution of boric acid until the liquid attains an alkaline reaction. It is easily soluble, crystallises in hexagonal prisms having the formula $K_2B_4O_7,5H_2O$ and possesses a faint alkaline taste. If hot solutions of boric acid and potassium carbonate be mixed together, in the proportion of one molecule of the former to two molecules of the latter, glittering rhombic crystals of *potassium triborate*, $2KB_3O_5,5H_2O$, separate out, and when a hot solution of caustic potash is saturated with boric acid, rhombic pyramids of *potassium pentaborate*, $KB_5O_8,4H_2O$, are deposited.

Potassium Perborate, $KBO_3,4H_2O$, is precipitated by alcohol from a solution of the borate in hydrogen peroxide, and has the characteristic oxidising properties of this class of salts (Vol. I., p. 737; this vol., p. 288).

Potassium and Carbon.

178 *Potassium Carbide*, K_2C_2, closely resembles the sodium compound (p. 289), and is prepared in a similar manner. The

compound with acetylene, C_2K_2,C_2H_2, crystallises in brilliant silky, rhombohedral lamellæ.[1]

Normal Potassium Carbonate, K_2CO_3.—This salt, well-known under the name of potashes, was originally obtained solely from the ashes of wood and other land plants, as the name implies, boiled in pots. Even to the present day this compound is sometimes obtained according to the old process, especially in Canada, North America, Moravia, the Steppes of Southern Russia, Hungary, and other districts where wood is plentiful. The ashes are lixiviated in wooden tubs, and the dark brown lye thus obtained evaporated to dryness or to the point of crystallisation, and the residue calcined in a reverberatory furnace to remove organic matter. The crude product has usually a red, yellow, or green colour, due to the presence of iron or manganese, and also contains potassium chloride, sulphate and silicate, as well as sodium salts, and, where caustic lime is added, as in the preparation of American potash, considerable quantities of caustic potash; the latter may be converted into carbonate by calcining the crude ash with sawdust. To purify the crude ash it is redissolved in two parts of boiling water, the filtered solution is allowed to stand for some days, then poured off from separated salts, consisting chiefly of potassium sulphate, and the clear solution evaporated till the salt commences to crystallise out. After cooling, it is drained and washed with small quantities of water to remove the adherent mother-liquor. To the white salt thus obtained the name *pearl-ash* is given.

Owing to the high price of potashes and the gradual extinction of forests, and in consequence of this alkali being a substance largely needed in manufacturing processes, other sources of potassium compounds have been sought. The suggestion has frequently been made that felspar and other silicates of potash should be employed for the purpose, and this proposition seems a very plausible one, inasmuch as it is by the slow decomposition of these silicates that all fruitful soils obtain their potash salts. Hitherto, however, it has not been found possible to obtain potash commercially from this source, and fortunately other richer sources of potassium compounds have been discovered. Amongst these the first to be noted is that from the manufacture of beet-root and cane-sugar. Beet-root is a potash plant, its ash being particularly rich in potassium compounds. The first attempt

[1] Moissan, *Compt. rend.*, 1898, **126**, 302; 1898, **127**, 911.

to obtain potash from this plant was made by incinerating the leaves. This process, however, did not prove satisfactory, and the molasses or uncrystallisable sugar, which contains large quantities of potash salts, is now evaporated, and either heated in a furnace to remove the organic matter, or distilled and the nitrogen recovered in the form of ammonia and cyanides. In either case a residue of potash salts and carbon is left, from which the salts are removed by lixiviation.

Another remarkable source of potash is sheep-wool. It has already been mentioned that sheep withdraw a considerable quantity of potash salts from the soil. Chevreul first pointed out that the sweat or suint of sheep contains no less than one-third of its weight of potash salts. The brown liquors in which the wool has been washed are evaporated to dryness, and the solid residue calcined in retorts, by which means ammonia and a gas used for illuminating purposes are evolved; the residual mixture of charcoal and alkaline salts is again lixiviated, and treated as before described.

Potashes are also manufactured from potassium sulphate, which is obtained in considerable quantity from the Stassfurt beds, from sea-water, by heating potassium chloride with sulphuric acid, and in the manufacture of dichromate. For the purpose of converting the sulphate into the carbonate it is heated in a reverberatory (black-ash) furnace with the requisite quantity of limestone and coal, the process being worked exactly according to Leblanc's process for obtaining carbonate of soda from salt-cake (p. 298).

The greater part of the potassium carbonate which is made from the Stassfurt salt is manufactured by the magnesia–potash process from potassium chloride. This depends on the fact that in the presence of magnesium carbonate, potassium chloride is decomposed below 24° by carbon dioxide, with formation of an insoluble double salt, $KHCO_3,MgCO_3,4H_2O$, and magnesium chloride. The precipitated salt is washed and then decomposed by warm water, or by magnesium hydroxide below 20°, and the solution of potassium carbonate is evaporated and calcined.[1]

In order to prepare chemically pure potassium carbonate, it was customary formerly to employ pure cream of tartar (hydrogen potassium tartrate), which was heated in covered iron crucibles. A mixture of carbon and potassium carbonate

[1] German Patents 135329; 143408; 143409; 157354. Davis, *J. Soc. Chem. Ind.*, 1906, **25**, 791.

was thus obtained, and by lixiviating the residue with water and evaporating the solution in a silver basin the pure salt was deposited. This salt even now retains the name of salt of tartar. Instead of the expensive tartar it is now customary to employ the much cheaper hydrogen potassium carbonate or bicarbonate of potash, which can be easily prepared in the pure state, and which on heating yields water, carbon dioxide, and potassium carbonate:

$$2KHCO_3 = H_2O + CO_2 + K_2CO_3.$$

When prepared on the manufacturing scale, the carbon dioxide which is evolved is made use of for the preparation of a fresh portion of bicarbonate.

Pure potassium carbonate occurs either in the form of a white granular powder, or as a white solid mass, which possesses a strong alkaline reaction, and has an alkaline and slightly caustic taste. It has the sp. gr. 2·29, melts at 879°, and then loses a small quantity of carbon dioxide; it is converted into caustic potash and carbon dioxide at a red heat in a current of steam or hydrogen. At a white heat it is volatilised. It is extremely hygroscopic and very soluble in water, and when exposed to the air it soon deliquesces to an oily liquid which received the name of "oleum tartari per deliquium." One hundred parts of water dissolve of the salt [1] at

0°	26°	40°	60°	80°
105	113·5	117	127	140 parts.

At 135° the boiling point of the saturated solution, 100 parts of water dissolve 205 parts of the salt. The hydrate which is stable in contact with water from −6·8° to 135° contains $2H_2O$.[2] For the specific gravity of solutions of this salt, Gerlach's tables may be consulted.[3] When the concentrated solution is allowed to stand, monoclinic crystals, possessing a glassy appearance and having the composition $2K_2CO_3,3H_2O$, are deposited. These on heating to 100° fall to a white powder having the composition K_2CO_3,H_2O, and this at 130° loses all its water.

Potassium carbonate is largely used in the manufacture of soft soap, other potassium compounds, and crystal glass.

Hydrogen Potassium Carbonate, $KHCO_3$.—This salt, also known

[1] Meyerhoffer, Landolt-Börnstein, *Physikalisch-Chemische Tabellen*.

[2] See also Lescoeur, *Bull. Soc. Chim.*, 1897, [3], **17**, 18.

[3] *Zeit. anal. Chem.*, 1869, **8**, 279.

as potassium bicarbonate, is obtained by passing carbon dioxide through a concentrated solution of the normal salt, when the bicarbonate, which is much less soluble, crystallises out. Another process is to pass a current of carbon dioxide over the slightly moistened purified potashes, the product being recrystallised from warm water. It forms large, transparent crystals belonging to the monoclinic system, which possess a saline taste and a slightly alkaline reaction. One hundred parts of water dissolve at 10° 27·7 parts, and at 60°, 60 parts of the salt. When the solution is boiled carbon dioxide is given off, and when the dry salt is heated to 190° it is completely decomposed into the normal carbonate, carbon dioxide, and water.

Potassium Percarbonate, $K_2C_2O_6$, see Vol I., p. 835.

Potassium Sulphocarbonate, K_2CS_3, is prepared by the interaction of carbon disulphide and potassium sulphide. The salt has a yellow colour, and is readily soluble in water.

Potassium Cyanide, KCN.—Commercial potassium cyanide was formerly prepared according to Liebig's method as follows. Eight parts of dry ferrocyanide of potassium (for the manufacture of which see under Iron) are melted in an iron crucible together with three parts of potassium carbonate:

$$K_4Fe(CN)_6 + K_2CO_3 = 5KCN + KOCN + CO_2 + Fe.$$

As is seen from this equation, the cyanide thus prepared contains cyanate; for some purposes this is of no consequence. A purer product can be obtained by heating the dry ferrocyanide to a bright red heat:

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2.$$

To avoid the loss of cyanogen which thus takes place in both these reactions it is now usual to heat the completely dehydrated ferrocyanide with metallic sodium:

$$K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe.$$

The resulting mixture of potassium and sodium cyanides is known commercially as potassium cyanide. A large amount of potassium cyanide is now made by Beilby's process, which consists in treating a fused mixture of potassium carbonate and charcoal with ammonia, the product being a molten cyanide of high strength, which is filtered from the small amount of insoluble matter present and is then cast in moulds, thus yielding massive crystalline cakes of pure white cyanide.[1] It is also

[1] Beilby, "Advances in Chemical Industry during the Nineteenth Century," *Proc. Roy. Phil. Soc.*, Glasgow, 1904.

manufactured on a commercial scale from the waste product known as " Schlempe " of the beet-sugar refineries. The process is one of destructive distillation. Chemically pure potassium cyanide is best prepared by passing the vapour of hydrocyanic acid into an alcoholic solution of potash, the salt then separating out as a white, crystalline powder.

Potassium cyanide has a sharp bitter taste; it is exceedingly soluble in water, and dissolves slightly in cold, and somewhat more readily in hot, alcohol. When the concentrated aqueous solution of the salt is allowed to evaporate over strong sulphuric acid, it deposits crystals in the form of regular octahedra. Potassium cyanide is readily fusible, and on cooling solidifies in cubes. The weakest acids, even carbonic acid, decompose the salt with evolution of hydrocyanic acid. The salt is, moreover, partially hydrolysed in its aqueous solution, which possesses an alkaline reaction and always smells of hydrocyanic acid. It is itself as poisonous as the acid.

Potassium cyanide is used in very large quantities in the Macarthur-Forrest process for recovering the last portions of gold from the tailings of the gold mines [1] (see Gold); in the laboratory it is also used as a reducing agent. This is due to the fact that when in the fused state it withdraws oxygen from many oxides and is converted into potassium cyanate. When heated with nitric acid or potassium chlorate violent explosions occur. Potassium cyanide and sulphur when melted together combine directly, forming potassium thiocyanate. This compound is also formed when the cyanide is heated with some metallic sulphides.

Potassium Cyanate, KCNO or CO.NK, is prepared by heating four parts of very carefully dried potassium ferrocyanide and three parts of fused potassium dichromate in an iron dish, and extracting the product with hot 80 per cent. methylated spirit. It crystallises on cooling in transparent plates, which are readily soluble in water and alcohol, the aqueous solution gradually decomposing into ammonia and potassium hydrogen carbonate:

$$KCNO + 2H_2O = NH_3 + KHCO_3.$$

The cyanate can also be readily prepared by the electrolytic oxidation of a solution of potassium cyanide containing caustic

[1] *J. Soc. Chem. Ind.*, 1890, **9**, 270; Maclaurin, *Journ. Chem. Soc.*, 1893, **63**, 724; 1895, **67**, 199.

potash.[1] Potassium cyanate is employed in the preparation of certain organic compounds.

Potassium Thiocyanate, KCNS or CS:NK, is formed by the direct union of potassium cyanide and sulphur, but is usually prepared by gently heating a mixture of 46 parts of dry potassium ferrocyanide, 17 parts of potassium carbonate, and 32 parts of sulphur. The mass after cooling is extracted with boiling alcohol, and the salt crystallises from the cooled solution in long striated prisms, which readily melt when heated and deliquesce in moist air. One hundred parts of water dissolve 217 parts of the salt at 20°, a considerable amount of heat being absorbed; thus if 500 grams of the salt be mixed with 400 grams of water the temperature of the mass sinks to — 20°; hence the salt has been used as a refrigerant.

It melts at 172°, and on heating to 430° becomes coloured blue, the blue colour changing to white again on cooling.[2]

This salt occurs in minute amounts in human saliva.

Potassium and Silicon.

179 *Potassium Silicates.*—When silica is fused with potassium carbonate, carbon dioxide is evolved, and according to the proportions of the two substances employed, the temperatures and the duration of heating, the silicates K_2SiO_3, $K_4Si_3O_8(2K_2O,3SiO_2)$, and $K_8Si_3O_{10}(4K_2O,3SiO_2)$ are obtained.[3] Attempts to obtain the orthosilicate, K_4SiO_4, have all been unsuccessful, and in all probability it does not exist. The action at a high temperature of limited amounts of water upon specially prepared potash glasses [4] produces *potassium hydrogen disilicate*, $KHSi_2O_5$, and *potassium disilicate*, $K_2Si_2O_5$. The former is very little affected by water, even at 100°, but the latter is hygroscopic and readily acted upon by water.

Potassium Metasilicate, K_2SiO_3, obtained by fusing equal molecular proportions of silica and potassium carbonate, forms a glassy mass which deliquesces on exposure to moist air. It also absorbs carbonic acid from the air, and is gradually transformed into a transparent jelly which in time shrinks together, and after some weeks becomes hard enough to scratch glass. It is probable

[1] Paternò and Pannain, *Gazz.*, 1904, **34**, [2], 152.

[2] Paternò and Mazzucchelli, *Atti R. Accad. Lincei*, 1907, [5], **16**, i, 465.

[3] Scheerer, *Annalen*, 1860, **116**, 149.

[4] Morey, *J. Amer. Chem. Soc.*, 1914, **36**, 215.

that opal and flint are formed in a similar manner (Kuhlmann). Van Helmont was aware that the substance obtained by fusing silica with an excess of alkali became liquid on exposure to air, and Glauber termed this *liquor silicum.*

Soluble potash glass is prepared in a similar manner to soluble soda glass (p. 293), and closely resembles it in properties. It has been used for a variety of purposes, but its place has mostly been taken by the cheaper soda glass.

Potassium Silicofluoride, K_2SiF_6, is obtained when hydrofluosilicic acid is brought into contact with a solution of a potassium salt. When the acid is added in small quantities no precipitate is observed to form, but soon the liquid begins to exhibit iridescent colours, and after a time the insoluble potassium fluosilicate separates out as a semi-transparent mass. After washing with water and drying, the salt is obtained as a fine white powder sparingly soluble in cold, though easily soluble in hot, water. By slow cooling it may be obtained in the form of bright octahedra, which sometimes show cubic faces (Marignac).

Detection and Estimation of Potassium.

180 The best indication of the presence of potassium compounds is the violet colour which they impart to the non-luminous flame. This tint is, however, not seen if even a small quantity of a sodium compound is present, and it is then necessary to examine the flame by means of the spectroscope. The spectrum thus obtained is that of the metal itself and contains only two characteristic lines :—viz., the double line Kα (7697 and 7663), in the outermost red, approaching the ultra-red rays and below the dark line A of the solar spectrum; and a second line Kβ (4044), situated far in the violet rays, towards the other end of the spectrum, also identical with a dark solar line. Owing to the position of the two lines, Kα and Kβ, both situated near the limit at which our eyes cease to be sensitive to the rays, this reaction for potassium is not very sensitive, but $\frac{1}{100}$ of a milligram can be readily detected. The absorption spectrum of potassium has been mapped by Roscoe and Schuster.[1] It is totally different from the emission spectrum just described, being a

[1] *Proc. Roy. Soc.*, 1874, **22**, 362.

channelled space spectrum. Observed at a low temperature, the green-coloured vapour exhibits a well-marked series of bands, one group in the red (α) and two groups (β and γ) at each side of the sodium line being seen. These bands are all shaded off towards the red, and in general appearance resemble those of the iodine spectrum.

In order to detect and estimate soluble potassium compounds they must be precipitated either as the perchlorate, the phosphotungstate, the acid tartrate, or the chloroplatinate K_2PtCl_6.

Potassium may be detected microchemically by the yellow precipitate or coloration produced with sodium cobaltinitrite and acetic acid,[1] and the same reagent has been proposed for its estimation.[2] Cunningham and Perkin have, however, shown that the method is not reliable.[3]

For the separation of this metal from sodium and for its quantitative estimation, an excess of chloroplatinic acid, H_2PtCl_6, is added to the mixed chlorides; the liquid is then evaporated on the water-bath, and the cooled residue mixed with strong alcohol, in which the excess of chloroplatinic acid and the sodium double salt easily dissolve. The potassium double salt is then collected, dried, and weighed, or its amount estimated indirectly from the amount of platinum or chlorine which it contains. Potassium may also be estimated by adding perchloric acid and alcohol to the concentrated solution, the precipitated potassium perchlorate being washed with a mixture of alcohol and water, dried, and weighed. The perchlorate method is now usually employed for the assay of potassium salts.

The mixed chlorides of potassium and sodium can also be weighed, and then converted into sulphates by treatment with strong sulphuric acid, and the weight of these determined. From these data the amount of potassium (x) and of sodium (y) present can readily be calculated when the molecular weights of the several salts are known. Thus :

$K = 39{\cdot}10$	$Na = 23{\cdot}00$	$K_2 = 78{\cdot}20$	$Na_2 = 46{\cdot}00$
$Cl = 35{\cdot}46$	$Cl = 35{\cdot}46$	$SO_4 = 96{\cdot}07$	$SO_4 = 96{\cdot}07$
74·56	58·46	174·27	142·07

[1] Macallum, *Journ. Physiol.*, 1905, **32**, 95.
[2] Adie and Wood, *Journ. Chem. Soc.*, 1900, **77**, 1076.
[3] *Journ. Chem. Soc.*, 1909, **95**, 1562.

If A represent the weight of the mixed chlorides, and B that of the mixed sulphates, we have :

$$A = \frac{74{\cdot}56}{39{\cdot}10}x + \frac{58{\cdot}46}{23{\cdot}00}y$$

$$B = \frac{174{\cdot}27}{78{\cdot}20}x + \frac{142{\cdot}07}{46{\cdot}00}y$$

Hence the values of x and y can be readily obtained.

A similar result may be obtained by simply ascertaining the amount of chlorine present in the mixed chlorides by titration with silver nitrate solution, but neither of these indirect methods is susceptible of great accuracy.

The atomic weight of potassium was determined by Stas. As a means of eight experiments he found that 100 parts of potassium chlorate yielded 60·846 parts of potassium chloride on ignition. Moreover, 69·103 parts of potassium chloride were needed, as a mean of nineteen experiments, to precipitate 100 parts of silver from solution : and 100 parts of silver, as a mean of seven experiments, gave 132·8445 parts of silver chloride. These experiments give the number 38·85 as the mean for the atomic weight of potassium, the number 35·18 for that of chlorine, and the number 107·12 for that of silver when H = 1 (or K = 39·15, Cl = 35·45, and Ag = 107·93, when O = 16).

A closely agreeing result has been obtained by the analysis of the chloride by Archibald,[1] who found that 100 parts of silver were precipitated as chloride by 69·114 parts of potassium chloride, and that 100 of silver chloride were produced by 52·028 of potassium chloride. Finally, Richards and Staehler[2] have carefully analysed potassium chloride prepared from potassium nitrate, and have found the ratios KCl : Ag = 69·1072 : 100; KCl : AgCl = 52·0118 : 100. The atomic weight of potassium is therefore 38·821 when Ag = 107·12, and Cl = 35·207; or 39·114 when Ag = 107·93, and Cl = 35·473.

The international atomic weight of potassium (1922) is 39·10.

RUBIDIUM. Rb = 85·45. At. No. 37.

181 In the year 1860 Bunsen[3] announced the discovery by means of spectrum analysis of a new alkali metal, to which he

[1] *Trans. Roy. Soc., Canada* [2], **10**, iii., 47.
[2] *Ber.*, 1906, **39**, 3611.
[3] *Berlin Akad. Ber.*, May 10, 1860.

gave the name of *Cæsium*, and in 1861 he discovered by the same method a second new alkali metal, and to this he gave the name *Rubidium*.

These two metals and their compounds possess so close a resemblance, and at the same time give reactions so similar to those of potassium, that they cannot be distinguished either from the well-known alkali or from one another by any of the common wet reactions or blowpipe tests. The only means by which their presence can be readily detected is by their spectrum reactions, and these are so delicate and so characteristic that they serve for the certain recognition of the minutest trace of these two new bodies, whether present alone or mixed with the other alkalis. The metals were first met with by Bunsen in the waters of Dürkheim in the Palatinate, and in the mineral petalite. In these, however, they are contained in such small quantity that, although their presence can be easily recognised in a few drops of the water or in a few grains of the mineral, it was requisite to boil down 40 tons of the water, and to work up 150 kilograms of the mineral, in order to obtain enough of the new metals to serve for the investigation of their compounds.

The following extract from Bunsen and Kirchhoff's second memoir on Spectrum Analysis[1] gives a clear idea of the method by which the presence of the two new metals was first detected:

"If a drop of the mother-liquor of the Dürkheim water be brought into the flame of the spectrum apparatus, the characteristic lines of sodium, potassium, lithium, calcium, and strontium are at once seen. If the lime, strontia, and magnesia be separated according to well-known processes, and if the residual alkali bases in the form of nitrates be washed out with alcohol, and the lithium removed as completely as possible by precipitation with carbonate of ammonium, a mother-liquor is obtained which in the spectrum apparatus shows the lines of sodium, potassium, and lithium, but, besides these, two splendid blue lines situated close together, and almost coinciding with the blue strontium line Srδ. As no known elementary body produces two blue lines in this portion of the spectrum, we may consider the existence of this hitherto unknown alkali element as thus placed beyond doubt.

"The facility with which a few thousandths of a milligram of

[1] *Phil. Mag.*, 1861, [4], **22**, 330.

this body may be recognised by the bright blue light of its incandescent vapour, even when mixed with large quantities of the more common alkalis, has induced us to propose for it the name *Cæsium* (and the symbol Cs), derived from the Latin *cæsius*, used to designate the blue of the clear sky.[1]

"If Saxony lepidolite be treated by any of the known plans for separating the alkalis from the other constituents, and if the solution of the alkalis thus obtained be precipitated with dichloride of platinum, an abundant precipitate is formed, which, when examined in the spectrum apparatus, shows only the bright potassium lines. If this precipitate be repeatedly washed with boiling water, and the residual salt occasionally examined in the apparatus, two splendid violet lines, lying between the strontium line Srδ and the blue potassium line Kβ, will be noticed on the gradually fading continuous background of the potassium spectrum. These new lines increase in brilliancy as the washing is continued, and a number more appear in the red, yellow, and green portions of the spectrum. None of these lines belong to any previously known body. Amongst them are two which are especially remarkable as lying beyond Fraunhofer's line A and the potassium line Kα coincident with it, and therefore situated in the outermost portion of the red solar rays. Hence we propose for this new metal the name *Rubidium* (and the symbol Rb), from the Latin *rubidus*, which was used to express the darkest red colour." [2]

Since this discovery, rubidium has been shown to be widely distributed (see also p. 171), generally accompanying the other alkalis, but in very minute quantities. Rubidium occurs in many minerals, such as lepidolite and triphylite, in Vesuvian leucite, in the porphyrites of the Palatinate, in mica, in Stassfurt carnallite,[3] and in orthoclase. It is also present in nearly all iron ores, except red hæmatite, in many meteorites and in some aluminous minerals, such as bauxite and shale.[4]

The following is the analysis of the lepidolite from Rozena in

[1] Aulus Gellius in his *Noctes Atticæ*, ii., 26, quotes Nigidius Figulus as follows: "Nostris autem veteribus cæsia dicta est, quæ a Græcis γλαυκῶπις ut Nigidius ait, de colore cœli quasi cœlia."

[2] Aulus Gellius, *Noctes Atticæ*, ii, 26. "Rubidus autem est rufus atrior et nigriore multo mustus."

[3] Feit and Kubierschky, *Chem. Zeit.*, 1892, **16**, 335.

[4] Hartley and Ramage, *Journ. Chem. Soc.*, 1897, **71**, 533, 547; *Sci. Proc. Roy. Dublin Soc.*, 1898, N.S., **8**, 703.

Moravia in which Kirchhoff and Bunsen first discovered rubidium:

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Rb_2O.	Cs_2O.	Li_2O.	LiF.
50·32	28·54	0·73	1·01	0·51	0·24	trace	0·70	0·99

NaF.	KF.	H_2O.
1·77	12·06	3·12

A large number of brine springs and mineral waters also contain this alkali. Thus the hot springs of the Ungemach contain in one litre 1·3 milligrams of chloride of rubidium (Bunsen); the mineral water of Bourbonne-les-Bains contains 18·7 milligrams of the same salt, and 32·5 milligrams of cæsium chloride.

The celebrated waters of Ems, Kissingen, Nauheim, Selters, Vichy, Wildbad-Gastein, and many others contain rubidium, and some of them also cæsium compounds. Rubidium has been found in sea-weed and in sea-water (Sonstadt),[1] and also in the mother-liquors (bitterns) from the salterns of Villefranche (Grandeau). Rubidium salts are also widely met with in the vegetable kingdom. Beet-root takes up these salts from the soil, and in the saline residue obtained by calcining the fermented molasses considerable quantities of rubidium salts are contained. Thus 100 parts of the saline residue contain 0·18 part of chloride of rubidium (Grandeau). It has also been found in samples of tobacco grown in the most distant quarters of the globe—such as Algiers, Havana, Kentucky, France, and Macedonia. Rubidium likewise occurs in several kinds of coffee and tea (Grandeau): in the ash of the oak, *Quercus pubescens*, in that of beech trees grown on a basaltic soil, in crude cream of tartar, and in potashes from various sources. Plants cannot, however,, absorb rubidium salts in place of potassium salts, and they die if these latter are not present (Lucanus).

Mode of Preparation of Rubidium Compounds.—According to Bunsen, the best source of rubidium is the saline residue left from the preparation of lithium salts from Saxon lepidolite. This consists of the chlorides of sodium, potassium, and lithium, and traces of the chlorides of cæsium and rubidium. The separation of these metals is based upon the fact that their chlorides form double chlorides with platinic chloride, which are more insoluble than the corresponding potassium double

[1] *Chem. News*, 1870, **22**, 25, 44.

chloride. One kilogram of the saline mixture is dissolved in 2·5 kilograms of water, and the cold liquid precipitated by a solution of thirty grams of platinum in aqua regia. The precipitate, having settled down, is collected, and boiled twenty-five times successively with small quantities of water, in all about 1·5 kilograms, the liquid in each case being added to the solution of the original salt. A fresh precipitate is then formed, this is again washed and treated as the first, and when the above series of operations has been repeated seven or eight times the rubidium is found to be nearly all extracted. Each of the platinum precipitates is then dried, the platinum reduced by hydrogen, and the alkali chlorides dissolved in water. In this way 125 grams of rubidium chloride are obtained, containing three or four per cent. of chloride of potassium, and a little chloride of cæsium. By a repetition of the precipitation and washing of the platinichloride this quantity of potassium impurity can be so completely removed that the well-known red potassium line (Kα) is not seen with a spectroscope when some of the salt is held in the flame (Bunsen).

Another method consists in decomposing lepidolite with sulphuric acid, recrystallising the alums of potassium, cæsium, and rubidium which are formed, decomposing by baryta, treating the alkaline solution with carbon dioxide and converting into the oxalates. These salts are then fractionally crystallised, the potassium salt being the least soluble.[1] Lepidolite may also be decomposed by heating with sulphuric acid and calcium fluoride and the alkalis separated by crystallisation of the alums.[2]

The most important source for the preparation of rubidium salts is the mother-liquor left over in the manufacture of potassium chloride from carnallite, which contains rubidium carnallite, $RbCl,MgCl_2$; by the addition of aluminium sulphate the alum is produced, and by fractional crystallisation the pure rubidium compound can be obtained. The solubilities of the alums (in grams per 100 grams of water) are as follows :

Potash Alum.	Rubidium Alum.	Cæsium Alum.
13·5	2·27	0·619

Numerous other methods for the separation of rubidium and cæsium from potassium have been proposed; amongst these may be mentioned precipitation with stannic chloride,[3] which

[1] Formánek, *Oesterr. Chem. Zeit.*, 1899, **2**, 309.
[2] Browning and Spehcer, *Amer. J. Sci.*, 1916, [4], **42**, 279.
[3] Feit and Kubierschky, *Chem. Zeit.*, 1892, **16**, 335.

converts them into the sparingly soluble stannic chlorides $2RbCl,SnCl_4$ and $2CsCl,SnCl_4$; conversion into the alums, both of which are only slightly soluble in water, and still less soluble in a solution of potash alum[1]; and conversion into the dichloro-iodides, which are much less soluble than the corresponding potassium compounds.[2]

To separate rubidium from cæsium, advantage is taken of the different solubilities of the sparingly soluble salts of the two metals. The platinichlorides do not give good results, but the alums, $Rb_2Al_2(SO_4)_4,24H_2O$ and $Cs_2Al_2(SO_4)_4,24H_2O$, have been successfully employed, the former being about four times as soluble as the latter.[3] The *hydrogen tartrates*, $RbHC_4H_4O_6$ and $CsHC_4H_4O_6$, may also be used, the latter being the more soluble,[4] and the chlorides may be precipitated by hydrogen chloride, the cæsium salt being the more soluble (Archibald).

The best method of separation is that of Godeffroy, which consists in the addition of antimony trichloride to a solution of the chlorides in concentrated hydrochloric acid, when the double cæsium antimony chloride, $3CsCl,2SbCl_3$, is precipitated, but not the rubidium salt.[5] This method is well adapted for obtaining pure cæsium salts, but not for removing the last traces of cæsium from rubidium salts.

182 Metallic rubidium is prepared in an analogous manner to potassium by heating a mixture of the carbonate and charcoal (obtained by the ignition of the hydrogen tartrate) to whiteness in an iron tube, and is also obtained by heating the carbonate or hydroxide with magnesium,[6] the hydroxide with aluminium, rubidium aluminate being then also formed,[7] or the chloride with metallic calcium.[8]

It is a silver-white metal of specific gravity 1·525 at 0°,[9] which at — 10° is still soft and wax-like, melts at 38·5°, boils at 696° (Ruff and Johannsen), and emits at incipient redness a blue

[1] Redtenbacher, *J. pr. Chem.*, 1865, **94**, 442; Setterberg, *Annalen*, 1882, **211**, 100.

[2] Wells, *Amer. Chem. J.*, 1901, **26**, 265; Archibald, *Journ. Chem. Soc*, 1904, **85**, 776.

[3] Redtenbacher, *loc. cit.*; Godeffroy, *Annalen*, 1876, **181**, 176.

[4] Allen, *Amer. J. Sci.*, 1862, [2], **34**, 367.

[5] *Ber.*, 1874, **7**, 375; 1895, **8**, 9; *Annalen*, 1876, **181**, 176; Muthmann, *Ber.*, 1894, **26**, 1019, 1425.

[6] *Ber.*, 1890, **23**, 51; Erdmann and Köthner, *Annalen*, 1896, **294**, 55.

[7] Beketoff, *J. Russ. Chem. Phys. Soc.*, 1888, 363.

[8] Hackspill, *Compt. rend.*, 1905, **141**, 106.

[9] Hackspill, *Ann. Chim. Phys.*, 1913, [8], **28**, 613.

coloured vapour. Like potassium, it appears to form an explosive compound with carbon monoxide. When thrown on water rubidium burns like potassium.

COMPOUNDS OF RUBIDIUM.

183 The compounds as a rule present the greatest similarity to those of potassium and ammonium, and are isomorphous with them (see p. 230).

Rubidium Oxides.—Rubidium *monoxide*, Rb_2O, is obtained by partial oxidation of the metal and subsequent distillation of the excess of rubidium. It forms light yellow, transparent crystals, which melt at 250° and react vigorously with water. The *peroxide*, Rb_2O_2, is obtained by heating rubidium in excess of oxygen; it is a light-yellow, crystalline body. When rubidium is heated for a long time in excess of oxygen, the *tetroxide*, Rb_2O_4, is produced. It is a yellowish-brown, crystalline substance, which melts between 600° and 650° when heated in oxygen. When heated in a vacuum to 600° oxygen is given off, and a blackish mass, the *trioxide*, Rb_2O_3, is left behind. Rb_2O_2 and Rb_2O_4 can also be obtained by the action of oxygen on rubidium dissolved in liquid ammonia at — 50°.[1]

Rubidium Hydroxide, RbOH, is best prepared by adding baryta water to a solution of rubidium sulphate. It forms a greyish-white, deliquescent mass, melts at a red heat, and is volatile in the flame of a Bunsen burner. It is a stronger base than potassium hydroxide.

Rubidium Hydride, RbH, forms colourless, prismatic needles of sp. gr. 2, which decompose below 300° *in vacuo*.[2]

Rubidium Chloride, RbCl.—Rubidium takes fire in chlorine gas, burning with a bright light. The salt crystallises in glittering cubes which melt at 710°. One hundred parts of water dissolve 84·4 parts of the salt at 10°, and 138·9 parts at 100°.

The *bromide* and *iodide* are very similar to the corresponding potassium salts. The latter reacts with liquid sulphur dioxide to form a crystalline sulphone, $RbI_3{,}3SO_2$.[3]

The rubidium halides unite with a large number of metallic chlorides, forming double salts which for the most part crystallise

[1] Rengade, *Compt. rend.*, 1906, **142**, 1533; 1907, **145**, 236; *Ann. Chim. Phys.*, 1907, **11**, 348.

[2] Moissan, *Compt. rend.*, 1903, **136**, 587.

[3] De Forcrand and Taboury, *Compt. rend.*, 1919, **168**, 1253; **169**, 162.

well. Rubidium also forms compounds with a larger number of halogen atoms much more readily than potassium, the compounds being also more stable. The following are known, and are all crystalline: $RbBr_3$, $RbClBr_2$, $RbCl_2Br$, RbI_3, $RbBr_2I$, $RbCl_2I$, $RbClBrI$, $RbCl_4I$.[1] The solid polyiodides, RbI_7 and RbI_9, exist at 25°, but have not been prepared pure.[2]

Rubidium Chlorate, $RbClO_3$, is obtained by the double decomposition of rubidium sulphate and barium chlorate. It crystallises in small prisms which taste like potassium chlorate and of which 2·8 parts dissolve in 100 parts of water at 4·7° and 5·1 parts at 19°.

Rubidium Perchlorate, $RbClO_4$, is a granular powder consisting of glittering microscopic crystals belonging to the rhombic system. When heated below redness it decomposes into rubidium chloride and oxygen. One hundred parts of water dissolve 1·085 parts of the salt at 21·3°.

Rubidium Sulphides.[3]—The *monosulphide*, $Rb_2S,4H_2O$, is obtained by the action of hydrogen sulphide on a solut on of the hydroxide, and precipitation with alcohol. The *tetrasulphide*, $Rb_2S_4,2H_2O$, is obtained by adding the calculated quantity of sulphur to a solution of the monosulphide. When an excess of sulphur is added to a solution of the monosulphide, and the mixture is heated in an atmosphere of hydrogen, the *pentasulphide*, Rb_2S_5, is produced. The pentasulphide when heated in an atmosphere of nitrogen is converted into the *trisulphide*, Rb_2S_3, but when heated in an atmosphere of hydrogen the *disulphide* is formed.

Normal Rubidium Sulphate, Rb_2SO_4, forms large rhombic crystals which taste like potassium sulphate. One hundred parts of water dissolve 42·6 parts at 10°, and 81·8 at 100°.

Rubidium Selenate, Rb_2SeO_4, has the density 3·9: 100 parts of water dissolve 158·9 parts of the salt at 12° (Tutton).

Rubidamide, $RbNH_2$, is formed by the action of rubidium on liquid ammonia, and by reaction with sodamide in that solvent forms *mono-* and *di*-rubidium ammonosodiates, $Rb[Na(NH_2)_2]$, and $Rb_2[Na(NH_2)_3]$.[4]

Rubidium Nitrate, $RbNO_3$, crystallises in needles or prisms,

[1] *Amer. J. Sci.* [3], 1892, **43**, 475; **44**, 42; 1893, **46**, 88, 269; *Amer. Chem. J.*, 1896, **18**, 847; *Zeit. physikal. Chem*, 1899, **28**, 523.

[2] Abegg, *Zeit. anorg. Chem.*, 1906, **50**, 403.

[3] Biltz and Wilke-Dorfurt, *Ber.*, 1905, **38**, 123; *Zeit. anorg. Chem.*, 1906, **50**, 67.

[4] Franklin, *J. Physical Chem.*, 1919, **23**, 36.

and is very soluble in water, 100 parts of which dissolve, at 0°, 19·5, and at 100°, 452 parts. It is distinguished from nitre by readily dissolving in concentrated nitric acid.

Rubidium Carbonate, Rb_2CO_3.—The normal salt is obtained by decomposing the sulphate with baryta water and evaporating the filtrate with ammonium carbonate. It is a deliquescent powder which is very soluble in water. If the solution of this salt be saturated with carbon dioxide and evaporated over sulphuric acid, glittering prisms of the acid salt, $HRbCO_3$, are obtained; these have a cooling taste, and are easily soluble in water.

Detection and Estimation of Rubidium.

184 The rubidium salts when brought into the non-luminous gas flame impart to it a tint of a rather more red shade than is produced by the potassium salts.

The flame spectrum (p. 158) exhibits two characteristic lines in the violet Rbα (4202) and Rbβ (4216). These are the most valuable as the means of recognising the rubidium salts. Two other rubidium lines, Rbδ (7950) and Rbγ (7799), are seen at the red end of the spectrum; they are both less refrangible than the red potassium lines. Besides these several other characteristic lines occur. The spectrum reaction for rubidium is so delicate that 0·002 mgrm. can be readily detected (Bunsen), and the method may be adapted for the approximate estimation of small amounts of rubidium in presence of potassium.[1]

Rubidium can be estimated in the same way as potassium either by precipitation as the platinichloride or the perchlorate.[2]

Bunsen determined the atomic weight of the metal by precipitating the pure chloride by silver nitrate. He found as a mean result the number 84·8 for the atomic weight of rubidium. Grandeau obtained a closely corresponding number by the analysis of the sulphate, the same number being also found by Godeffroy, whilst Archibald by the analysis of the bromide found the number 84·841 (H = 1); 85·485 (O = 16).[3] The value at present accepted (1922) is 85·45.

[1] Wilke-Dorfurt, *Zeit. anorg. Chem.*, 1912, **75**, 132.
[2] See also *Gazz.*, 1903, **33**, [2], 189.
[3] *Journ. Chem. Soc.*, 1904, **85**, 776.

CÆSIUM. Cs = 132·81. At. No. 55.

185 This metal is remarkable not only as having been the first one discovered by spectrum analysis, but also because even before Bunsen's discovery of this metal, chemists had investigated certain cæsium compounds, which, however, they had mistaken for potassium salts. Thus, in the year 1846, Plattner analysed a rare mineral found in the island of Elba and termed pollux,[1] with the result given in column I.

	I.	II.
Silica	46·20	44·03
Alumina	16·39	15·97
Ferric oxide	0·86	0·68
Potash	16·51	—
Soda	10·47	3·88
Water	2·32	2·40
Lime	—	0·68
Cæsia	—	31·07
	92·75	101·71

Plattner, being a careful experimentalist, sought for an explanation of the fact that his analysis did not add up to 100 parts, although he searched in vain for all other constituents. The explanation of the enigma was given by the discovery of cæsium, for Pisani,[2] in the year 1864, found on analysis of another sample of the same mineral that the alkali which Plattner had mistaken for potassium was in reality cæsium. His analysis is given in column II.

If now we calculate the quantity of cæsium oxide corresponding to the amount of potash found by Plattner as the platinum double salt, we obtain the number 35·69; if next we subtract the weight of the chloride of cæsium thus found from the weight of the mixed chlorides of cæsium and sodium as found by Plattner, we obtain the number 1·72 as the amount of soda present. These numbers correspond satisfactorily with Pisani's results, especially when we remember that the quantity of mineral analysed by Plattner was very small. Both analyses, therefore, lead to the following formula for pollux:

$$10SiO_2 + 5(Cs_2O,Na_2O,CaO) + 2(Al_2O_3,Fe_2O_3) + 2H_2O.$$

[1] *Pogg. Ann.*, 1846, **99**, 443. [2] *Compt. rend.*, 1865, **60**, 714.

The mineral pollux, or *pollucite*, is the best source of cæsium, which may be extracted from it by treatment with hydrochloric acid and purified by recrystallisation of the alum.[1]

It has already been mentioned under rubidium that cæsium occurs generally together with this and the other alkali metals. Cæsium alone is found in the mineral waters of Frankhausen, of Monte Latino in Tuscany, as well as in the Wheal Clifford Spring, one litre of this latter water containing 1·71 mgrms. of cæsium chloride (Yorke). It is a remarkable fact that plants do not take up any cæsium compounds from the soil, and in absence of potassium compounds cæsium acts as a poison upon vegetable life (Lucanus). The sources from which cæsium is derived, and its separation from other metals and finally from rubidium, have already been described under the latter metal. Cæsium was obtained by Setterberg by the electrolysis of a mixture of cæsium and barium cyanides, and by Beketoff by heating cæsium hydroxide with aluminium to a bright red heat in a nickel retort. It can also be prepared by heating the carbonate [2] or hydrate [3] with magnesium, or the chloride with calcium [4] in a vacuum. The metal is of silver-white colour, takes fire when heated in the air, melts at 26·4°, boils at 670° (Ruff and Johannsen), and has a specific gravity of 1·903 at 0°.[5] When exposed to the air it gradually melts and takes fire, and when thrown into water it remains on the surface and burns with a reddish-violet flame (Graefe and Eckardt). In the presence of mercury an amalgam is formed which is more electro-positive than rubidium amalgam, and hence metallic cæsium is the most electro-positive of the metals.

COMPOUNDS OF CÆSIUM.

186 The cæsium compounds are isomorphous with those of potassium, rubidium, and ammonium (p. 230). They colour the flame a still more reddish tint than do the salts of rubidium.

Cæsium Monoxide, Cs_2O, may be obtained by exposing cæsium to an insufficient amount of oxygen in a silver boat, exhausting

[1] Browning and Spencer, *Amer. J. Sci.*, 1916, [4], **42**, 279.

[2] Erdmann and Menke, *J. Amer. Chem. Soc.*, 1899, **21**, 259.

[3] Graefe and Eckardt, *Zeit. anorg. Chem.*, 1899, **22**, 158.

[4] Hackspill, *Compt. rend.*, 1905, **141**, 106.

[5] Hackspill, *Ann. Chim. Phys.*, 1913, [8], **28**, 613; see also Setterberg, *Annalen*, 1882, **211**, 100; Eckardt and Graefe, *Zeit. anorg. Chem.*, 1900, **23**, 378; Menke, *J. Amer. Chem. Soc.*, 1899, **21**, 420.

the apparatus and distilling off the excess of metal.[1] It forms orange-red crystals, which become darker when heated and melt at 450–500° and then lose cæsium, forming a higher oxide. It absorbs water and carbon dioxide from the air, and is rendered incandescent by the addition of water, a colourless solution of the hydroxide being produced.

Cæsium Hydroxide, CsOH, is obtained by a process similar to that by which rubidium hydroxide is prepared, and resembles it closely; it is the strongest of all bases.

Peroxides of Cæsium.—When molten cæsium is exposed to oxygen and the mass heated to 300–350°, the *peroxide*, CsO_2, is formed as a yellow crystalline powder, which readily dissociates when further heated and is decomposed by water with formation of cæsium hydroxide and hydrogen peroxide, and evolution of oxygen. This oxide is also formed by the action of oxygen on cæsium dissolved in liquid ammonia, the oxides Cs_2O_2 and Cs_2O_3 being intermediate products.[2]

Cæsium Chloride, CsCl, crystallises in small cubes of sp. gr. 3·972, which melt at a dull red heat, and volatilise even more readily than potassium chloride. It deliquesces in moist air; 100 parts of water dissolve 174·7 parts of the salt at 10°. The *bromide*, sp. gr. 4·38, and *iodide* are similar to the corresponding potassium salts, and the latter forms a sulphone, $CsI_3,3SO_2$, with liquid sulphur dioxide, analogous to those of sodium and rubidium. Like the rubidium halides, the cæsium derivatives form a very large number of well-crystallised double salts with other metallic halides. A number of polyhalide salts are also known, most of which are crystalline; among these may be mentioned $CsBr_3$, $CsBr_5$, CsI_3, and $CsCl_4I$ (Wells, Penfield, and Wheeler). The polyiodide, CsI_9, exists at 25°, but has not been isolated (Abegg).

Cæsium Sulphides.—Cæsium forms the same series of sulphides as rubidium, and their preparation is similar. The *pentasulphide* melts at 202°.

Normal Cæsium Sulphate, Cs_2SO_4, forms short, hard, prismatic crystals of sp. gr. 4·24, insoluble in alcohol, though readily soluble in water. The *acid salt*, $CsHSO_4$, crystallises in rhombic prisms.

Cæsium Selenate, Cs_2SeO_4, has the sp. gr. 4·4528; 100 parts of water dissolve 244·8 parts of the salt at 12°.[3]

[1] Rengade, *Compt. rend.*, 1906, **143**, 592.

[2] *Ibid.*, 1905, **140**, 1183; 1906, **142**, 1149; *Zeit. anorg. Chem.*, 1906, **50**, 67.

[3] Tutton, *Journ. Chem. Soc.*, 1897, **71**, 846.

Cæsium Nitrate, $CsNO_3$, crystallises in small glittering prisms which possess the cooling taste of saltpetre, and are slightly soluble in alcohol. One hundred parts of water at 3·2° dissolve 10·58 parts of this salt. It has the sp. gr. 3·687, and melts at 414°.

Normal Cæsium Carbonate, Cs_2CO_3.—This salt separates out from a syrupy solution in the form of ill-defined hydrated deliquescent crystals. They melt on heating, leaving a residue of the anhydrous salt as a sandy powder. It is soluble in absolute alcohol. One hundred parts of alcohol dissolve at 19°, 11·1, and at the boiling point, 20·1 parts of the anhydrous salt. The *acid salt*, $CsHCO_3$, crystallises from aqueous solution in large prisms.

Cæsium Hydride,[1] CsH, and *Cæsium Amide*,[2] $CsNH_2$, closely resemble the corresponding potassium compounds.

Detection and Estimation of Cæsium.

The spectrum of cæsium contains, in addition to the two characteristic bright blue lines, Csα and Csβ (4555 and 4593), several other less distinct lines.

The atomic weight of cæsium has been ascertained by the analysis of the halogen salts by means of silver nitrate. Johnson and Allen as well as Bunsen thus obtained the number 132·0, whilst Godeffroy obtained the number 131·6.

Richards and Archibald [3] by the analysis of the chloride and bromide, and by heating the nitrate with silica, have obtained the value 131·874 (H = 1), 132·879 (O = 16). The material employed was purified by recrystallisation of the dichloroiodide, $CsCl_2I$. The value at present accepted (1922) is 132·81.

AMMONIUM COMPOUNDS.

187 The name *volatile alkali* was long ago given to ammonia as pointing out its similarity to the fixed alkalis potash and soda. In 1808, Seebeck made the interesting discovery that when mercury is brought into a strong aqueous solution of ammonia, and an electric current passed through it, the metal increases rapidly in bulk, giving rise to an amalgam-like mass. The same observation was made almost simultaneously by Berzelius and Pontin, whilst Davy, as soon as he was informed of the fact.

[1] Moissan, *Compt. rend.*, 1903, **136**, 587.
[2] Rengade, *Compt. rend.*, 1905, **140**, 1536.
[3] *Zeit. anorg. Chem.*, 1903, **34**, 353.

repeated the experiment and discovered that a piece of sal-ammoniac moistened with water might be employed instead of aqueous ammonia. Davy also noticed that the same amalgam-like mass is formed when an amalgam of potassium is thrown into a concentrated solution of sal-ammoniac. Hence he, like Berzelius, concluded that ammonia must contain oxygen, and that in this experiment it, like potash and soda, had been reduced by the electricity to a metal-like body. To this metal-like substance, which was supposed to exist in this amalgam, they gave the name of *ammonium*. This view of the constitution of the ammonium compounds was objected to by Gay-Lussac and Thénard, who, from their observation that the amalgam undergoes rapid spontaneous decomposition into mercury, ammonia, and hydrogen gas, concluded that the formation of the amalgam is due to a combination of the ammonia with hydrogen. Arguing from analogy, the French philosophers were inclined to believe that in like manner potassium and sodium could not be considered to be true metals, but were rather the hydrogen compounds of the alkalis. In reply to these objections, Davy and Berzelius showed that the hydrogen which was evolved might arise from the decomposing action of the metallic ammonium upon the water which adhered to it, in the same way as hydrogen is evolved when sodium and potassium are thrown into water. Berzelius continued for many years to hold the view that oxygen is contained in ammonia, and he explained the fact that this element could not be detected in the ammonia, by assuming that nitrogen itself is an oxide of an element hitherto not isolated, to which he gave the name of *nitricum*.

Ampère was the first, in the year 1816, to endeavour to explain the analogy of the ammoniacal salts with those of the fixed alkalis. He showed that the differences in composition between the salts of a fixed and those of the volatile alkali disappear when we assume that, in the latter class of salts, a compound radical exists composed of one volume of nitrogen to four volumes of hydrogen, so that sal-ammoniac or hydrochloride of ammonia may be regarded as the chloride of the metal-like substance to which the name of ammonium had been given. In 1820 Berzelius gave up his old view, and accepted the ammonium theory. He showed that aqueous ammonia must be regarded as a solution of ammonium oxide, and assumed that when anhydrous ammonia unites with a hydrogen acid (a substance to which we now give

the simple name of acid) the ammonia combines with the hydrogen of the acid to form the metal-like radical ammonium, and that this becomes an oxide by union with the oxygen of the water.

According to our present views, the ammonium salts are considered as being derived from acids by the replacement of their hydrogen by the radical ammonium, NH_4. These salts are isomorphous with the salts of potassium, rubidium, and cæsium, and exhibit a close analogy with them (p. 230).

Ammonium Amalgam.—This substance, as has already been mentioned, is formed when a piece of moistened sal-ammoniac is laid in a platinum basin, a small quantity of mercury poured upon it, and this brought in contact with the negative pole of an electric battery, the positive pole being connected with the platinum basin. It may be obtained still more readily by throwing sodium amalgam containing 1 per cent. of sodium into a concentrated solution of sal-ammoniac. The mercury increases in bulk to upwards of twenty times its original volume, and then contains from 0·6 to 0·9 per cent. of its weight of ammonium. It is also produced by the action of sodium amalgam on ammonium chloride dissolved in liquid ammonia at $-35°$.[1] This amalgam forms, at the ordinary temperature, a light, soft, buttery mass which at $-80°$ becomes a very hard metallic mass, and begins to liquefy at $-40°$, and decomposes, even at $-29°$, with evolution of two volumes of ammonia and one volume of hydrogen.

The nature of this remarkable substance has been the subject of much discussion. Some chemists have supposed that it must be regarded merely as a solution of ammonia and hydrogen in mercury, or as a metallic froth. Against this view, however, it is to be remembered that neither of these gases, either alone or when mixed together, dissolves at all in mercury. Others again support the view that ammonium amalgam is a true amalgam containing the metallic radical ammonium. Ammonium amalgam differs, however, from the amalgams of the alkali metals, inasmuch as it does not reduce the salts of silver and copper at the ordinary temperature,[2] and this fact was for long considered to be strong evidence against this opinion. It has, however, been found that at 0° this reduction readily occurs, and that the amalgam is even capable

[1] Moissan, *Compt. rend.*, 1901, **133**, 803.

[2] Landolt, *Annalen*, 1868, Suppl., **6**, 342.

of reducing the salts of cadmium and zinc.[1] The view that ammonium amalgam is in reality analogous to the amalgams of sodium and potassium is confirmed by the fact that the depression of the freezing point of mercury produced by the presence of the ammonium is similar to that produced by sodium or potassium.[2] Moreover, the effect of the amalgam on the magnitude of polarisation of a battery is comparable with that of the amalgams of the alkali metals.[3]

When ammonium amalgam decomposes, it appears to give off positively charged ions, the nature of which is unknown.[4]

All efforts to isolate the radical ammonium, either from the amalgam or from the salts, have hitherto failed. It does not appear to be produced by the electrolysis of ammonium iodide in liquid ammonia at $-95°$ [5]; nor is it formed in various reactions, such as the interaction of calcium with ammonium chloride at a low temperature in presence of liquid ammonia.[6] In all these cases ammonia and hydrogen are the products and hence it is probable that "ammonium" can only exist, if at all, at very low temperatures.

Potassammonium and Sodammonium. — When metallic potassium or sodium is added to liquid ammonia, a blue solution is formed which on evaporation leaves a copper-coloured mass of the composition NH_3K or NH_3Na.

Similar substances are formed by lithium, rubidium, cæsium, calcium, strontium, and barium.[7] They are also formed when ammonia is passed over these metals, and for each metal there is a limit of temperature above which the change does not occur. It has hitherto been supposed that these substances are compounds of ammonia with the metals in question, but the experiments of Ruff and Geisel [8] show that in all probability the change consists simply in the formation of a solution of the metal in ammonia, the copper-coloured residue being composed of the solid metal and its saturated solution, which can be separated by filtration through a cloth under pressure.

[1] Coehn, *Zeit. anorg. Chem.*, 1900, **25**, 430.

[2] Rich and Travers, *Journ. Chem. Soc.*, 1906, **89**, 872.

[3] Le Blanc, *Zeit. physikal. Chem.*, 1890, **5**, 467.

[4] Coehn, *Chem. Centr.*, 1906, ii., 409; *Zeit. Elektrochem.*, 1906, **12**, 609.

[5] Ruff, *Ber.*, 1901, **34**, 2604.

[6] Moissan, *Compt. rend.*, 1901, **133**, 715, 771.

[7] Joannis, *Ann. Chim. Phys.*, 1906 [8], **7**, 5; Roederer, *Compt. rend.*, 1905, **140**, 1252; Moissan, *Compt. rend.*, 1892, **127**, 685; 1901, **133**, 715; 1903, **136**, 1177.

[8] *Ber.*, 1906, **39**, 828.

All the solutions of the metals in ammonia gradually decompose, forming the amide of the metal and free hydrogen; platinised asbestos much accelerates the change.

The metals in this form are extremely reactive, and these solutions have been employed in the preparation of many metallic compounds.

Ammonium Peroxide.—A crystalline compound of the composition $(NH_4)_2O_2,H_2O_2$, melting at 14°, is formed when an ethereal solution of hydrogen peroxide is saturated with ammonia at — 10°. It decomposes slowly at this temperature into ammonia and hydrogen peroxide, but at the ordinary temperature yields ammonia, water, and oxygen, a small amount of ammonium nitrite being also formed.[1]

By the continued action of ammonia on ethereal hydrogen peroxide at — 40° a heavy oily layer separates which freezes to solid crystalline ammonium peroxide, $(NH_4)_2O_2$ melting at — 2° and readily losing ammonia even at —10°.[2]

Ammonium and the Halogens.

188 *Ammonium Fluoride,* NH_4F, is obtained by saturating hydrofluoric acid with ammonia. The commercial hydrofluoric acid, however, generally contains lead and other metals which must be previously removed by the addition of a small quantity of ammonium carbonate and sulphide. The clear acid liquid is saturated with solid ammonium carbonate and then evaporated in a platinum basin, ammonium carbonate being added at intervals to prevent the formation of the acid fluoride. Ammonium fluoride crystallises in hexagonal tablets or prisms. It has a sharp saline taste and deliquesces in moist air, is more easily soluble in water than sal-ammoniac, and decomposes at the ordinary temperature when in the moist state. It decomposes silicates on being heated with them, with evolution of silicon tetrafluoride, and hence it is largely used in mineral analysis and for etching upon glass. This may be readily accomplished by allowing a solution of the salt to dry upon the place which it is desired to etch. It cannot be preserved in glass bottles, but must be kept in vessels either of platinum, silver, or guttapercha.

[1] Melikoff and Pissarjewsky, *Ber.*, 1897, **30**, 3144; 1898, **31**, 152, 446.
[2] D'Ans and Wedig, *Ber.*, 1913, **46**, 3075.

By the action of dry ammonium fluoride on sulphuric acid containing about 70% of sulphur trioxide, *ammonium fluorosulphonate*, NH_4SO_3F, is produced, as a crystalline salt melting at 245°.[1]

Hydrogen Ammonium Fluoride, NH_4F,HF, is formed when a solution of the normal salt is evaporated at a temperature of about 40°. It crystallises in colourless rhombic prisms which deliquesce slightly in the air and on heating evolve highly irritating and acrid fumes.

Ammonium Chloride, NH_4Cl.—The history of this salt, well known under the name of sal-ammoniac, has already been given in Vol. I., p. 504. It is found in the fumeroles of Vesuvius, Etna, Hecla, and other volcanoes, as well as in the cracks and fissures in recent lava streams. Its formation has also been observed when large masses of coal undergo combustion, as when a coal pit is on fire. The salt has also been observed in guano from the Chincha Islands.

Sal-ammoniac originally served as the source from which all the ammoniacal salts were prepared. At present, however, these are usually obtained from ammonium sulphate, which is prepared from the ammoniacal liquor of the gasworks on an enormous scale. For the manufacture of the chloride, gas liquor is sometimes distilled with lime in the manner described under ammonium sulphate, and the ammonia evolved absorbed in hydrochloric acid of sp. gr. 1·1 contained in a stone saturator. More usually now, a crude fairly concentrated *liquor ammoniæ* is first prepared by the distillation of gas-liquor, as described in Vol. I., p. 511, and then neutralised with hydrochloric acid, or a solution of ammonium sulphate is boiled with the equivalent quantity of sodium chloride, when double decomposition takes place:

$$(NH_4)_2SO_4 + 2NaCl = 2NH_4Cl + Na_2SO_4.$$

The sodium sulphate separates first on concentration and is removed by "fishing." The solution of ammonium chloride obtained by any of these methods is then evaporated to the crystallisation point, and the crude product purified by recrystallisation or more frequently by sublimation. The vessel employed for this purpose consists of two parts. The lower one is either a semicircular earthenware vessel embedded in an iron one, or consists entirely of a cast-iron basin. The sal-

[1] Traube, Hoerenz, and Wunderlich, *Ber.*, 1919, **52**, [*B*], 1272.

ammoniac in the solid state is brought into this, and then a semicircular dome-like cover, either of earthenware, lead, or iron, is placed over it, and this is luted tight with clay. In the centre of the dome there is an opening which is left open during the sublimation. Pure sal-ammoniac is also obtained by employing the same apparatus, but, instead of the impure salt, a mixture of common salt, NaCl, and ammonium sulphate, $(NH_4)_2SO_4$, is heated, when sodium sulphate remains behind. sal-ammoniac subliming as before.

Pure ammonium chloride is colourless and odourless and has a sharp saline taste. It crystallises from a saturated solution in arborescent or feather-like growths which consist of an aggregation of small regular octahedra, and other forms of the regular

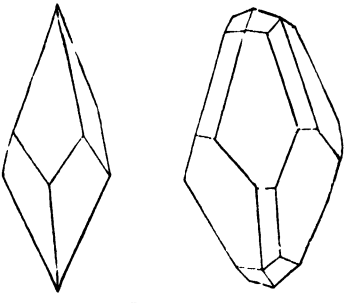


FIG. 107.

system (class 29, p. 209), so that the crystals appear to belong to the hexagonal or tetragonal system (Fig. 107). From a solution containing urea, sal-ammoniac crystallises in cubes. When the salt is sublimed, and the vapour quickly cooled, it is precipitated in the form of a light crystalline powder known as flowers of sal-ammoniac. The common sublimed sal-ammoniac is a semi-transparent, fibrous, crystalline mass, which is so tough that it is difficult to powder. For the purpose of obtaining it in a fine powder, a concentrated solution is evaporated down and constantly stirred. Ammonium chloride exists in two enantiotropic forms, the transition point being 184·5°.[1]

When sal-ammoniac dissolves in water a considerable reduction of temperature takes place; 30 parts of salt dissolve in 300 parts of water at 13·3°, and the temperature is reduced to — 5·1° (Rüdorff). One hundred parts of water dissolve, at 0°, 29·7, at

[1] Wallace, *Centr. Min.*, 1910, **33**; Scheffer, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1498.

10°, 33·3, and at 110°, 83·8 parts of the salt; the boiling point of the saturated solution is 115·6°.

Sal-ammoniac is very sparingly soluble in absolute alcohol, of which 100 parts dissolve 0·62 part of the salt at 19°. The specific gravity of sal-ammoniac is 1·52.

The salt is slightly hydrolysed in aqueous solution,[1] and when the solution is boiled, ammonia escapes in small quantity, the liquid, which is at first neutral to litmus, becoming slightly acid. It is not volatile at the ordinary temperature of the air, but at higher temperatures it evaporates completely, giving rise to a colourless vapour, which, according to Bineau, has the specific gravity 0·89, corresponding to a vapour density of 13·345, whilst the molecular formula, NH_4Cl, requires a density of 26·69. From the fact of the abnormal density it has been argued that the sal-ammoniac vapour consists of a mixture of equal molecules of ammonia and hydrochloric acid. The truth of this supposition was first experimentally demonstrated by Pebal,[2] who allowed the vapour of sal-ammoniac to diffuse into an atmosphere of hydrogen, when the lighter ammonia was found to diffuse out and the heavier hydrochloric acid to remain behind. Karl von Than[3] then showed that if ammonia and hydrogen chloride be brought together at a temperature of upwards of 350°, at which point sal-ammoniac is gaseous, no change either of temperature or of the volume of the gases is observed, whereas if chemical union had taken place a change of both of these would naturally have been expected. Marignac[4] further observed that in the volatilisation of sal-ammoniac nearly the same amount of heat is absorbed as is evolved when ammonia and hydrochloric acid combine. It has also been shown that under diminished pressure and in an atmosphere of ammonia the vapour density of ammonium chloride is 24·2–24·6, showing that under these conditions nearly the whole of the ammonium chloride volatilises without dissociation,[5] whilst if the ammonium chloride employed be absolutely dry it has the normal vapour density even under atmospheric pressure.[6]

This fact of the dissociation of sal-ammoniac can be readily shown by igniting a small piece of the solid in a closed platinum crucible. On removing the lid after the salt has been volatilised,

[1] Veley, *Journ. Chem. Soc.*, 1905, **87**, 26.
[2] *Annalen*, 1862, **123**, 199.
[3] *Annalen*, 1864, **131**, 129.
[4] *Compt. rend.*, 1869, **68**, 877.
[5] Neuberg, *Ber.*, 1891, **24**, 2543.
[6] Baker, *Journ. Chem. Soc.*, 1894, **65**, 615.

and plunging a moistened piece of blue litmus paper into the crucible, the litmus paper will be turned bright red, proving the presence of free hydrochloric acid, the lighter ammonia having escaped.

Sal-ammoniac is used in medicine. In former days that which came from Egypt was especially esteemed as a drug. Large quantities are used in the processes of dyeing, and workers in metal employ it in the processes of soldering and tinning, as at a high temperature it either reduces the metallic oxide or converts it into fusible chloride and thus gives rise to a bright metallic surface. It is also of value in the laboratory, both as a reagent and as a convenient source of ammonia.

Ammonium Bromide, NH_4Br, is very soluble in water, and crystallises in white cubes which taste like sal-ammoniac. Like the chloride, it exists in enantiotropic forms, the transition temperature being 137·3°.[1]

Ammonium Iodide, NH_4I, is best obtained by saturating ammonia with hydriodic acid. It crystallises in colourless cubes readily soluble in water and in alcohol, and appears to exist in one form only.[2] It deliquesces in moist air and gradually assumes a yellow colour due to the slow liberation of iodine.

A *dibromoiodide*, NH_4Br_2I, analogous in composition to the rubidium trihalogen compounds, has been described.[3]

Ammonium Chlorate, NH_4ClO_3.—When ammonia is saturated with chloric acid and the solution evaporated, this salt crystallises out in small needles, which have a strongly acrid taste and are very soluble in water and slightly soluble in absolute alcohol. Heated to 102° the salt decomposes (Wächter), chlorine, oxygen, nitrous oxide, and aqueous vapour being evolved, and sal-ammoniac remaining behind. Occasionally the salt undergoes spontaneous decomposition. When thrown on to a hot plate it decrepitates like ammonium nitrate.

Ammonium Perchlorate, NH_4ClO_4, is obtained by saturating ammonia with perchloric acid. It forms rhombic crystals, which are isomorphous with potassium perchlorate and dissolve in 5 parts of cold water. It has been employed as a constituent of explosives, for which purpose it may be prepared by the interaction of concentrated solutions of ammonium nitrate and sodium perchlorate.[4]

[1] Scheffer, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1498.
[2] Smith and Eastlack, *J. Amer. Chem. Soc.*, 1916, **38**, 1500.
[3] Jackson and Derby, *Amer. Chem. J.*, 1900, **24**, 15.
[4] Alvisi, *Gazz.*, 1899, **29**, [1], 121, 478.

Ammonium and Sulphur.

189 The method of preparing volatile compounds of sulphur has long been known. Thus, for instance, the writer who assumed the name of Basil Valentine states that a blood-red oil may be obtained by distilling together common sulphur, quicklime, and sal-ammoniac. He also says: "Take grey sulphur and quicklime a pound, sal-ammoniac a fourth part; rub these together, when a splendid red oil is obtained, which fixes and refines." Beguin was also acquainted with this mode of preparation in the seventeenth century, and this salt was known as *spiritus sulphuris volatilis Beguinii*. Boyle in 1663 observed that the vapours of this body possessed the power of blackening metals, and he therefore termed it a volatile tincture of sulphur, and this same substance was known to the later chemists as *spiritus fumans Boylei*. This is a mixture of several sulphides of ammonium. Boerhaave in 1732 was the first to mention the fact that flowers of sulphur dissolve in ammonia, the substance thus obtained being known as volatile liver of sulphur. The preparation of the compound by leading sulphuretted hydrogen into ammonia was described by Kirwan in 1786.

Ammonium Sulphide, $(NH_4)_2S$, is obtained in colourless micaceous crystals by passing a mixture of sulphuretted hydrogen with a slight excess of ammonia into a vessel cooled to $-18°$, ammonium hydrosulphide being also formed. At the same time a very volatile liquid is condensed, which has the composition $(NH_2)_2S,2NH_3$. Ammonium sulphide readily dissolves in water, but the properties of the solution render it probable that it is at the same time partially dissociated into ammonium hydrosulphide and ammonia.[1]

Ammonium Hydrosulphide, NH_4HS, is obtained by mixing sulphuretted hydrogen and ammonia in equal volumes at the ordinary temperature, and forms a porcelain-like mass; it is also formed if the sulphuretted hydrogen be present in slight excess, but is not the only product in presence of excess of ammonia. Its aqueous solution is obtained by saturating ordinary strong ammonia solution, diluted with four times its volume of water, with sulphuretted hydrogen, the strongest solution obtainable containing 16–19 per cent. of NH_4HS. If the solution of ammonia be more concentrated, compounds of the general formula

[1] Bloxam, *Journ. Chem. Soc.*, 1895, **67**, 283.

$(NH_4)_2S,xNH_4HS$ are formed, the value of x decreasing step by step with the increase in the concentration of the solution. Thus with ammonia of specific gravity 0·880 the compound formed has the composition $(NH_4)_2S,2NH_4HS$, and separates, when the solution is cooled to 0°, in leaf-like crystals. Crystals having the composition $(NH_4)_2S,6NH_4HS$, $(NH_4)_2S,12NH_4HS$, and $(NH_4)_2S,18NH_4HS$ have also been prepared. The ammonium sulphide solution employed in the laboratory consists, therefore, of ammonium sulphide, hydrosulphide, hydroxide, and free ammonia in proportions varying with the concentration, and it also almost always contains a small quantity of polysulphides, which impart to it a yellow colour, these being formed by the action of the solution on the sulphur obtained from its partial oxidation.

Ammonium Polysulphides. — Compounds containing more sulphur than the foregoing are obtained by the action of sulphur on solutions of ammonium sulphide; these were first examined by Fritsche, who described the tetrasulphide, $(NH_4)_2S_4$, the pentasulphide, $(NH_4)_2S_5$, and the heptasulphide, $(NH_4)_2S_7$, and regarded these as formed by the direct addition of sulphur to ammonium sulphide. The subject has again been investigated by Bloxam,[1] who has found that the formation of these compounds does not proceed in so simple a manner. The solutions of ammonium sulphide, which as above mentioned usually contains the hydrosulphide, sulphide, and free ammonia, acts on the sulphur with evolution of sulphuretted hydrogen and formation of two tetrammonium polysulphides, viz, the *enneasulphide*, $(NH_4)_4S_9$, and the *heptasulphide*, $(NH_4)_4S_7$, both of which crystallise in yellow needles, and contain respectively seven and four molecules of water. These compounds by their decomposition give rise to the diammonium polysulphides, of which the following have been obtained in the crystalline form:

Ammonium tetrasulphide, $4(NH_4)_2S_4,H_2O$.
Ammonium pentasulphide, $(NH_4)_2S_5,H_2O$.
Ammonium heptasulphide, $3(NH_4)_2S_7,4H_2O$.
Ammonium enneasulphide, $2(NH_4)_2S_9,H_2O$, and $5(NH_4)_2S_9,4H_2O$.

190 *Normal Ammonium Sulphate*, $(NH_4)_2SO_4$.—We find this salt mentioned by Libavius, but more accurately described by Glauber, who recommended its use as a medicine. It was long

[1] *Journ. Chem. Soc.*, 1895, **67**, 283. But compare Thomas and Rule, *Trans. Chem. Soc*, 1917, **111**, 1063.

known by the name of *sal ammoniacum secretum Glauberi*. This salt is found in certain volcanic districts, especially in the neighbourhood of the boric acid fumeroles of Tuscany, and it is termed by mineralogists mascagnite. Ammonium sulphate is prepared on the large scale by heating ammoniacal gas liquor with milk of lime, and passing the ammonia evolved into sulphuric acid.

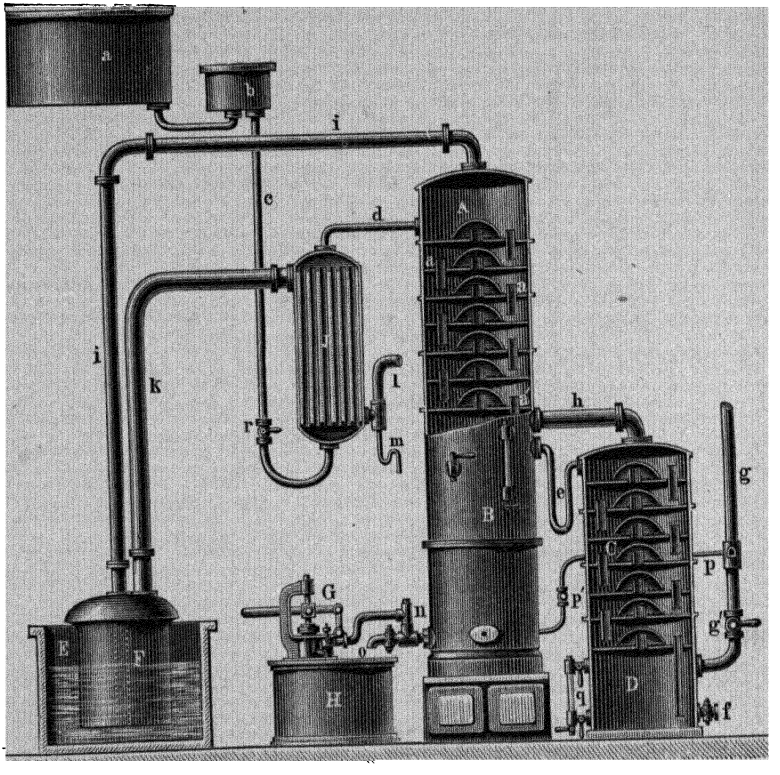


FIG. 108.

The distillation is best carried out in a continuous still, the construction of which is analogous to the well-known Coffey still, used in the distillation of alcohol. A typical form of still, devised by Feldmann,[1] is shown in Fig. 108. The ammoniacal liquor passes from the storage tank *a* into the supply tank *b*, and thence through the economiser J, where it is warmed by the hot waste gases coming from the saturator E. It flows thence into the top chamber of the column A, falls from chamber

[1] Patent No. 3643 (1882).

to chamber by the overflow pipes *a*, and is subjected in each to a current of steam subdivided into a number of small streams, which completely removes the volatile ammonia, *i. e.* the ammonia present as sulphide and carbonate. In the chamber B it is mixed with milk of lime introduced by the pump G, and then passes into the top of the second column C, where it is again subjected to the action of the current of steam and freed from the fixed ammonia, *i.e.*, that present as sulphate, chloride, thiosulphate, thiocyanate, etc., the acids remaining in combination with the lime. The waste liquor passes away from the bottom D, and is almost completely free from ammonia.

The steam required is introduced by the pipe *g* into the bottom of the column C, passes from the bottom to the top of A, and leaves the latter, carrying with it the whole of the ammonia, sulphuretted hydrogen, and carbon dioxide, by the pipe *i*, through which it is conveyed to the saturator E, which consists of an iron or wooden tank lined with lead and filled with sulphuric acid of 142° Tw. The latter absorbs the ammonia, forming ammonium sulphate, which is fished out as it separates and allowed to drain, the waste gases being retained within the bell F, and passing thence through the economiser J to the pipe *l*, by which they are conveyed to plant for further treatment and prevention of nuisance arising from them.

These gases consist chiefly of sulphuretted hydrogen and carbon dioxide, with some hydrocyanic acid, hydrocarbon vapours, and small amounts of other impurities, and they are usually treated for the recovery of the sulphur. In some cases they are burnt with the requisite quantity of oxygen in a Claus kiln (p. 316), and the sulphur recovered as such, but in most cases the sulphuretted hydrogen is removed by absorption with oxide of iron, as in the purification of coal-gas (Vol. I., p. 883). Other methods of treatment are to burn the gas completely and pass the products of combustion with those from pyrites burners into sulphuric acid chambers, or, where no chambers are available, into a tower containing limestone, down which water flows, the sulphur being thus converted into a solution of calcium sulphite.

The ammonium sulphate thus obtained is always slightly damp and contains a small quantity of free acid, but may be purified by recrystallisation. It forms large transparent crystals isomorphous with those of potassium sulphate, has a specific gravity of 1·77, and a sharp, bitter, and saline taste. One hundred

parts of water dissolve, at 0°, 71 parts, and at 100°, 103·3 parts of the salt, but it is only slightly soluble in aqueous alcohol and insoluble in absolute alcohol.

Ammonium sulphate is used for the manufacture of other ammonium salts, but its chief employment is as a nitrogenous manure, this salt and Chili saltpetre being the two chief sources of inorganic nitrogenous matter employed in agriculture. It is estimated that in 1912 the world's consumption of these salts for manurial purposes was no fewer than 2,555,200 tons of Chili saltpetre, and about 1,300,000 tons of ammonium sulphate.[1] The whole of the ammonia of commerce, as already mentioned, is obtained as a by-product in the distillation of coal, by far the greatest quantity being obtained from the coal-gas manufacture. Increasing quantities of ammonia, are, however, being recovered in other industries where coal is distilled, namely, from coke-ovens, blast-furnaces, shale-works, bone-works, and in the manufacture of producer gas from bituminous fuel (Vol. I., p. 903).

Ammonium Persulphate, $(NH_4)_2S_2O_8$.—This salt is obtained by the electrolysis of a solution of ammonium sulphate in dilute sulphuric acid, and crystallises in large prisms which are very soluble in water.[2] In presence of silver salts it undergoes a remarkable decomposition, one-eighth of the nitrogen being oxidised to nitric acid :[3]

$$8(NH_4)_2S_2O_8 + 6H_2O = 7(NH_4)_2SO_4 + 9H_2SO_4 + HNO_3.$$

It is now prepared on the manufacturing scale for use as an oxidising agent, also for the preparation of other persulphates, as it is the most soluble of all these salts.

Ammonium Selenate, $(NH_4)_2SeO_4$, is not isomorphous with the rhombic sulphate, but forms monoclinic crystals. In the presence of a small amount of sulphate, however, mixed crystals of the rhombic system are obtained.[4]

Ammonium and Nitrogen.

191 *Ammonium Azoimide* or *Ammonium Nitride*, N_4H_4 or $NH_4,N<\overset{N}{\underset{N}{\|}}$, is formed by neutralising a solution of azoimide

[1] Compare Guye, *J. Soc. Chem. Ind.*, 1906, **25**, 568.

[2] Marshall, *Journ. Chem. Soc.*, 1891, **59**, 777.

[3] Marshall, *Proc. Roy. Soc. Edin.*, 1900, **23**, 163; Marshall and Inglis, *ibid.*, 1902, **24**, 88.

[4] Tutton, *Journ. Chem. Soc.*, 1906, **89**, 1059.

with ammonia, but is best obtained by saturating an alcoholic solution of diazohippuramide, $C_9H_8NO_2{\cdot}NH{\cdot}N{:}N{\cdot}OH$, with ammonia gas; it crystallises in large lustrous prisms, which become opaque and slowly volatilise in the air, and on careful heating sublime in small lustrous prisms. It is very soluble in water, has an alkaline reaction, melts and decomposes violently at 110°, and explodes with great violence when quickly heated.[1] When it is vaporised the salt dissociates completely.[2]

Ammonium Nitrite, NH_4NO_2, is best obtained by passing the nitrous fumes prepared by the action of nitric acid on arsenious oxide over ammonium carbonate kept cool by ice, the resulting mass being treated with alcohol, and precipitated with ether. It forms colourless deliquescent crystals which ordinarily explode on heating to 60–70°, whilst in acid solution similar decompositions sometimes occur at the ordinary temperature.[3] It can be vaporised by the use of special precautions, and the vapour density is then found to be normal.[4] It can also be prepared from ammonium sulphate and sodium nitrite.[5] The solution decomposes on heating with formation of nitrogen and water (Vol. I., p. 496):

$$N_4NO_2H = N_2 + 2H_2O.$$

Ammonium Nitrate, NH_4NO_3.—This salt was first prepared by Glauber and was originally known by the name of *nitrum flammans*. It has a specific gravity of 1·72, and melts at 166°. It is tetramorphous, forming a cubic modification which is stable above 125·6°, a hexagonal modification stable from 125·6° to 82·8°, a rhombic form stable from 82·8° to 32·4°, and finally a second rhombic form stable below this temperature,[6] which is the form obtained by the evaporation of the solution at the ordinary temperature. It is very soluble in water, a large amount of heat being absorbed; 100 parts of water dissolve 118·3 parts of the salt at 0°, 241·8 parts at 30°, and 580 parts at 80°. The cryohydric temperature is −17·35° (de Coppet). It is

[1] Curtius, *Ber.*, 1891, **24**, 3348.

[2] Curtius and Rissom, *J. pr. Chem.*, 1898, [2], **58**, 261.

[3] Sorensen, *Zeit. anorg. Chem.*, 1894, **7**, 33.

[4] Rây, Dhar, and De, *Trans. Chem. Soc.*, 1912, **101**, 1185.

[5] Biltz and Gahl, *Zeit. Elektrochem.*, 1905, **11**, 409.

[6] Lehmann, *Zeit. Kryst. Min.*, 1877, **1**, 106; Schwarz, *Preisschrift, Göttingen*, 1892, 42; Tammann, *Ann. Chim. Phys.*, 1899, [2], **68**, 553, 629; Muller and Kaufmann, *Zeit. physikal. Chem.*, 1903, **42**, 497; Nicol, *Zeit. anorg. Chem.*, 1897, **15**, 397; *Vogt. Physikal. Zeitsch.*, 1911, **12**, 1129. Compare Wallerant, *Compt. rend.*, 1906, **142**, 217.

also easily soluble in alcohol and dissolves in liquid ammonia. When the dry salt is thrown on a red-hot plate it decomposes, with the production of a yellow flame and a slight explosion, into nitrogen, water, and nitric oxide, whereas if it be gently heated it decomposes into water and nitrous oxide, a small portion of the salt subliming unchanged. It is chiefly employed in the manufacture of nitrous oxide for anæsthetic purposes, and is also used for the preparation of freezing mixtures, and as a constituent of certain explosives.[1] The salts $NH_4NO_3,2HNO_3$, melting at 29·5°, and NH_4NO_3,HNO_3 have been described.[2]

Ammonium and Phosphorus.

192 *Normal Ammonium Phosphate*, $(NH_4)_3PO_4$, is obtained as a crystalline semi-solid mass when hydrogen di-ammonium phosphate is supersaturated with concentrated aqueous ammonia. It crystallises from its solution in dilute ammonia in short prismatic needles. These contain $3H_2O$, and are moderately stable in the air, but on boiling the aqueous solution two-thirds of the ammonia is evolved.

Di-ammonium Hydrogen Phosphate, $(NH_4)_2HPO_4$, occurs in guano from Ichaboe (Herapath), and is easily formed when a solution of phosphoric acid containing an excess of ammonia is allowed to evaporate; transparent monoclinic prisms are thus deposited.

Ammonium Dihydrogen Phosphate, $(NH_4)H_2PO_4$, is formed when aqueous phosphoric acid is added to ammonia until the solution reddens litmus paper and is no longer precipitated by barium chloride. It crystallises in tetragonal prisms and is isomorphous with the corresponding potassium salt.

Hydrogen Ammonium Sodium Phosphate or *Microcosmic Salt*, $HNaNH_4PO_4,4H_2O$.—The old alchemists were aware that this peculiar salt could be obtained from urine, but Marggraf was the first to examine with care the salt which crystallised from evaporated urine and to show that it contained a volatile alkali, whilst Proust found in 1775 that sodium was contained in this compound. The salt was first termed *sal urinæ fixum*, in contradistinction to the *sal urinæ volatile* or ammonium carbonate, but it was also termed *sal microcosmicum*, being obtained from the human body. This compound is also found in guano (Herapath).

[1] See Marshall, *Explosives*, 1918.

[2] Groschuff, *Ber.*, 1904, **37**, 1486; *Zeit. anorg. Chem.*, 1904, **40**, 1.

In order to prepare the compound, five parts of common rhombic sodium phosphate are dissolved in hot water together with two parts of crystallised ammonium phosphate, and the solution is allowed to cool. Transparent monoclinic prismatic crystals separate out, having a specific gravity of 1·55 and possessing a strongly saline taste. They melt readily on heating, giving off water and ammonia, leaving a residue of the dihydrogen sodium orthophosphate, which at a high temperature melts with loss of water, forming a clear liquid; this on cooling yields a glassy mass of sodium hexametaphosphate. This substance is used largely as a blowpipe reagent.

Ammonium and Carbon.

193 *Carbonates of Ammonia.*—Commercial carbonate of ammonia, *sal-volatile*, or salt of hartshorn, forms the starting-point for these compounds. This substance was well known to the later alchemists, who prepared it by the dry distillation of evaporated and decomposed urine, hartshorn, bones, and other animal matter. Its preparation from sal-ammoniac was first described in the works attributed to Basil Valentine, but long after the 15th century it was supposed that the volatile alkaline salts obtained from various sources possessed different medicinal power. Even up to the end of the 17th century *English drops*, which were really nothing more than carbonate of ammonia mixed with an ethereal oil, were sold at high prices, and it was stated by some that the volatile alkali contained in this substance was prepared by the destructive distillation of silk, whilst others gave the remarkable receipt that 5 lb. of skulls of persons who had been hanged, or had otherwise come to an unnatural end, must be distilled with 2 lb. of dried vipers, hartshorn, and ivory. More rational views concerning the composition of these compounds were arrived at towards the end of the 18th century. Dossie in his *Elaboratory laid Open*, published in 1758, distinctly states that the same animal substances always yield an equally efficacious kind of volatile alkali.

Commercial Carbonate of Ammonia is obtained by subliming a mixture of two parts of chalk and one part of sal-ammoniac or ammonium sulphate. This operation is conducted in iron retorts furnished with leaden receivers, and ten parts of sal-ammoniac yield from seven to eight parts of the carbonate. This salt is then resublimed with the addition of some water,

and is thus obtained as a white, semi-transparent, fibrous mass, which has a strongly ammoniacal smell and a pungent caustic taste. This salt possesses the composition $N_3H_{11}C_2O_5$, and consists of hydrogen ammonium carbonate along with ammonium carbamate (Vol. I., p. 865); thus, $(NH_4)HCO_3 + NH_4{\cdot}CO_2NH_2$. By treating the salt with strong alcohol the carbamate can be dissolved whilst the ammonium bicarbonate remains undissolved. This same decomposition takes place when the salt is exposed to the air, the carbamate undergoing slow volatilisation.

The impurities liable to occur in the commercial salt are thiosulphate, sulphate, and chloride of ammonia, lead from the receiver, and lime and calcium chloride from the chalk employed.

Normal Ammonium Carbonate, $(NH_4)_2CO_3,H_2O$. — Dalton first prepared this salt by treating sal-volatile with a quantity of water insufficient to dissolve it completely. It is also obtained when ammonium carbamate is dissolved in water, a condition of equilibrium between the two salts being finally attained : [1]

$$CO\begin{cases}NH_2\\ONH_2\end{cases} + H_2O \rightleftharpoons CO\begin{cases}ONH_4\\ONH_4\end{cases}.$$

It is, however, most readily prepared by digesting the common commercial carbonate of ammonia for two hours at a temperature of 12° with strong aqueous ammonia, and drying the crystalline powder which remains behind between blotting paper.

Transparent tabular or prismatic crystals are deposited from a solution prepared at a temperature of from 30° to 35°. These possess an ammoniacal odour, attract moisture from the air, and become opaque from loss of ammonia and formation of hydrogen ammonium carbonate and water (Divers).[2]

Hydrogen Ammonium Carbonate or *Ammonium Bicarbonate*, $(NH_4)HCO_3$.—Crystals of this salt are sometimes found in Patagonian guano, and in the purifiers of gas-works. It is formed when the foregoing compound is allowed to lie exposed to the air, or when its solution is treated with carbon dioxide. It forms a white mealy powder, or, when slowly crystallised, large rhombic crystals, which have a cooling saline taste and do not smell of ammonia when in the dry state. At 60° it slowly undergoes decomposition with evolution of carbon dioxide, ammonia, and water. When it is more strongly heated in such

[1] Macleod and Haskins, *J. Biol. Chem.*, 1906, **1**, 319. See also Burrows and Lewis, *J. Amer. Chem. Soc.*, 1912, **34**, 993.

[2] *Journ. Chem. Soc.*, 1870, **23**, 171.

a way that a small quantity of water condenses and the gases are not allowed to recombine, the ordinary commercial carbonate of ammonia is formed (Divers). This salt dissolves at 15° in 8 parts of water. Its solution when exposed to the air, as well as when heated above 36°, loses carbon dioxide, but its saturated solution can be crystallised by cooling out of contact with air. It is not soluble in alcohol, but if alcohol be added and the mixture be allowed to stand in the air carbon dioxide is evolved and normal ammonium carbonate dissolves. It forms a double salt with the former compound, having the composition

$$2(NH_4)HCO_3,(NH_4)_2CO_3,H_2O,$$

which is known as ammonium sesquicarbonate; this may be most easily obtained by treating the commercial salt at 30° with a moderate amount of tolerably concentrated ammonia, and crystallising. This double salt forms flat rhombic prisms or thin six-sided tablets, smells strongly of ammonia, and dissolves at 15° in 5 parts of water. It is decomposed by an excess of water with formation of the bicarbonate. Aqueous solutions of the carbonates are completely decomposed on boiling, the ammonia and carbon dioxide passing over with the steam.

194 *Ammonium Cyanide*, NH_4CN.—When a mixture of sal-ammoniac and dry ferrocyanide of potassium, or mercury cyanide, is heated, this salt sublimes in colourless cubes which smell of both ammonia and hydrocyanic acid. It is also produced when a mixture of ammonia, nitrogen, and hydrogen is passed over wood charcoal at 1000°.[1] It is easily soluble in both water and alcohol, and evaporates at a temperature of 36°. The vapour is inflammable and burns with a yellow flame. It is an extremely poisonous salt, and decomposes, especially in the moist state, into azulmic acid.

Ammonium Cyanate, NH_4OCN, is formed, mixed with urea and cyamelide, when the vapour of cyanic acid is brought into contact with dry ammonia, but is obtained nearly pure by mixing ethereal solutions of ammonia and cyanic acid at 20°,[2] and is formed in solution when concentrated solutions of potassium cyanate and ammonium sulphate are mixed. It forms a friable mass, easily soluble in water and sparingly soluble in absolute alcohol. This salt easily undergoes intramolecular change, forming the isomeric urea, $CO(NH_2)_2$ (Vol. I., p. 866).[3]

[1] Lance, *Compt. rend.*, 1897, **124**, 819.

[2] Walker and Wood, *Proc. Chem. Soc.*, 1898, 108; *Journ. Chem. Soc.*, 1900, **77**, 21.

[3] See Chattaway, *Trans. Chem. Soc.*, 1912, **101**, 170.

Ammonium Thiocyanate, NH_4CNS, is formed when a solution of yellow ammonium sulphide which contains polysulphides is warmed with hydrocyanic acid :[1]

$$(NH_4)_2S + HCN + S = NH_4CNS + NH_4HS.$$

It is obtained on the large scale by this reaction from the hydrocyanic acid present in crude coal-gas (Vol. I., p. 887), but in the laboratory is most readily prepared by mixing together 600 grams of 95 per cent. alcohol, 800 grams of ammonia (specific gravity 0·912), and 350 to 400 grams of carbon disulphide, and allowing to stand for several days, then distilling off a portion of the liquid, and allowing the remainder to crystallise.[2] Ammonium thio-carbonate, $(NH_4)_2CS_3$, is first formed in this reaction, but decomposes on heating into the thiocyanate and sulphuretted hydrogen :

$$(NH_4)_2CS_3 = NH_4CNS + 2H_2S.$$

It is very readily soluble in water and alcohol, crystallising out in colourless plates. Its solution in water is attended with great absorption of heat; thus if 100 grams of the salt be dissolved in an equal weight of water at 17°, the temperature sinks to −12° (Rüdorff). The perfectly dry salt melts at 159° and when slowly melted is partially converted into the isomeric thio-urea $CS(NH_2)_2$[3] (Vol. I., p. 869).

Ammonium thiocyanate is always found amongst the products of the dry distillation of organic substances containing nitrogen and sulphur, and is therefore always present in gas liquor. Its formation is brought about partly by the combination of the hydrocyanic acid in this gas with ammonium polysulphide, partly by the interaction of the ammonia, sulphuretted hydrogen, and carbon disulphide, in the manner already explained.

HYDROXYLAMINE SALTS.

195 Hydroxylamine, NH_2OH, the preparation of which has already been described (Vol. I., 525), forms salts with acids which are analogous to those of ammonia; the most important of these are as follows :

Hydroxylamine Hydrochloride, NH_2OH,HCl, crystallises from

[1] Liebig, *Annalen*, 1847, **61**, 126.

[2] Schultz, *J. pr. Chem.*, 1883, [2], **27**, 518.

[3] Reynolds and Werner, *Journ. Chem. Soc.*, 1903, **83**, 1; Findlay, *ibid.*, 1904, **85**, 403.

a hot alcoholic solution in monoclinic prisms or plates, which are very soluble in water but less so in alcohol. When heated it decomposes into ammonium chloride, hydrochloric acid, water, and nitrogen. When a concentrated solution of this salt is treated with an alcoholic solution of hydroxylamine, it yields the salt $(NH_2OH)_2HCl$ as a crystalline precipitate, which when mixed with concentrated solutions of the normal salt yields large, well-formed crystals having the composition $(NH_2OH)_32HCl$, and melting at 95° with decomposition.

Hydroxylamine Hydriodide, NH_2OH,HI, forms flat, colourless, very hygroscopic needles,[1] which are obtained by evaporating the solution *in vacuo* below 26°. The compounds $(NH_3O)_3HI$ and $(NH_3O)_2HI$ are also known.[2]

Hydroxylamine Sulphate, $(NH_2OH)_2,H_2SO_4$, crystallises from aqueous solution in large monoclinic prisms, according to Lang, or triclinic prisms according to Dathe, and is precipitated in needles on addition of alcohol to the aqueous solution.

Hydroxylamine Nitrate, NH_2OH,HNO_3, is obtained by decomposing a solution of the hydrochloride with silver nitrate, or of the sulphate with barium nitrate. On evaporating the solution over sulphuric acid an oily liquid remains, which, when pure, forms crystals melting at 48°, and readily remains in superfusion. It is very readily soluble in water and alcohol, and its aqueous solution decomposes on the water-bath with evolution of nitrous fumes.

HYDRAZINE SALTS.

196 Hydrazine, N_2H_4, like ammonia, readily combines with acids to form salts, which may for convenience be described here, although they do not correspond to the ammonium salts and those of the alkalis, hydrazine being a di-acid base. The mon-acid salts, $N_2H_5.X$, are as a rule much more stable than the di-acid salts, $N_2H_6:X_2$. The salts are for the most part obtained by neutralising hydrazine hydrate (Vol. I., p. 519) with the appropriate acid, and evaporating the solution to the point of crystallisation.

Hydrazine Dihydrochloride, $N_2H_4,2HCl$, crystallises in regular octahedra, which rapidly attract moisture from the air. It melts at 198°, losing hydrogen chloride and forming the *mono*-hydrochloride, N_2H_4,HCl, as long needles melting at 89°.

[1] Wolffenstein and Groll, *Ber.*, 1901, **34**, 2417.

[2] Dunstan and Goulding, *Journ. Chem. Soc.*, 1896, **69**, 839.

Hydrazine Dihydrobromide, $N_2H_4,2HBr$, and *Hydrazine Hydrobromide*, N_2H_4,HBr, are very similar to the hydrochlorides, and melt at 195° and 80° respectively.

Hydrazine Dihydriodide, $N_2H_4,2HI$, can only be obtained by the action of fuming hydriodic acid on benzalazine, $C_6H_5.CH:N.N:CH.C_6H_5$, and is a very hygroscopic substance which melts at 220°, and becomes brown in the light. The *monohydriodide*, N_2H_4,HI, is formed by the action of iodine on an alkaline solution of hydrazine hydrate:

$$5N_2H_4,H_2O + 2I_2 = 4N_2H_4,HI + 5H_2O + N_2.$$

It forms long colourless prisms, melts at 127°, and explodes violently at a higher temperature.

Trihydrazine Dihydriodide, $3N_3H_4,2HI$.—This salt is prepared by the addition of iodine to a solution of hydrazine hydrate in a little alcohol till crystals separate in quantity. It crystallises in large white needles melting at 90°.

Hydrazine Nitrate, N_2H_4,HNO_3, crystallises in long prisms, melts at 69°, and explodes when quickly heated. The *di-acid salt* is very unstable,[1] and decomposes when heated, yielding azoimide, ammonium nitrate, nitrogen, nitric acid, and water. *Hydrazine Nitrite*, N_2H_4,HNO_2, forms white hygroscopic crystals, which detonate when struck or heated.[2]

Hydrazine Sulphate, N_2H_4,H_2SO_4.—The method of preparation of this salt has been already mentioned in describing the preparation of hydrazine (Vol. I., p. 517). It crystallises in thick lustrous tablets or long thin prisms belonging to the rhombic system, and is sparingly soluble in cold but readily soluble in hot water, and insoluble in alcohol. It melts at 254°, and simultaneously undergoes decomposition, yielding hydrazine sulphite, sulphur dioxide, sulphuretted hydrogen, and sulphur. Hydrazine sulphate in liquid ammonia is decomposed quantitatively into hydrazine, which remains in solution, and ammonium sulphate, which is precipitated.[3]

Hydrazine Nitride or *Hydrazine Azoimide*, N_5H_5 or $N_2H_4,HN<^{N}_{N}$, is obtained by the action of hydrazine hydrate on ammonium azoimide, or azoimide itself, and forms large vitreous

[1] Sabanieff, *Zeit. anorg. Chem.*, 1899, **20**, 21.

[2] Sommer, *Zeit. anorg. Chem.*, 1913, **83**, 119.

[3] Friedrichs, *J. Amer. Chem. Soc.*, 1913, **35**, 244. See also Browne and Welsh, *ibid.*, 1911, **33**, 1728.

prisms, melting at 65°, which deliquesce in the air, and gradually volatilise. It is sparingly soluble in alcohol, from which it crystallises in lustrous plates, and explodes with great violence when quickly heated or touched with a white-hot wire.[1] It burns like gun-cotton when a light is applied to it.

[1] Curtius, *Ber.*, 1891, **24**, 3348.

THE COPPER GROUP

Copper, Cu. Silver, Ag. Gold, Au.

197 The metals of this sub-group, as has already been pointed out, differ very considerably from the other metals of the same group. Like the alkali metals, they form a series of characteristic salts in which each atom of the metal replaces one of hydrogen, but, except in the case of silver, other series of salts are known which are more stable than the first-named series. As is frequently the case with metals having very high atomic weights, gold differs in many respects from the elements of the same sub-group which have a lower atomic weight, and also shows considerable resemblance to the elements having nearly the same atomic weight; thus gold resembles platinum and iridium in many respects, and is sometimes classed with them.

COPPER. Cu = 63·57. At. No. 29.

198 Copper of all the metals was probably the one first employed by man. This is explained by the fact that copper occurs in the native condition, and thus requires no metallurigcal treatment. In the Hebrew Scriptures copper is termed *Nehósheth*, a word derived from the root *nahásh*, to glisten. This is translated by Χαλκός in the Septuagint, and this again by *Aes* in the Vulgate. By both the latter words the ancients understood, not only copper, but brass and bronze. Copper was afterwards specially designated as *aes cyprium*, or simply *cyprium*, a name which afterwards became *cuprum*.

The Latin Geber appears to have noticed that copper is easily attacked by acid liquids, and hence it was termed *meretrix metallorum* by the alchemists. Inasmuch as it was obtained from Cyprus, copper was considered to be the metal specially sacred to Venus, and in the writings of the alchemists it is generally known by the name of this goddess and symbolised by ♀. In the works attributed to Basil Valentine we find

noted the power possessed by iron to precipitate metallic copper from solutions of its salts. In his *Last Testament* we read: "The cement or *ley* from Schmölnitz in Hungary eats iron into slime, and when the iron mud is taken out of the trough it is found to be good ♀ (copper)." In his *Currus Triumphalis Antimonii* he says, "From iron a ♀ (copper) can be got by natural means, as, for instance, by an acrid ley from Hungary which gives to it (the iron) such a metallic colour that it is converted into the best copper."

It would thus appear that this change was regarded as a transmutation of iron into copper, and Paracelsus and many other chemists seem to have held similar views with respect to this reaction. Wedel in 1664 made special inquiry into the nature of the wonderful transmutation of iron into copper by means of this Hungarian liquor; and so late as 1690 Stisser, who was professor of chemistry in Helmstedt, believed that the formation of copper precipitate was a proof of the possibility of the transmutation of metals.

It was long before these erroneous views concerning this precipitation of copper were corrected, although Van Helmont rightly surmised that the copper existed in the solution from which it was precipitated by the iron. Boyle first proved this to be the case, and in his *History of Fluidity and Firmness*,[1] published in the year 1661, he describes the precipitation of copper from its solution by metallic zinc, and in 1675, in his *Treatise on the Mechanical Causes of Chemical Precipitation*,[2] explains the action of iron upon copper solutions by the supposition that the solvent permits the metal to be precipitated in order to take up the precipitant.

Copper occurs in the native state in various parts of the world, especially in the copper region of Lake Superior, where, sometimes in enormous masses, it occurs in veins traversing red sandstone and trap. It is also found in the same condition in Cornwall, the Faroe Islands, Siberia, and the Urals, and in many localities in North and South America. Native copper almost invariably contains small quantities of silver and a few other metals, such as bismuth, lead, etc. Cupric oxide, CuO, black oxide of copper, also occurs in nature, as tenorite or melaconite, and cuprous oxide, Cu_2O, occurs in larger quantities, as cuprite or red copper ore. Many copper salts occur native; of these the most important are malachite, $CuCO_3,Cu(OH)_2$;

[1] *Op.* 1, p. 377. [2] *Op.* 4, p. 329.

azurite or blue carbonate of copper, $2CuCO_3,Cu(OH)_2$. Copper also occurs widely distributed in combination with sulphur as vitreous copper, chalcocite, or copper glance, Cu_2S; covellite or indigo copper, CuS; copper pyrites or chalcopyrite, $CuFeS_2$, and erubescite or purple copper ore, Cu_3FeS_3.

Copper is found in the animal kingdom in the blood of certain crustacea and arthropoda as a faintly-blue compound called *hæmocyanin*, which has similar oxygen-carrying properties to hæmoglobin, the compound of iron contained in the blood of vertebrates, whilst the livers of some of the cephalopods also contain copper.[1] This element also forms about 7 per cent. of the red pigment turacin which occurs in the feathers of birds of certain species.[2]

It has also been detected in small quantities in plants grown in ordinary soils,[3] and in larger quantities when the plants have been grown in soils containing copper.

199 *Copper Smelting.*—The methods in use for the extraction of copper differ considerably, according to the nature of the ore from which the metal is to be obtained. Both dry and wet processes of extraction are employed, the greater quantity of the metal being obtained by the former.

Two different classes of dry processes are successfully at work; (1) smelting in reverberatory furnaces, and (2) smelting in blast furnaces. The first class comprises the *Welsh* or *English process*, formerly carried out in the Swansea district of South Wales but now modified in many directions, and also the modern method of smelting in reverberatory furnaces carried out in many important districts.

In the old *Welsh process*, a mixture of copper ores was usually employed, consisting of copper pyrites and copper carbonates, mixed with iron pyrites containing silicates and gangue, mostly consisting of quartz. To obtain the pure metal six distinct operations were required, viz.:

(1) Calcining the mixed ore.
(2) Preparing "coarse metal."
(3) Calcining the "coarse metal."
(4) Preparing "fine metal."
(5) Roasting to obtain metallic copper.
(6) Refining.

[1] Henze, *Zeit. physiol. Chem.*, 1901, **33**, 417.
[2] Church, *Proc. Roy. Soc.*, 1893, **51**, 399.
[3] MacDougal, *Bot. Gaz.*, 1899, **27**, 68.

The calcination of the crude ores was generally carried out in kilns or reverberatory furnaces.

Figs. 109 and 110 show the construction of the ordinary

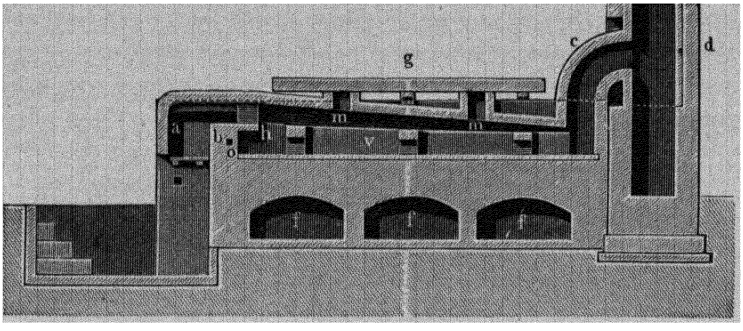


Fig. 109.

calcining furnace, into which the mixture of ore, weighing about three-and-a-half tons, was introduced from the trough *g*.

This charge was exposed to the oxidising action of the air for from twelve to twenty-four hours, the result of this operation

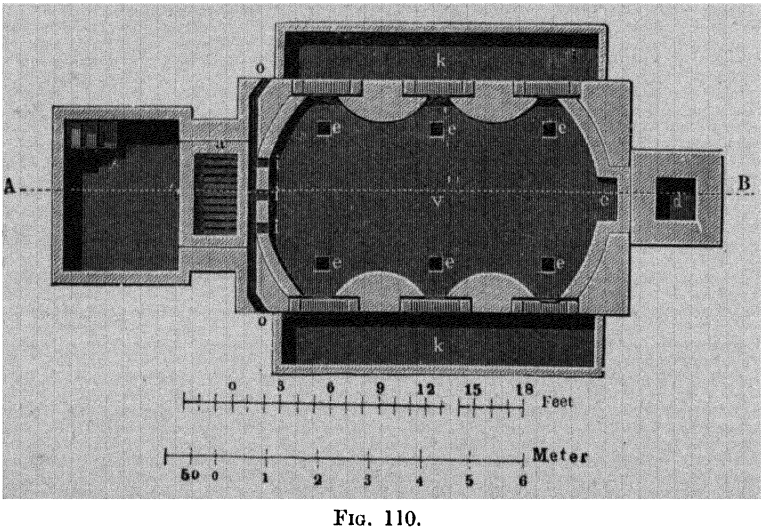


Fig. 110.

being the partial oxidation of the sulphides of copper and iron, with the formation of the corresponding oxides, and the conversion of any copper carbonate present into oxide.

In the second operation the roasted ore was mixed with "metal slag" derived from the "fine metal" operation, and

strongly heated in a smelting reverberatory furnace, Figs. 111 and 112, which had a much larger grate area in proportion to the size of the hearth than the calcining furnace, as it was desired to obtain a fused mass or *regulus* consisting of a mixture of the sulphides of copper and iron, termed *coarse metal*, and at the same time a slag consisting of a silicate of iron, and containing

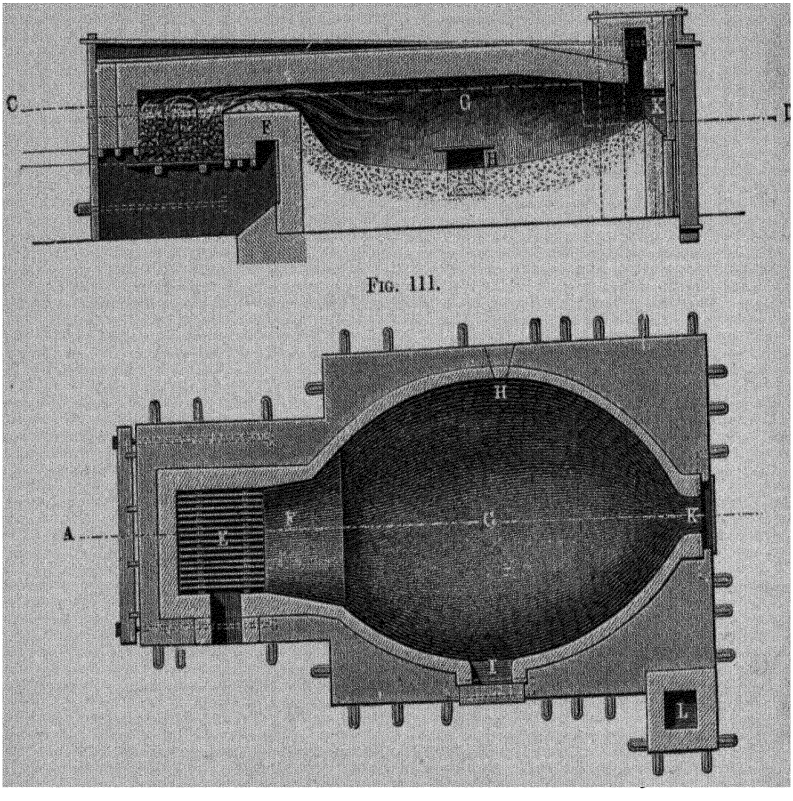


Fig. 111.

Centimeter 1 0.75 0.5 0.25 0 1 2 3 4 5 Meter.

Fig. 112.

little or no copper, called *ore-furnace slag*. When thus smelted the copper oxide of the roasted ore reacts with a portion of the sulphide of iron with formation of copper sulphide and oxide of iron, this latter oxide then combining with the silica present to form a fusible slag of iron silicate. In order to obtain by this means an ore-furnace slag free from copper, it was found that the mixture of ore should not contain more than 14 per cent. of copper, whilst, on the other hand, the percentage of copper should not

be below 9, otherwise the consumption of fuel became extravagant. The coarse metal, or crude copper sulphide, usually contained about 35 per cent. of copper. The slag was drawn off, and the fused coarse metal run out through the tap-hole into a granulator, into sand beds or into iron moulds.

The third operation consisted of the calcination of the granulated or crushed regulus or coarse metal, for the purpose of oxidising a portion of the sulphur, leaving only sufficient to combine with the copper present, so that when again smelted, in the fourth operation, with the addition of *roaster-slag*, *refinery-slag*, and a certain proportion of oxidised ores, such as the carbonate or oxide, a nearly pure cuprous sulphide, Cu_2S, called *white metal* or *fine metal*, and containing about 75 per cent. of copper, was obtained.

In such an operation if the amount of oxidised ore be insufficient, the product contains sulphide of iron and is then known from its colour as " blue metal," whilst if an excess be employed some of the copper sulphide is reduced, and sulphur dioxide evolved; the latter in its attempt to escape gives the surface a pimply appearance, the product being therefore known as " pimple-metal."

The smelting furnace used in this operation was identical in construction with that employed in the first fusion, and the slags formed chiefly consisted of iron silicate, but contained some quantity of copper, and were termed *metal slags*; these were retreated, as has been stated, in the first smelting process.

The fifth operation, consisting of the roasting of white metal to metallic copper, is used to a considerable extent in present day practice and for this purpose the pigs are now charged into a reverberatory furnace, in such a manner that air can circulate round each pig, thus subjecting them to a slow roasting process. In this way the oxide formed reacts with the unoxidised sulphide with the production of metallic copper and sulphur dioxide:

$$2Cu_2O + Cu_2S = 6Cu + SO_2.$$

The metal thus reduced is filled with cavities and covered with blisters, hence it is termed *blister-copper*. It still contains from 2 to 3 per cent. of foreign matter, chiefly consisting of sulphur and iron.

To remove the impurities, the blister-copper is subjected to the sixth, or refining operation, which is also used at the present time. For this purpose the blister-copper is again fused in a

smelting-furnace constructed like the others except that its floor is inclined towards a point near the door and near the chimney. Upon this floor a charge of about eight tons of blister-copper is brought, and the slags having been removed by skimming from the surface of the molten metal, this is well stirred up, or *rabbled*. The metal in this condition is termed *dry copper*. In this state it is, however, unfit for use, as it contains a proportion of oxygen, present as cuprous oxide, which renders it brittle. To eliminate this, the metal has to be *toughened*. This is effected by covering the surface of the molten metal with a thin layer of anthracite, and plunging a pole of wood into the molten metal. Large volumes of reducing gases consisting of hydrocarbons and carbon monoxide are thus evolved, and the metal boils up violently, the oxide being reduced. After the *poled* metal has remained quiescent for a few minutes a sample is removed by the refiner, cast into a mould, and the casting cut half through with a cold chisel and broken. From the appearance and colour of the fractured surface an experienced eye can at once decide whether the copper has arrived at what is termed the *tough-pitch*, in which condition it contains just sufficient oxygen to overcome the injurious effects of the small quantities of impurities present. When this is reached, the charge must be withdrawn from the furnace as rapidly as possible and cast in iron moulds, in order to prevent a second oxidation occurring. Sometimes the molten metal becomes what is called *over-poled*, and if this is the case the metal must be exposed to the air for a short time to bring it back again to the tough-pitch condition.

Figs. 113 and 114 (p. 419) show the construction of a smelting furnace with a gas-generator (A) fired with coal which is filled from the shaft (C). The air necessary for the combustion of the generated gas is admitted by the openings (*b b*), whilst that required for the oxidation of the charge enters by the openings (K K).

The subject of the toughening of copper and of the removal of the non-metallic impurities contained in commercial copper is somewhat complex, and has received much attention from metallurgists. From the experiments of Abel [1] it appears that toughened copper always contains a certain amount of oxygen present as suboxide, and this agrees with the observation of copper smelters, who find that the whole charge may become over-poled in a few seconds, this being explained by the fact

[1] *Journ. Chem. Soc.*, 1864, **17**, 164.

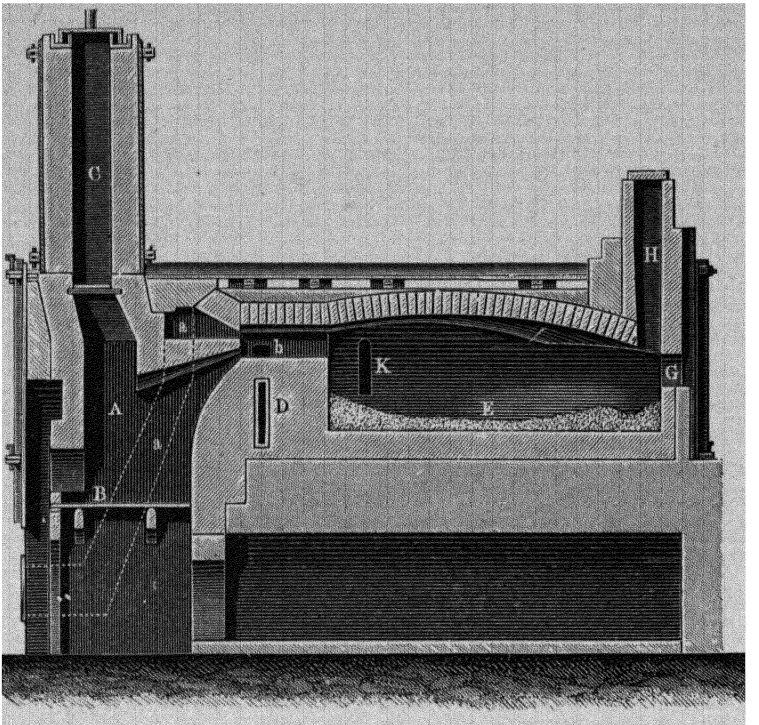


FIG. 113.

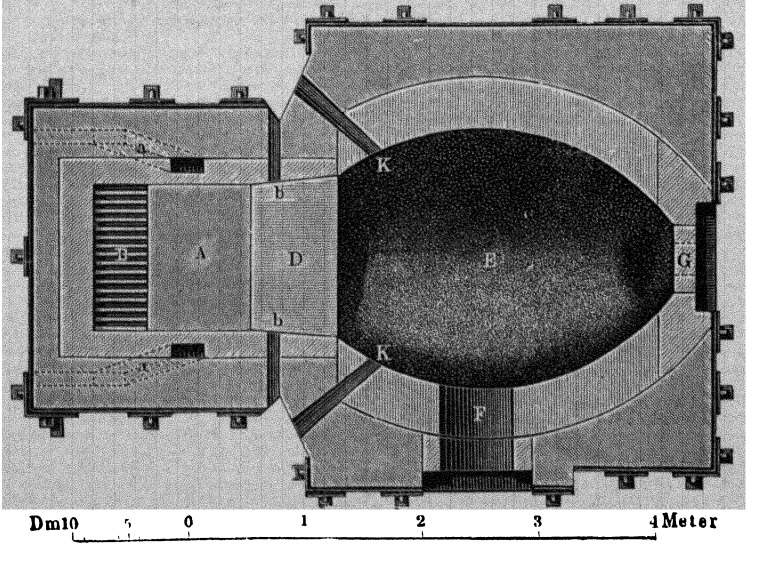


FIG. 114.

that the whole of the oxygen has been withdrawn. According to Hampe,[1] on the other hand, the phenomenon of the over-poling of copper depends on the reduction of small quantities of lead oxide and bismuth oxide which the copper contains, so that if these bodies be not present no over-poling occurs.

This method of copper smelting is seldom used exactly as described, but is improved by the use of one or more of the following modifications.

Large mechanical furnaces are often used for the calcination of the ore and coarse metal, in place of the old-fashioned calcining furnace. In some cases revolving cylinders, similar in principle to the Oxland calciner employed in roasting tin ores (see Tin), and, in other cases, long-bedded reverberatory furnaces fitted with mechanical rabbles, such as the O'Hara, are used. A large number of other mechanically worked calciners have also been designed and worked with success, such as the Pearce Turret furnace, the Brown Horseshoe, the Merton, the Edwards, the MacDougal, and others.

In some cases also it is the practice to use shaft-furnaces or small blast furnaces for the second operation, that is for the smelting of the roasted ores for the production of "coarse-metal." This effects a considerable economy in labour and fuel. In some cases also shaft-furnaces are used for the fourth operation, the production of "white metal."

The use of gas-fired reverberatory furnaces for the refining operation, having regenerators for heating the gas and air necessary has also been introduced.

In modern smelting, *reverberatory furnaces* are used for matte-smelting of finely-divided ores such as concentrates. Before charging, the ore is partially roasted, generally in one of the types of mechanical roasters, and during the smelting the remaining sulphur unites with copper and iron, forming the matte, and the silica of the gangue unites with the oxide of iron, lime, and alumina, forming a fusible slag.[2]

There has also been a considerable development in size and method of working smelting reverberatories. Furnaces capable of smelting from 200 to 300 tons per 24 hours, with hearths measuring up to 119 feet in length, are now used as against the furnaces capable of smelting only 12 tons per 24 hours, measur-

[1] *Chem. Centr.*, 1875, 378.

[2] Full information concerning copper smelting may be found in *The Principles of Copper Smelting*, by Peters (Hill Publishing Co., 1907), and *The Practice of Copper Smelting*, by Peters, 1911.

ing 15 feet in length, commonly used in 1880. The increase in smelting capacity is not only due to increase in size of furnace, but to certain improvements in the method of working, such as rapid charging of the hot calcined ore, preheating air by conduction through channels in the brickwork, rapid skimming through four doors simultaneously, and tapping after several charges have been smelted, thus keeping the hearth well covered with matte.

Important innovations have been introduced recently into American copper smelting practice in the use of oil and powdered coal in reverberatory furnaces. Oil-firing has been used in several works and has been found to result in a reduction of the cost of smelting, especially where the waste gases are utilised for the raising of steam in boilers. Powdered coal-firing has also been found to work satisfactorily and to result in considerable economy of fuel and in an increased output per furnace. The value of powdered coal for firing cement kilns has been realised since 1895, but it was not used successfully in copper smelting until 1911. At Anaconda,[1] this method is now used in reverberatory furnaces 144 feet long by 23 feet wide; with five coal-dust burners per furnace, as much as 760 tons of charge has been smelted in 24 hours with a consumption of 100 tons of coal dust.

Smelting of Copper Ores in Blast Furnaces.

200 *The Mansfield Process of Copper Smelting.*—The well-known cuprous schist or "kupferschiefer" of the Germans has been worked for copper for a long time. Agricola, writing in the middle of the sixteenth century, described the methods adopted in his time near Mansfield for the extraction of the metal. In this process the first operation consists in the roasting of the schist to burn off bituminous matter, expel the water and arsenic, and remove a portion of the sulphur.

In the second operation the roasted ore is mixed with slag from the "black copper" operation, and smelted in blast furnaces for coarse metal and a clean slag. The coarse metal, or "rohstein," is next re-roasted and smelted for fine metal or "spurstein."

The fine metal was formerly treated by the Ziervogel process (see Silver) for the extraction of the silver present, and the

[1] Austin, *Mining and Scientific Press*, Feb. 1916.

remaining copper oxide was smelted in a blast furnace for the production of black copper, which was refined.

Blast furnaces are sometimes employed in the smelting of oxidised copper ores, the charge consisting of ore, the necessary fluxes, and coke for fuel. The products are blister-copper, which is afterwards refined, and slag which invariably contains from 1·5 to 2·5 per cent. of copper.

Blast furnaces are very largely used in the smelting of

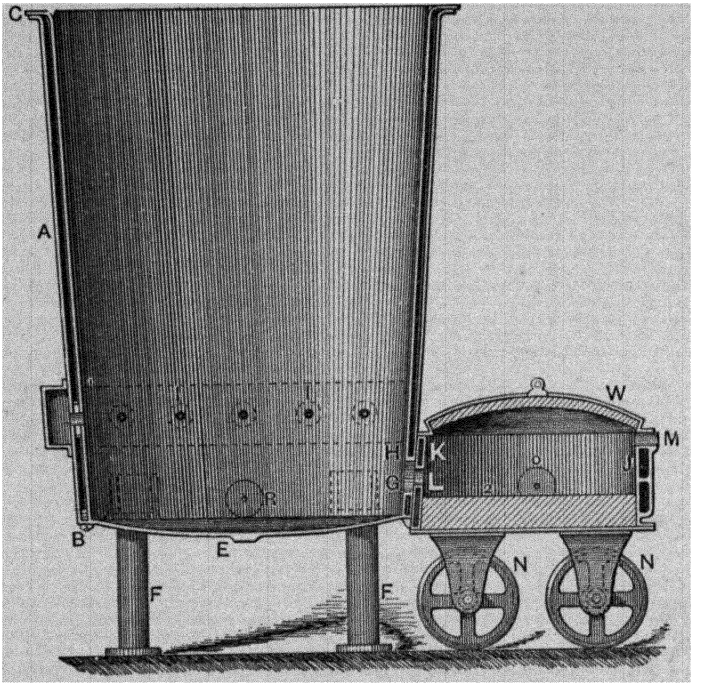


Fig. 115.

sulphide copper ores, the form mostly employed being water-jacketed iron furnaces. One of the types of furnace employed is that of Herreshoff, a sectional elevation of which is shown in Fig. 115, and a sectional plan in Fig. 116. The main furnace, A, has an elliptical section and consists of a double casing of iron, A, B, C, through which water is continually circulated; the bottom of the furnace, E, is lined with fire-brick or fire-clay. The roasted ore, mixed with coke or anthracite, and the slag from a later process, which consists chiefly of iron silicate with a little copper, is introduced at the top of the furnace, the air being forced through the tuyeres, I I. The products, which

consist of " matte " (corresponding to the " coarse metal " of the Welsh process) and slag, accumulate in the bottom of the furnace and then overflow continuously into the " fore-hearth," W, the end elevation of which is shown in Fig. 117; this is frequently mounted on wheels, N N, for convenience of moving.

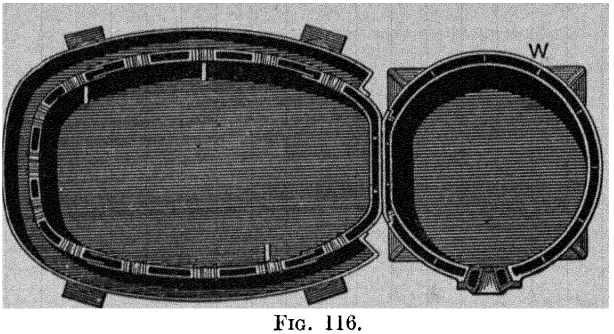


FIG. 116.

The slag then flows away almost continuously from the opening, M, the matte being run off by the tap-hole, O, as occasion requires. This matte is usually reduced to metallic copper in a " converter," the resulting metal being refined in reverberatory furnaces or by the electrolytic method.

The water-jacketed blast furnaces, generally rectangular in

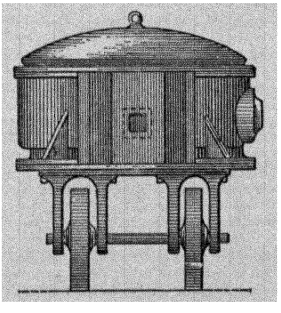


FIG. 117.

form, are not only more easily constructed than the ordinary brick furnaces, but can be much more rapidly heated and cooled, the blowing-in of the furnace and its cooling down for repairs being thus greatly facilitated. The manipulation of the furnace during the smelting is also rendered much simpler.

During recent years great developments have taken place in the sizes of water-jacketed blast furnaces used in the smelting

of copper.[1] Up to the year 1885 the largest furnaces were 96 inches long by 36 inches wide, and up to 1902, the largest furnaces were 120 inches by 42 inches. In 1902 the Anaconda Copper Company built a furnace 180 inches by 56 inches, and in 1904 the same company joined up two furnaces including a space of 21 feet between, making a furnace 52 feet in length; in 1905 this furnace was joined to another 15 feet furnace, including a space of 21 feet, making a furnace 87 feet long.

Pyritic Smelting.[2]—By this is meant the smelting of sulphide ores by the heat generated by their own oxidation, without the aid of carbonaceous fuel. In this direction great progress has been made in recent years. This process is applicable to auriferous, argentiferous, and cupriferous pyrites, and its object is to smelt for a matte in which the valuable metals will be concentrated.

In practice it is found advisable to add a small quantity, up to 5 per cent., of fuel to the charge forming a process of partial pyritic smelting. The furnaces most suitable are large, rectangular, water-jacketed blast furnaces with a larger number of tuyeres than usual for ordinary smelting.

One of the applications of this method is to smelt a mixture of pyrites, low in copper, with siliceous material carrying gold and silver; most of the sulphur and iron are oxidised, thus generating the heat, and leaving ferrous oxide which forms a slag with the silica. The unoxidised sulphur forms a matte with the copper and some iron, and this matte also carries practically the whole of the precious metals. This matte may be treated by the Bessemer process and the copper obtained refined electrolytically.

Collection of Furnace Dust.—Serious losses of copper may arise from the escape of fine particles of ore with the furnace gases and all well-equipped smelting works are provided with large flues and dust chambers for their collection. These losses occur in roasting and smelting furnaces and in blast furnaces; they vary with the pressure of the blast and with the proportion of fine ore contained in the charge, but are never less than 5 per cent. and in some cases reach 20 per cent. To collect the dust, the speed of the gases must be reduced, and this is effected by the provision of large flues and capacious settling chambers. The Cottrell process of electrostatic precipitation has also been

[1] See Gowland, *Trans. Inst. Min. and Met*, 1906–7, 265.

[2] "Pyritic Smelting," *Trans. Inst. of Min. and Met.*, 1905–6, 269.

applied with success to the treatment of furnace gases and consists in exposing the gases to a strong electrostatic field, which charges the particles of dust or fume and causes them to pass to a series of pipe collectors which act as the discharge electrodes.

The flue dust may be smelted in certain proportions with the fine ore charges for reverberatory furnaces or may be sintered or briquetted for blast furnace smelting. In some works, the dust is incorporated with molten converter slag or with molten low grade matte previous to retreatment in blast furnaces.

Application of the Bessemer Process to Copper Smelting.—By far the most important method of treating copper matte is in the Bessemer converter by the Manhès process. The principle involved is the same as that of the Bessemer iron process, viz., the removal of the foreign substances by the passage of air through the molten mass, but in the manufacture of steel from 5 to 10 per cent. of the charge only has to be oxidised, whereas in treating a 25 per cent. copper matte 75 per cent. has to be disposed of.

The operations consist in charging the converter with the molten matte, blowing air to concentrate the matte up to white-metal, pouring off the slag, adding more matte to the converter, blowing to metallic copper and pouring the charge. During the blow, the sulphur and iron become oxidised, the latter combining with the siliceous lining to form a ferrous silicate slag.

The converters (Fig. 118) are similar to the steel converters, but have side tuyeres slightly elevated above the bottom and a lining often 18 inches thick. A lining generally lasts only from four to six blows, and hence this is an expensive item in converting. In some works, therefore, a siliceous ore containing 5 to 10 per cent. of copper is used as a lining, the copper being extracted during the process; thus at the Detroit copper works 200 tons of such an ore are economically treated every month per converter.[1]

In order to obviate the necessity of constantly renewing the linings of these converters, basic linings have been introduced and are working successfully. These converters are lined with magnesite bricks, and after a small charge of matte, together with the siliceous material necessary to form a slag, has been

[1] See "Treatment of Copper Mattes in the Bessemer Converter," *Trans. Inst. of Min. and Met.*, 1899–1900, **18**, 2.

blown, it is poured. The slag which adheres to the sides of the converter now forms a suitable medium for retaining the charge of siliceous material necessary for the reactions which is put in the converter before the next charge of matte is introduced.

A converter installed at the smelter of the Anaconda Copper Co.[1] is 20 feet in diameter, and 17 feet high, and it has a lining

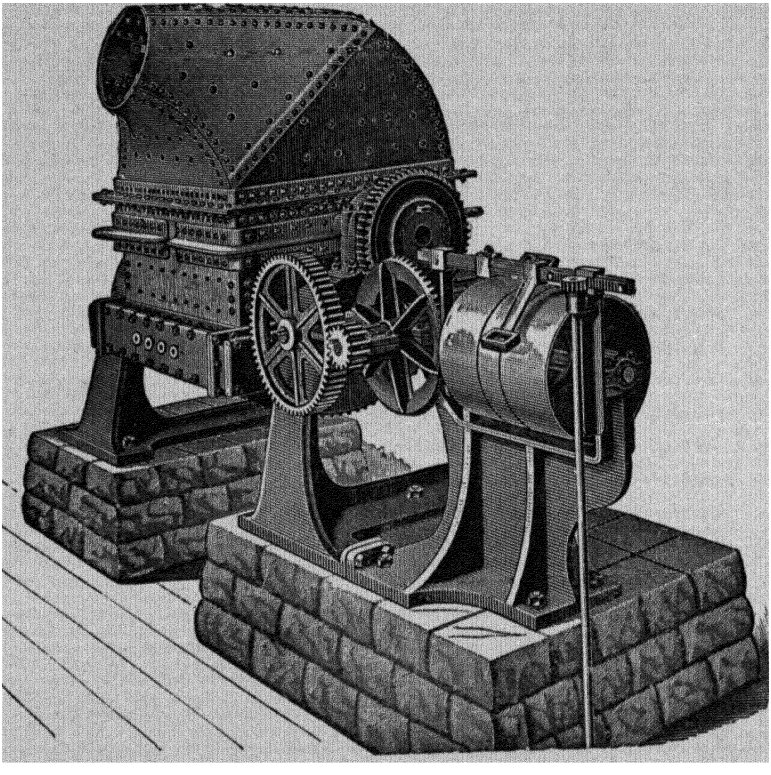


FIG. 118.

of magnesite bricks $2\frac{1}{2}$ feet thick on the tuyere side, and 2 feet thick on the opposite side. There are 62 tuyeres each of $1\frac{3}{4}$ inches diameter, and the air consumption is 25,000 cubic feet per minute. The total weight of this converter, filled with metal, is nearly 300 tons, and it is capable of producing 50 tons of copper at each pouring.

201 *Wet Copper Extraction Processes.*—Upwards of half a million tons of iron pyrites, containing on an average 3 per cent.

[1] *Mining and Scientific Press*, 1912, 222.

of copper, are annually burnt in the sulphuric acid works of this country. The residual oxide of iron, known as burnt pyrites, or *blue billy*, is too poor in copper to render it possible to apply to it any of the ordinary dry-smelting operations.

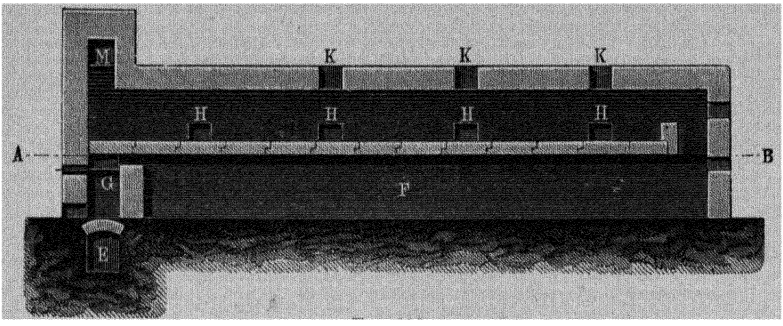


FIG. 119.

Processes for accomplishing this end have been proposed by Longmaid and Henderson, and are now carried out on a large scale. These operations depend upon the fact that if the ground burnt ore be mixed with from 12 to 15 per cent. of coarsely crushed rock-salt, and the mixture properly calcined, the whole

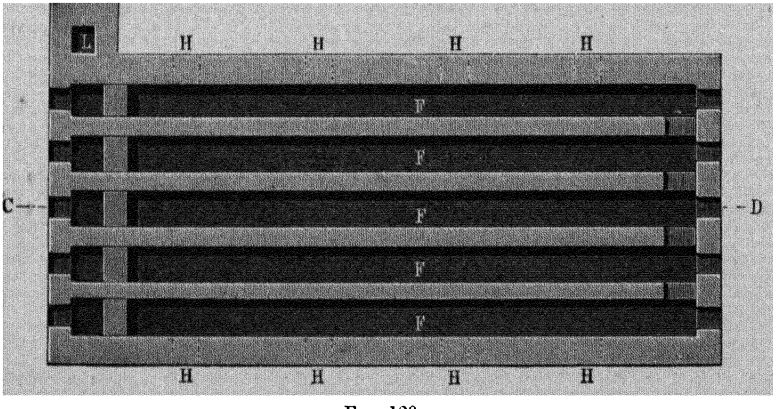


FIG. 120.

of the copper is converted into a soluble cupric chloride. The roasted mass is then lixiviated, and the copper contained in solution thrown down as metal by scrap-iron, any silver contained in the solution being previously recovered by the Claudet process (p. 471) as silver iodide by the addition of potassium or zinc iodide. The calcination is usually carried on in long furnaces shown in Figs. 119, and 120, the mixture of ore and salt being

introduced through hoppers placed above the furnace; the temperature is kept at a dull red heat, and the mass is frequently stirred. The ordinary furnace charge is 3 tons 5 cwt., and the operation lasts about six hours. It is found that the success of the working of the process depends upon the relative amounts of sulphur and copper existing in the ore, the sulphur exceeding the copper by about 0·5 per cent. If the proportion of sulphur in the burnt ore be less than this, a sufficient quantity of raw pyrites must be added. During the calcination considerable quantities of chlorine and hydrochloric acid gases are evolved, together with some vapours of ferric and cupric chlorides. In order to prevent these noxious vapours from passing into the atmosphere, the exit flue from the furnace is connected with a wash-tower filled with open brickwork, down which a current of water passes. The precipitate of metallic copper, thrown down from the liquors by scrap-iron, contains from 70 to 80 per cent. of copper, and it is either smelted direct for blister-copper, or fused with the fine metal, Cu_2S, of the dry process, then roasted, and afterwards worked up to marketable copper by the process already described.

Another extraction process is that of Hunt and Douglas.[1] According to this, the ores containing carbonates or oxides are simply heated, whilst those containing sulphides must be roasted, as it is necessary for the copper to be in the form of cupric oxide.

The ore is then treated with a solution prepared by dissolving 120 parts of common salt, or 112 parts of calcium chloride, and 280 parts of ferrous sulphate in 1,000 parts of water, and then adding 200 parts of common salt. The process depends upon the fact that ferrous chloride, $FeCl_2$, is thus formed, which in contact with common salt converts the copper oxides into chlorides. If cuprous oxide be present, metallic copper is at once precipitated.

$$3Cu_2O + 2FeCl_2 = 2Cu + 4CuCl + Fe_2O_3.$$

Cupric oxide is decomposed as follows:

$$3CuO + 2FeCl_2 = 2CuCl + CuCl_2 + Fe_2O_3.$$

Cuprous chloride, although insoluble in water, is held in solution in the presence of the other chlorides, and then decomposed by iron together with the cupric chloride.

The advantage of this process lies in its requiring smaller

[1] *Engineering*, 1876, 22, 419.

quantities of iron for the precipitation of the copper, since part of this is present as cuprous chloride. The objections are the formation of basic salts, the difficulty of separating the solution from the residue, and the difficulty of recovering any silver present. These objections have led to the adoption of a new Hunt and Douglas process, in which the copper oxide is dissolved by means of dilute sulphuric acid, and ferrous or calcium chloride added to convert the copper into cupric chloride, sulphur dioxide being then forced through to precipitate the copper as cuprous chloride :

$$CuCl_2 + CuSO_4 + SO_2 + 2H_2O = 2CuCl + 2H_2SO_4.$$

The cuprous chloride is separated and treated with iron for the formation of metallic copper, or with milk of lime for the formation of cuprous oxide, which is smelted with carbon for the production of copper. The solution from the cuprous chloride precipitate is freed from sulphur dioxide by blowing in hot air, and is then available for dissolving a further quantity of ore.

The Rio Tinto process, largely employed in Spain, consists in preparing heaps of about 100,000 tons of ore in such a manner that air circulates through the material. In this way the copper is oxidised to sulphate, and is afterwards leached out with water and precipitated on iron.

The leaching of oxidised ores of copper, especially those containing carbonates, with dilute sulphuric acid, and the subsequent recovery of the copper by precipitation on iron or by electrolysis has been adopted on many mines but generally speaking has not been very successful. It will be realised that only ores in which the copper occurs in an easily soluble form, associated with gangue minerals little affected by the solvent are suitable for this process, and it may be added that cheap acid and cheap iron or power are also necessary. Under favourable conditions, with large quantities of suitable ore, capable of being mined cheaply and with modern plant, capable of dealing with big tonnages, ores containing from 0·5 to 1·5 per cent. of copper may be treated at a profit.

For low grade oxidised ores associated with carbonates of lime and magnesia, which render them unsuitable for sulphuric acid leaching, solutions of ammonia together with an ammonium salt have been employed. The success of such a process depends on the following : Oxide of copper is soluble in ammoniacal solutions, yielding copper ammonium compounds; solutions of cupric

ammonium salts are capable of dissolving metallic copper, yielding cuprous ammonium salts which are capable of being oxidised to cupric ammonium salts by air or other oxidising agents; copper ammonium solutions, on distillation, are decomposed yielding copper oxide and ammonia, which latter may be recovered and used again.

The process has been applied to the treatment of old tailings at the Calumet and Hecla Mine,[1] where solutions containing 1 per cent. of ammonia are used for leaching. The copper-bearing solution is distilled, copper oxide being precipitated and ammonia and ammonium carbonate recovered and used for further leaching solution.

Solutions of sulphur dioxide have also been used in the Neill process for the extraction of copper from oxidised ores or from roasted sulphide ores. The ground material is charged into wooden revolving barrels with water and sulphur dioxide is passed through one of the trunnions. The copper dissolves readily, forming copper sulphite, and the solution thus formed is run into vats and heated to boiling point by means of steam. Sulphur dioxide is expelled and from 55 to 75 per cent. of the copper is precipitated as hydrated cupro-cupric sulphite, which is washed, dried, and reduced to copper in a reverberatory furnace. The copper remaining in solution is recovered by means of scrap iron.

Electrolytic Refining of Copper.

202 Copper is refined on the large scale by electrolytic methods, this process being especially applicable in the case of impure copper containing silver or gold. For this purpose the copper is cast into suitable slabs which are placed in a wooden tank lined with lead, and form the anodes, thin sheets of pure copper being employed as cathodes; the solution in the tank contains 5 to 10 per cent. of sulphuric acid and 15 to 20 per cent. of crystallised copper sulphate.

For the process to work successfully it is necessary to keep the bath acid by adding sulphuric acid from time to time, and to maintain the copper content by addition of copper sulphate. It is also necessary to keep the solution in the tanks in active circulation. Nearly all the impurities, including silver, gold, platinum, tin, arsenic, antimony, and lead, are ultimately found in the precipitate or slime, which is deposited at the bottom of

[1] C. H. Benedict, *Mining and Scientific Press*, April, 1915.

the tank, whilst iron, zinc, nickel, and cobalt remain in solution in the liquor.[1] This slime is usually worked up for the precious metals by treatment with sulphuric acid for the removal of the copper, iron, and arsenic, followed by treatment in the silver refinery.

Electrotyping Process.

203 The electrolytic method is employed, not only for the refining of metallic copper, but also very largely for obtaining a coating of metallic copper on any suitable object, the latter being employed as the cathode in a bath of copper sulphate solution, the anode consisting of slabs of metallic copper. This industry dates back much further than that of the electrolytic refining of copper; the latter being in reality an offspring of the electrotyping process.

In the year 1836 De la Rue, when using a Daniell's battery, observed "that the copper plate is covered with a coating of metallic copper which is continually being deposited; and so perfect is the sheet of copper thus formed, that on being stripped off it has the counterpart of every scratch of the plate on which it is deposited."[2] This observation was followed up by other physicists, and in 1839 Jacobi of St Petersburg published his galvano-plastic process, "a method of converting any line however fine, engraved on copper, into a relief by galvanic process, applicable to copper-plate engravings, medals, stereotype plates, ornaments, and to making calico-printing blocks, and patterns for paper-hanging."[3] In the same year T. Spencer of Liverpool read a paper on the "Electrotype Process" to the Liverpool Polytechnic Society, and also in 1839 J. C. Jordan published results of experiments made with the same object.[4]

Electrotyping in copper has become a most important branch of industry, statues and other works of art being largely reproduced in this way.

For the purpose of reproducing statues, busts, and similar objects, casts of the original in gypsum or models in gutta-percha are saturated with oil, coated with graphite to give the surface the necessary conducting power, guiding wires connected to various parts of the surface, and the object then made

[1] Kiliani, *Berg.- und Hutten. Ztg.*, 1885, 249.

[2] *Phil. Mag.*, [3], 1836, 9, 484. [3] *Athenæum*, May 4, 1839.

[4] For a detailed account of these discoveries, see Gore's *Art of Electro-Metallurgy*.

the cathode in a bath of copper sulphate solution. When the coating is $\frac{1}{10}$th of an inch thick the process is stopped, the copper cut through in several places and the plaster core extracted. The inner surface of the various parts is then subjected to the action of sulphuretted hydrogen to coat it with a thin layer of sulphide, and these are again placed in the copper sulphate bath as the cathode. As soon as the deposit on the interior is of sufficient thickness the parts are removed, the thin outer shell of copper is torn off, and the parts are then joined together.

For the purpose of covering iron, an alkaline solution of copper cyanide in potassium cyanide is employed. On dipping the iron or steel article into this solution a thin deposit of copper is obtained, and upon this a coating of silver or gold can easily be deposited. For the purpose of obtaining a thicker deposit of copper on iron, the operation is conducted as described and the object then placed in a copper sulphate depositing bath. The solution, according to Wilde's process, is maintained in a constant state of rotation, and the iron heated to 90° before it is placed in the warm solution of cyanide, no hydrogen then being liberated on the copper, so that the latter adheres more closely to the iron. The process is now successfully applied to the economical production of coppered cast-iron rollers for calico-printing. When a new pattern is required one-half of the copper is turned off and the roller restored to its original thickness by electro-deposition at a small cost. The maintenance of the rollers to a standard size is a great advantage.

204 The following table shows the amount of copper produced in 1918, by the chief copper-producing countries :[1]

Africa	31,110	metric tons.
Australasia	33,838	,, ,,
Canada	52,693	,, ,,
Chili	85,850	,, ,,
Germany	40,000	,, ,,
Japan	95,800	,, ,,
Peru	44,800	,, ,,
Mexico	75,529	,, ,,
Spain and Portugal	41,000	,, ,,
United States	848,203	,, ,,
Other countries	46,337	,, ,,
	1,395,160	,, ,,

[1] *Mineral Industry*, 1919, **28**, 150.

205 *Alloys of Copper.*—Copper unites with a number of other metals to form alloys, many of which are of great technical importance. Among these may be mentioned brasses, alloys of copper and zinc, bronze, gun-metal and bell-metal, which are alloys of copper and tin, and German silver, which is an alloy of copper, nickel, and zinc. A description of these will be found under the metal forming the second constituent of the alloy.

206 *Properties of Copper.*—Commercial copper usually contains traces of the other metals which are present in the ores, and in addition to these not infrequently arsenic, sulphur, and oxygen. Pure metallic copper is obtained either by heating the pure oxide in hydrogen, or by the electrolysis of a solution of pure copper sulphate by means of platinum electrodes.

Copper possesses a peculiar red colour and bright metallic lustre. The true copper-red colour is, however, not seen by a single reflection, and is only observed when the light entering the eye has been many times reflected from the surface of the copper. This is well seen if a piece of straight copper foil be bent at an acute angle and held before the observer; the fine deep red copper colour is noticed near the point at which the two copper surfaces approach.

Copper is found in the native state crystallised in regular octahedra; crystals of the same form are also found as an artificial refinery product. If a piece of phosphorus be allowed to remain for some months in contact with a clean copper wire under a solution of copper sulphate, single octahedra of metallic copper are formed together with copper phosphide (Wohler), and a similar artificial formation of crystalline copper is observed in Golding Bird's decomposing cell,[1] as well as in the cells of Meidinger's battery. In both these cases the metal is deposited from solution very slowly.

Copper is one of the toughest of metals. It is very malleable, and may be hammered or rolled into thin leaf (Dutch metal), or drawn into fine wire. After hammering it possesses a finely fibrous silky fracture, but very slight admixture of other metals makes it more brittle, and imparts to it a less distinctly fibrous nature. Native copper has a specific gravity of 8·94; cast copper, probably because it always contains small cavities, has a specific gravity of 8·92; rolled or hammered copper 8·95; and pure electrolytic copper 8·945 (Hampe). Copper which has been distilled in a vacuum[2] has the specific gravity

[1] *Phil. Trans.*, 1837, **127**, 37.

[2] Kahlbaum, Roth, and Siedler, *Zeit. anorg. Chem.*, 1902, **29**, 177.

at 20°/4° of 8·933 and, after compression at 10,000 atmospheres, of 8·938. Very thin copper leaf transmits a greenish-blue light. When a solution of copper sulphate is allowed to remain in contact with pure zinc, pure metallic copper is deposited as a fine spongy mass, which after washing and drying forms a soft, impalpable dark-red powder.

Copper melts at 1084·1° (Holborn and Day),[1] and in the molten state possesses a greenish-blue colour. When heated at a temperature just below that of its melting point, copper becomes so brittle that it can be pulverised in a mortar. Molten copper possesses the power of absorbing sulphur dioxide and hydrogen, which are evolved in the form of bubbles when the metal cools, giving rise to the peculiar phenomenon known as "spitting," when a solid crust has already been formed on the surface. Spongy copper absorbs at a red-heat 0·6 times its volume of hydrogen, whilst copper wire absorbs 0·308 times its volume (Graham). Copper may be readily volatilised in an electric furnace, and condenses in the form of iridescent filaments having a red colour and a specific gravity of 8·16,[2] the vapour forming cupric oxide in contact with air.

If cupric oxide be reduced at 200° by means of hydrogen or carbonic oxide an active form of the metal is obtained which takes fire when brought into contact with bromine. The active properties are retained when the metal is kept in a vacuum, but disappear after hammering.[3]

There is some evidence [4] for the existence of two enantiotropic forms of copper with a transition temperature about 72°.

Colloidal Copper.—Copper has been obtained in the form of colloidal solutions in several ways. Thus the reduction of a solution of copper chloride by stannous chloride in the presence of an alkaline tartrate yields a reddish-brown solution of copper,[5] whilst by reducing ammoniacal copper sulphate with a dilute solution of hydrazine hydrate a solution of copper is obtained which is blue by transmitted light.[6] It has also been prepared by Paal and Leuze,[7] by adding sodium hydroxide to a mixture of

[1] *Amer. J. Sci.*, 1900, **10**, 171.

[2] Moissan, *Compt. rend.*, 1905, **141**, 853.

[3] Colson, *Compt. rend.*, 1899, **128**, 1458.

[4] Cohen and Helderman, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 628; 1914, **17**, 60; but see also Burgess and Kellberg, *J. Washington Acad. Sci.*, 1916, **5**, 657.

[5] Lottermoser, *Anorganische Colloide* (Stuttgart, 1901), p. 61.

[6] Gutbier and Hofmeier, *Zeit. anorg. Chem.*, 1905, **44**, 225.

[7] *Ber.*, 1906, **39**, 1550.

solutions of copper sulphate and sodium lysalbate or protalbate, products of the decomposition of albumin by sodium hydroxide, dialysing the resulting mixture and heating on the water-bath with the addition of hydrazine hydrate. If a concentrated solution of copper oxide is reduced in this manner the resulting copper solution is blue, whilst a dilute solution of the oxide yields a red copper solution.

When alcohol is added to a solution of anhydrous copper sulphate in concentrated sulphuric acid, so as to form a separate upper layer, a violet zone is first formed between the two liquids which gradually changes to brown owing to the production of a solution of colloidal copper.[1] Methyl alcohol, ether, acetone, acetic acid, and chloroform act similarly.

Colloidal copper has also been obtained by passing an electric arc under water, the cathode being composed of an iron wire that has previously been dipped in copper sulphate.[2]

207 Metallic copper is largely used for a great variety of technical and domestic purposes, being especially valuable for its toughness. Next to silver, copper is the best conductor of electricity, and hence pure copper is very largely employed for electric light mains and submarine telegraphs. The purest copper must be employed, as very small quantities of impurities lower the conductivity to a large extent.

COPPER AND OXYGEN.

208 These elements form six compounds as follows :—

Copper quadrantoxide, Cu_4O.
Copper trientoxide, Cu_3O.
Cuprous oxide, Cu_2O.
Cupric oxide, CuO.
Copper peroxide, Cu_2O_3.
Copper dioxide or cupric peroxide, CuO_2.

Of these oxides the third and fourth have long been known, as they are formed when metallic copper is heated in the air. Copper scale, which falls from hot metallic copper when it is worked with the hammer, is a mixture of these two oxides. The

[1] A. Rassenfosse, *Bull. Acad. roy. Belg.*, 1910, 738. Consult *Grundriss der Kolloid Chemie*, Wo. Ostwald (Dresden, Steinkopff, 1911); also *Physics and Chemistry of Colloids*, by Emil Hatschek (Churchill, 1913).

[2] Billitzer, *Ber.*, 1902, **35**, 1929.

portion of the scale next to the metal consists of the red cuprous oxide, while the outside portion is composed of black cupric oxide. Dioscorides and Pliny mention the existence of the red compound, indeed they distinguished two varieties, the one obtained in the form of a finely divided powder by pouring water on to the surface of freshly melted copper, and termed *flos aeris*, and the other obtained as copper scale and termed *aeris squama*. The Latin Geber explained the calcination of copper by the combustion of the sulphur which this metal was supposed to contain (Vol. I., p. 5), and many later chemists speak of copper as being more or less calxed. It was not, however, until the year 1798 that Proust distinctly stated that the black and red calces of copper were two distinct oxidation products.

They have the composition Cu_2O and CuO respectively, and give rise to characteristic series of salts, known as the *cuprous* and *cupric* salts. In addition, lower oxides of the formulæ Cu_4O and Cu_3O, and peroxides, Cu_2O_3 and CuO_2, have been prepared, none of which yield salts. Hydrated mixed oxides of the formulæ $Cu_3O_2,2H_2O$ and $Cu_4O_3,5H_2O$ have also been described by Siewert.[1]

Cuprous Oxide, Cu_2O.—This oxide occurs as cuprite or red copper ore, crystallising in octahedra and in other forms of the regular system (Class 29, p. 209) having a specific gravity of 5·75. It possesses a bright red or brownish-red colour, frequently exhibiting a diamond lustre, and also occurs in the massive state. In the mineral chalcotrichite it forms a hair-like mass consisting of small cubical crystals elongated in the direction of one of the axes.

Cuprous oxide may be artificially obtained by heating thick copper wire in a muffle for half an hour at a white heat, and then for some hours to dull redness; small dark crystals of the oxide then cover the surface of the metallic bead. It is also obtained by heating cupric oxide in a similar manner, but if too strongly heated the cuprous oxide loses a further quantity of oxygen. Cuprous oxide is formed on the surface of molten copper when exposed to the air. The metal is capable of dissolving considerable quantities of this oxide, forming bodies which behave like true alloys. A eutectic is formed with 3·5 per cent. of the oxide, having a melting point of 1065°. The equilibrium between cuprous and cupric oxides and oxygen has been studied by Smyth and Roberts.[2] The finely-divided copper

[1] *Zeit. Chem.*, 1866, 363. [2] *J. Amer. Chem. Soc.*, 1920, **42**, 2582.

obtained by reducing a copper salt in hydrogen at as low a temperature as possible combines with atmospheric oxygen on exposure to the air with formation of cuprous oxide. By reducing an alkaline copper solution with sugar cuprous oxide is deposited on warming as a bright red crystalline powder.

Cuprous oxide is also formed by the slow oxidation of the metal under water. Sage, in the year 1773, pointed out that the remains of a statue which had long lain under water were partially converted into this oxide, and J. Davy observed that an antique helmet, found in the sea near Corfu, was covered with crystals of metallic copper as well as of cuprous oxide. It has also been obtained in the crystalline state by the slow electrolytic decomposition of copper sulphate.[1] Cuprous oxide is prepared on a large scale by electrolysis of a hot solution of sodium chloride with copper anodes enclosed in diaphragms. The product, which is practically anhydrous and of a beautiful scarlet colour, is largely used as a poisonous pigment in anti-fouling compositions.

Commercial cuprous oxide has a specific gravity of from 5·34 to 5·37, and the more finely it is divided the finer red does its colour become. It fuses at a red heat, and colours glass red, a property known to the ancients and in the middle ages. The knowledge of the process was, however, completely lost in later times, and it was not until about the year 1827 that Bontemps in France and Engelhardt in Germany succeeded in reviving the manufacture of this ancient red glass.

Cuprous Hydroxide.—When cuprous chloride is decomposed by potash or soda, a yellow precipitate is produced, which was considered to be a partially dehydrated cuprous hydroxide, of the formula $Cu_8O_3(OH)_2$ or $4Cu_2O,H_2O$. When the method of preparation is varied, however, the amount of water present in the dry substance also varies, and it is therefore probably not a true hydroxide.[2] The same yellow compound may be prepared electrolytically, using a platinum plate as cathode and one of copper as anode in a solution of potassium chloride,[3] or by adding caustic alkali to a solution of a cupric salt containing glucose.[4]

It absorbs oxygen readily and becomes of a blue colour when

[1] Golding Bird, *Phil. Trans.*, 1837, **127**, 37.
[2] Groger, *Zeit. anorg. Chem.*, 1902, **31**, 326.
[3] Lorenz, *ibid.*, 1896, **12**, 436. See also Moser, *ibid.*, 1919, **105**, 112.
[4] Sarma, *Chem. News*, 1921, **122**, 99.

exposed to moist air. It dissolves in ammonia, as does red cuprous oxide, forming a colourless liquid which on exposure to the air quickly oxidises and becomes of a dark blue colour.

Cuprous oxide corresponds to the series of cuprous salts in which each atom of copper replaces only one atom of hydrogen. These are mostly white salts which are insoluble in water, and readily oxidise to cupric salts.

Cupric Oxide, CuO.—This substance occurs as tenorite and melaconite, as a dark earthy mass or in bright lustrous laminæ and more rarely in cubes. It can be artificially produced by the gentle ignition of the nitrate, carbonate, or hydroxide. Thus obtained it is a black hygroscopic powder which commences to decompose when heated to 1025°, cakes together, and then fuses at about the melting point of copper, losing oxygen and forming Cu_2O or Cu_3O according to the temperature. If the amorphous oxide be ignited with five times its weight of caustic potash it becomes crystalline, and regular tetrahedra possessing a metallic lustre are formed (Becquerel). In copper refineries the occurrence of a crystalline oxide has also been observed. It is reduced by carbon at 700°.[1] When heated in the presence of hydrogen, carbon monoxide, marsh-gas, and other carbon compounds, it is easily reduced to the metallic state with formation of water and carbon dioxide, and hence it is largely used in the ultimate analysis of organic compounds. Cupric oxide when brought in contact with fused glass imparts to it a fine light green colour; this was known to the ancients as well as to the later alchemists, who rediscovered the fact and found that artificial emeralds could be prepared by means of copper. The writer known as Basil Valentine says, "the emerald contains sulphur veneris," and the writers of the sixteenth century who treat of the artificial production of gems all mention the fact that copper calx colours glass green.

Cupric Hydroxide, $Cu(OH)_2$, is obtained as a light blue precipitate by decomposing a solution of a cupric salt in the cold with an alkali. This precipitate, however, almost always contains a considerable quantity of alkali, and the hydroxide is obtained in a purer state by adding sal-ammoniac to the solution before precipitation, and then washing the precipitate well with warm water. It may also be obtained by passing an electric current through a well-stirred solution of potassium nitrate, using a copper plate as anode and one of platinum as cathode.[2]

[1] Doeltz and Graumann, *Metallurgie*, 1907, **4**, 420.

[2] Lorenz, *Zeit. anorg. Chem.*, 1896, **12**, 436.

The hydroxide, after having been dried over lime, does not undergo loss of water on heating to 100°, but the freshly precipitated compound in the presence of water undergoes spontaneous dehydration, slowly in the cold, very rapidly at 100°, with formation of a black substance [1] having the composition $Cu_4O_3(OH)_2 = Cu(OH)_2 + 3CuO$. This compound when kept in a dry vacuum continues to lose water slowly, until its composition corresponds to the formula $6CuO,Cu(OH)_2$ (Sabatier). A hydrated cupric oxide of the composition $6CuO,H_2O$ has been obtained as a brown powder by the action of chlorine on cupric hydroxide suspended in a solution of potassium hydroxide.[2]

If copper hydroxide is precipitated together with a large excess of aluminium hydroxide,[3] *e.g.*, by adding a slight excess of caustic soda to a solution of sulphates containing about 5 per cent. CuO and 95 per cent. Al_2O_3, a pale bluish product is obtained which retains its blue colour on drying at 100° and even on ignition in a Bunsen flame.

Cupric hydroxide dissolves readily in aqueous ammonia, yielding a beautiful dark blue liquid, which is also produced when copper is allowed to remain in contact with aqueous ammonia and the liquid exposed to the air. When largely diluted with water or treated with strong caustic potash, cupric hydroxide separates out from the solution, and on heating this the black hydroxide is precipitated. A solution of copper oxide in ammonia (Schweizer's reagent) possesses the property of dissolving cellulose (cotton-wool, linen, filter-paper, etc.).[4]

The above oxide and hydroxide yield the cupric salts on treatment with acids, the copper acting as a dyad. Many of the salts formed with colourless acids are colourless when anhydrous, but the hydrated salts are blue or green, the aqueous solutions having a similar colour; anhydrous cupric bromide and cupric chloride, however, are coloured. They combine with ammonia, forming compounds which dissolve in water, forming deep blue solutions. The soluble salts have an unpleasant metallic taste and an acid reaction to litmus.

In large doses the copper salts are poisonous, causing vomiting, but in small doses they have very little action, the cases of poisoning formerly supposed to have taken place from the

[1] Sabatier, *Compt. rend.*, 1897, **125**, 101, 301.
[2] Mawrow, *Zeit. anorg. Chem.*, 1900, **23**, 233.
[3] Schenck, *J. Physical. Chem.* 1919, **23**, 283.
[4] Schweizer, *J. pr. Chem.*, 1857, **72**, 109.

presence of copper in food being probably due to the presence of organic decomposition products.[1]

Both cupric hydroxide and the black hydroxide form basic salts with other copper salts, and double basic salts with many other metals,[2] while basic salts are also known corresponding to the hydroxide, $6CuO,Cu(OH)_2$ (Sabatier).

Copper Quadrantoxide, Cu_4O, is formed by careful addition of a solution of copper sulphate to a well cooled dilute solution of stannous chloride in caustic potash, the cupric hydroxide first formed being reduced by the stannous chloride with formation of the quadrantoxide and potassium stannate :[3]

$$4Cu(OH)_2 + 12KOH + 3SnCl_2 = Cu_4O + 6KCl + 3K_2SnO_3 + 10H_2O.$$

Copper quadrantoxide is an olive-green powder which undergoes no change under water if the air be completely excluded. Exposed to air, it rapidly absorbs oxygen. The composition of this compound is ascertained from the action of dilute hydrochloric or sulphuric acid upon it, when the following decomposition takes place :

$$Cu_4O + 2HCl = 2CuCl + 2Cu + H_2O$$
$$Cu_4O + H_2SO_4 = CuSO_4 + 3Cu + H_2O.$$

Copper Trientoxide, Cu_3O, is prepared by heating cupric oxide at temperatures between 1500° and 2000°, as a yellowish-red mass hard enough to scratch glass. It is unaffected by concentrated mineral acids with the exception of hydrofluoric acid, but is dissolved by fused caustic potash.[4]

Copper Peroxide, Cu_2O_2, has been obtained by the anodic oxidation of copper in 12–14*N*-caustic soda solutions with a current density greater than 0·1 ampere per sq. cm.[5] It has been obtained also by passing chlorine into a strong solution of sodium hydroxide previously saturated with copper hydroxide.[6] This oxide is yellow, is very unstable, and possesses marked oxidising power, decomposing hydrochloric acid, forming aldehyde from alcohol, and nitrite from ammonia.

[1] Lehmann, *Trans. Inter. Cong. Hygiene and Demography* (London), 1891, **5**, 63.

[2] Mailhe, *Compt. rend.*, 1902, **134**, 42; Recoura, *ibid.*, 1901, **132**, 1414.

[3] Rose, *Pogg. Ann.*, 1861, **120**, 1.

[4] Bailey and Hopkins, *Journ. Chem. Soc.*, 1890, **57**, 269.

[5] E. Muller and F. Spitzer, *Zeit. Elektrochem.*, 1907, **13**, 25.

[6] E. Muller, *Zeit. anorg. Chem.*, 1907, **54**, 417.

Copper Dioxide, CuO_2,H_2O, is best obtained by allowing finely divided cupric hydroxide to stand with aqueous hydrogen peroxide in the cold for several days, the mixture being frequently shaken. A crystalline precipitate is thus formed, which, after washing with water, alcohol, and ether at 0°, is dried in a vacuum. It has a yellowish-brown colour, and when moist readily decomposes above 6°; when dry it does not undergo change at 170°, but at 180° decomposes, forming cupric oxide.[1]

Cuprous Compounds.

209 *Cuprous Hydride*, $(CuH)_n$.—This compound, discovered by Wurtz,[2] is deposited as a yellow or reddish-brown precipitate, when a solution of copper sulphate is treated with hypophosphorous acid or its sodium or zinc salt at a temperature not exceeding 70°. At higher temperatures it decomposes into copper and hydrogen according to Wurtz, but according to Bartlett and Merrill[3] cupric hydride and hydrogen are really formed. It readily ignites in chlorine gas, and is decomposed by hydrochloric acid as follows:

$$CuH + HCl = CuCl + H_2.$$

Cuprous Fluoride, CuF, is best obtained by heating cuprous chloride in a current of hydrogen fluoride at 1100-1200°, at which temperature the fluoride volatilises. It forms a ruby-red crystalline mass, or red powder, which dissolves in boiling hydrochloric acid, but, unlike cuprous chloride, is not reprecipitated by addition of water.[4]

Cuprous Chloride, CuCl.—This substance was first obtained by Boyle[5] by the action of copper on mercuric chloride. He compared the substance thus obtained, which he found turned green on exposure to air, to resin or gum, and hence he gave to it the name of *resina cupri* or *cuprum gummatosum*. Proust obtained the same compound by the action of the dichloride on the salts of the monoxide, and J. Davy showed that cuprous chloride is formed together with the cupric salt when copper foil or copper filings are thrown into chlorine gas, when they burn with the evolution of a red light. If hydrogen chloride be passed over hot copper contained

[1] Kruss, *Ber.*, 1884, **17**, 2593. [2] *Compt. rend.*, 1844, **18**, 102.
[3] *Amer. Chem. J.*, 1895, **17**, 185. [4] Poulenc, *Compt rend*, 1893, **116**, 1446.
[5] *Considerations and Experiments about the Origin of Qualities and Forms*, 1664.

in a glass tube this compound is formed, and is seen to condense in transparent drops (Wöhler). It may readily be prepared on a large scale by a number of methods, all of which consist eventually in the reduction of cupric to cuprous chloride. For this purpose a mixture of copper and cupric oxide may be boiled with strong hydrochloric acid, or a hydrochloric acid solution of cupric chloride with copper; the metallic copper may be replaced by zinc dust or the cupric chloride by a mixture of cupric sulphate and sodium chloride, and the reduction may also be effected by sulphur dioxide. In all cases the cuprous chloride remains dissolved in the excess of hydrochloric acid, but separates out when the solution is poured into a large bulk of water as a heavy white crystalline precipitate which may be purified by washing. It crystallises from hot hydrochloric acid in white tetrahedra, has a sp. gr. of 3·7, and melts at about 434°, solidifying to a brown mass.

On exposure to light the moist substance quickly assumes a dirty violet tint, but if dried in absence of air and light, it only assumes a faint yellow colour on exposure. When allowed to remain n moist air it absorbs oxygen and is converted into green cupric oxychloride, $3CuO,CuCl_2,4H_2O$,[1] whilst repeated treatment with water in the presence of air converts it into cuprous oxide and cupric chloride.[2] If treated with water in an atmosphere of hydrogen or carbon dioxide, the chlorine passes completely into solution and a red residue of copper and cuprous oxide is obtained (Gröger).

Cuprous chloride readily dissolves in ammonia, forming, if air be completely excluded, a colourless solution which rapidly turns blue in the air owing to the absorption of oxygen and formation of cupric salts; this reaction has been used as a means of estimating the dissolved oxygen in water.[3]

Cuprous Chloride and Carbon Monoxide.—Cuprous chloride dissolves readily in hydrochloric acid, and this solution as well as the ammoniacal solution absorbs carbon monoxide, forming an unstable compound which separates out in nacreous scales when the concentrated solution is saturated with the gas, or when a thin paste of cuprous chloride and hydrochloric acid is saturated with carbon monoxide and water then added.[4]

[1] Gröger, *Zeit. anorg. Chem.*, 1901, **28**, 154.
[2] Lean and Whatmough, *Journ. Chem. Soc.*, 1898, **73**, 149.
[3] Ramsay and Homfray, *J. Soc. Chem. Ind.*, 1901, **20**, 1071.
[4] Jones, *Amer. Chem. J.*, 1899, **22**, 287.

Under certain conditions, a crystallised compound corresponding to $2CuCl,CO,H_2O$ is obtained.[1]

Cuprous Chloride and Acetylene.—When acetylene is passed into a solution of cuprous chloride in potassium chloride acidified with hydrochloric acid a red precipitate having the composition $(CuCl)_2,C_2H_2$ is formed. If the solution is neutral the precipitate has the composition $C_2H_2,(CuCl)_2,Cu_2O$ or $C_2H_2[(CuCl)_4KCl]_2$, according to the conditions of the experiment.[2]

The solution of cuprous chloride in ammonia absorbs acetylene, forming a blood-red precipitate of cuprous acetylide, Cu_2C_2 or Cu_2C_2,H_2O, which is very explosive.[3] On addition of acids to this compound it is decomposed with evolution of acetylene, and has been used as a means of preparing pure acetylene (Vol. I., p. 790). Ammoniacal cuprous chloride also absorbs other hydrocarbons of the acetylene series.

Cuprous Bromide, CuBr, is formed with ignition when bromine is brought into contact with copper heated below a red heat. It forms a brownish crystalline mass which turns blue on exposure to sunlight, and has a specific gravity of 4·72.

Cuprous Iodide, CuI.—This is the only known iodide of copper. It is obtained by the direct combination of the two elements when heated together, or when copper is dissolved in a hot concentrated solution of hydriodic acid. If potassium iodide be added to a solution of a cupric salt, cuprous iodide is precipitated, half the iodine being liberated. The production of iodine can be prevented by the previous addition of sulphurous acid or ferrous sulphate:

$$2CuSO_4 + 2FeSO_4 + 2KI = 2CuI + Fe_2(SO_4)_2 + K_2SO_4.$$

A convenient way of preparing cuprous iodide is to heat copper foil, torn into shreds, in a porcelain crucible and to add iodoform in small quantities at a time. A violent reaction takes place, violet clouds of iodine are evolved, and, on cooling, the copper is covered with a black scale which readily peels off, leaving a clean copper surface. This black scale consists of about 98 per cent. of cuprous iodide, and contains a little carbon and copper oxide.[4] The copper may then be reheated with iodoform until all is converted into the iodide.

[1] Berthelot, *Ann. Chim. Phys.*, 1901, [7], **23**, 32.

[2] Chavastelon, *Compt. rend.*, 1901, **132**, 1489.

[3] Keiser, *Amer. Chem. J.*, 1892, **14**, 285. See also Scheiber, *Ber.*, 1908, **41**, 3816.

[4] Lean and Whatmough, *Journ. Chem. Soc.*, 1898, **73**, 149.

Cuprous iodide is a white crystalline powder which undergoes little alteration on exposure to light, and has a specific gravity of 5·653 at 15°.[1] It melts at 628°, solidifying again to form a brown mass, which yields a green powder. It is almost insoluble in water, 1 part dissolving in 233,000 parts of water. When cuprous iodide is heated with cupric chloride (or bromide) it is converted into cuprous chloride (or bromide).[2]

Cuprous Sulphide, Cu_2S, occurs in nature as chalcocite, copper-glance, or vitreous copper, in rhombic six-sided tablets or prisms having a blackish lead-grey streak and a metallic lustre, which is often tarnished green or blue. As produced artificially from copper and sulphur in the vacuum furnace, it has a specific gravity of 5·785, 25°/4°, melts at 1130° ± 1°, and does not dissociate below 1200°. The sulphides formed by fusing copper and sulphur together under ordinary conditions are variable in composition and are really solid solutions of cuprous and cupric sulphides. Similar products result when cuprous sulphide is heated in hydrogen sulphide or sulphur vapour, and for this reason the melting points under these conditions are 1096° and 1057° respectively. Cuprous sulphide is dimorphous, the inversion temperature being 91°.[3]

The black substance left when copper is dissolved in sulphuric acid is stated to be cuprous sulphide.[4]

Cuprous Sulphite, Cu_2SO_3,H_2O.—This salt is obtained by passing sulphur dioxide into a hot solution of cuprous acetate in acetic acid, and separates as a heavy white precipitate consisting of microscopic nacreous plates. It combines with the alkali sulphites, forming a number of double salts which are colourless crystalline compounds. The double salt, $(NH_4)_2SO_3,2Cu_2SO_3$, when heated yields a bright red powder or scales of cupro-cupric sulphite, $Cu_2SO_3,CuSO_3,2H_2O$. A dark red crystalline precipitate of cupro-cupric sulphite is also obtained in the Neill process (p. 430).

Colourless crystals of the double salt, $Cu_2SO_3,Na_2SO_3,12H_2O$, are deposited from aqueous solutions of cupric sulphate and sodium sulphite kept in a closed vessel at the ordinary temperature.[5]

Cuprous Sulphate, Cu_2SO_4, is obtained by heating powdered

[1] Spring, *Rec. trav. chim.*, 1901, **20**, 79

[2] Barbieri, *Atti R. Accad. Lincei*, 1907, [5], **6**, i, 528.

[3] Posnjak, Allan, and Merwin, *Economic Geology*, 1915, **10**, 491.

[4] Adie, *Proc. Chem. Soc.*, 1899, 133.

[5] Baubigny, *Compt. rend.*, 1912, **154**, 434, 701.

cuprous oxide with methyl sulphate at 160° until methyl ether ceases to be evolved:

$$(CH_3)_2SO_4 + Cu_2O = Cu_2SO_4 + (CH_3)_2O.$$

The salt is obtained as a greyish-white powder which should be washed in ether, excluding air, and dried in a vacuum. When dry, it is stable in dry air, but is immediately decomposed by water with the development of heat, forming cupric sulphate and copper. It oxidises at 200°, yielding $CuO,CuSO_4$.[1]

Cuprous Nitride, Cu_3N.—Nitrogen gas does not act upon red-hot copper, but ammonia is decomposed into its elements when passed over the hot metal, the copper being rendered spongy and brittle, and losing its metallic lustre. This alteration in the metal seems to point to the formation and subsequent decomposition of a nitride which is only stable within a short range of temperature.[2] The nitride may be obtained by heating precipitated cuprous oxide in a current of ammonia gas, when a dark green powder is formed which contains 93 per cent. of cuprous nitride.[3] When potassamide is added to a solution of copper nitrate in liquid ammonia, an olive-green precipitate is produced.[4] If this precipitate be heated to 160° in a vacuum, nitrogen is evolved, and cuprous nitride remains as a black amorphous mass. The reaction is represented thus:

$$3Cu(NO_3)_2 + 6KNH_2 = Cu_3N + 6KNO_3 + 4NH_3 + N.$$

An intermediate product of the decomposition of the green precipitate is *cuprous imide*, Cu_2NH. *Potassium ammoniocuprite*, $CuNK_2,3NH_3$, is obtained from cuprous nitride and potassamide in liquid ammonia: it forms well defined colourless crystals.[5] Cuprous nitride is decomposed into its elements at about 300°, whilst acids and alkalis hydrolyse it with formation of ammonium salts or ammonia.

Nitrocopper, Cu_2NO_2, a maroon-coloured powder obtained by passing pure and dry nitrogen peroxide over finely divided copper (obtained by the reduction of copper oxide) at 25–30°, has been shown to have no real existence, the observed phenomena being probably due to surface formation of anhydrous copper nitrate.[6]

[1] Recoura, *Compt. rend.*, 1909, **148**, 1105.

[2] Beilby and Henderson, *Journ. Chem. Soc.*, 1901, **79**, 1245.

[3] Guntz and Bassett, *Bull. Soc. chim.*, 1906, [3], **35**, 201.

[4] E. F. Fitzgerald, *J. Amer. Chem. Soc.*, 1907, **29**, 656.

[5] Franklin, *J. Amer. Chem. Soc.*, 1912, **34**, 1501.

[6] Tartar and Semon, *J. Amer. Chem. Soc*, 1921, **43**, 494; *cf.* Sabatier and Senderens, *Compt. rend.*, 1892, **115**, 236; 1893, **116**, 756.

Cuprous Phosphide.—Copper and phosphorus unite to form cuprous phosphide, Cu_3P, which yields a series of alloys with metallic copper.[1] Alloys containing up to 15 per cent. of phosphorus may be prepared by heating copper and phosphorus together or by adding phosphorus to molten copper. Alloys containing more than 15 per cent. of phosphorus must be prepared in closed vessels owing to the volatility of the phosphorus. The compound Cu_3P (14 per cent. of phosphorus) melts at 1022°,[2] and forms a eutectic with metallic copper, melting at 707° and containing 8·2 per cent. of phosphorus. Cuprous phosphide is also formed when phosphine is passed over heated cuprous chloride or precipitated copper at 180–200°, or over cold moist precipitated cuprous oxide, when it is obtained as a grey amorphous powder which oxidises in oxygen, very slowly at ordinary temperatures, rapidly and with incandescence at 100°, forming phosphorus pentoxide and copper.[3]

A black powder of the composition Cu_5P_2,H_2O is obtained when phosphine is passed into a solution of copper sulphate.[4]

Cuprous Cyanide, CuCN.—When a solution of potassium cyanide is added to a solution of copper sulphate a red precipitate of cupric cyanide is first formed; when the liquid is boiled cyanogen gas is given off and a white precipitate of cuprous cyanide deposited. This same compound is formed by the action of potassium cyanide on cuprous chloride, and dissolves in an excess of the reagent. It may also be formed by heating copper acetate with aqueous ammonia in a sealed tube for two hours at 180°, when a colourless liquid is obtained containing in suspension finely divided copper and cuprous cyanide in crystalline plates.[5] Cuprous cyanide forms a number of double compounds with other cyanides.[6]

Cuprous Thiocyanate, CuCNS.—Potassium thiocyanate gives a black precipitate of cupric thiocyanate when added to a solution of copper sulphate. This on long standing and washing is converted into white cuprous thiocyanate. If a reducing agent such as ferrous sulphate or sulphur dioxide be present the white compound is at once precipitated. This reaction is often employed for the quantitative separation of copper from other metals and also for the separation of thiocyanates.

[1] Heyn and Bauer, *Zeit. anorg. Chem.*, 1907, **52**, 129.
[2] Huntington and Desch, *Trans. Faraday Soc.*, 1908, **4**, 51.
[3] Rubénovitch, *Compt. rend.*, 1899, **128**, 1398. [4] *Ibid.*, **127**, 270.
[5] Vittenet, *Bull. Soc. chim.*, 1899, [3], **21**, 261.
[6] Grossmann and van der Forst, *Zeit. anorg. Chem.*, 1903, **43**, 94.

Cupric Compounds.

210 *Cupric Hydride*, CuH_2.—This compound is obtained, according to Bartlett and Merrill,[1] by the action of heat on cuprous hydride. When freshly prepared it is a reddish-brown spongy mass, which changes after a time to a chocolate powder. It acts as a strong reducing agent, converting potassium chlorate in solution into the chloride, and the nitrate to nitrite and ammonia.

Cupric Fluoride, CuF_2.—When cupric oxide is dissolved in hydrofluoric acid and the solution evaporated, blue crystals having the composition $CuF_2,5H_2O,5HF$ separate out.[2] They are sparingly soluble in water, and are decomposed at 100° with separation of the oxyfluoride, CuF(OH). When heated with ammonium fluoride in a current of carbon dioxide, the crystals yield the anhydrous fluoride as a white amorphous powder, which becomes crystalline at 500° in an atmosphere of hydrogen fluoride.[3]

Cupric Chloride, $CuCl_2$, is formed when metallic copper is burnt in an excess of chlorine, or when the hydrated crystalline chloride is heated. The anhydrous salt may be prepared by adding a large excess of concentrated sulphuric acid very slowly to a solution of cupric chloride, care being taken that the temperature does not rise sufficiently high to decompose the chloride, when it separates out as a yellow precipitate.[4] Cupric chloride prepared from copper is a dark liver-coloured powder which on heating is converted into cuprous chloride with loss of chlorine. It readily dissolves in water, forming a green liquid; this is obtained also by dissolving the oxide or carbonate in hydrochloric acid. Greenish-blue rhombic prisms or needles having the composition $CuCl_2,2H_2O$ separate out on evaporation.

The solution saturated at 17° contains 75·6 parts of the anhydrous salt in 100 of water, and has an emerald-green colour, which on dilution with water changes to bluish-green. It is very deliquescent and is soluble in alcohol, the solution burning with a fine green flame and giving a characteristic channelled-space spectrum.

[1] *Amer. Chem. J.*, 1895, **17**, 185.
[2] Bohm, *Zeit. anorg. Chem.*, 1905, **43**, 326.
[3] Poulenc, *Compt. rend.*, 1893, **116**, 1446.
[4] Viard, *Compt. rend.*, 1902, **135**, 168.

Basic Cupric Chloride, or *Copper Oxychloride*, $Cu_3O_2Cl_2,4H_2O$ = $2CuO,CuCl_2,4H_2O$.— This compound forms a pale blue precipitate when caustic potash is added to an excess of a solution of cupric chloride. When it is heated it loses water and is converted into a brown or blackish powder, and when moistened, this takes up three molecules of water, and changes again to a green colour.

When a solution of cupric chloride is mixed with cupric hydroxide, or when caustic potash is added to the solution of the former salt in quantity insufficient to ensure complete precipitation, a compound having the composition $Cu_4O_3Cl_2,4H_2O$ is thrown down. This substance occurs native in the form of a green sand composed of small rhombic prisms found at Atacama, as well as in Peru, Bolivia, and other places, and hence termed atacamite. According to Field, this mineral is at the present day being formed on the south coast of Chili by the action of sea-water on copper pyrites. The same compound may be artificially obtained in the crystalline state by heating common salt with an ammoniacal solution of copper sulphate to 100° (Debray), the action being:

$$6NH_3 + 4CuSO_4 + 2NaCl + 3H_2O = 3(NH_4)_2SO_4 + Cu_4O_3Cl_2 + Na_2SO_4.$$

This compound is also formed when a solution of copper sulphate is boiled with a small quantity of bleaching powder solution; the product obtained occurs in commerce as a light, bright green powder, used in the arts as a pigment, and known under the name of *Brunswick green*. On heating it loses water and becomes black, but regains the green colour on moistening. Other oxychlorides of copper also are known, some being minerals and others artificial products. Cupric chloride also unites with other chlorides, forming crystalline double salts.

Cupric Perchlorate, $Cu(ClO_4)_2$, crystallises with $4H_2O$ or $8H_2O$ and is very deliquescent and readily soluble in water.[1]

Cupric Bromide, $CuBr_2$.—When cupric oxide is dissolved in hydrobromic acid and the solution allowed to stand in a vacuum over sulphuric acid, the anhydrous bromide separates out in dark crystals very similar to those of iodine. These are very deliquescent, and on heating in absence of air decompose into cuprous bromide and bromine.

Cupric Sulphide, CuS, occurs in nature as covellite or indigo-copper, occurring sometimes in hexagonal crystals but more

[1] Salvadori, *Gazz.*, 1912, **42**, [1], 458.

frequently in the massive state as at Mansfeld, on Vesuvian lavas, and in Chili. It has a semi-metallic lustre and an indigo-blue colour, and a specific gravity of 4·6. It is prepared artificially by heating cuprous sulphide with flowers of sulphur to a temperature not above that of boiling sulphur (Hittorf). It may also be prepared by triturating finely-powdered cuprous sulphide in a mortar with cold strong nitric acid until the action ceases; the powder is then washed, cupric sulphide remaining behind.[1] It may likewise be obtained as a blackish-brown precipitate by passing a current of sulphuretted hydrogen gas into a solution of a cupric salt. The finely-divided moist precipitate easily oxidises on exposure to the air. When cupric sulphide is gently heated in absence of air or in a current of hydrogen, it decomposes into sulphur and cuprous sulphide: this method is often used for the estimation of the metal (Rose).

Several *polysulphides of copper* have been described having the formulæ Cu_2S_5,[2] Cu_2S_6, Cu_4S_5, and Cu_2S_3.[3] These are all unstable bodies, which, on keeping, slowly decompose into cupric sulphide and sulphur.

Cupric Sulphate, $CuSO_4$. — This salt, commonly termed copper sulphate, copper vitriol, or blue vitriol, has long been known, being found in solution in the drainage water of copper mines. It was for a long time confounded with green vitriol or iron sulphate, this being partially due to the fact that both frequently occur in the same drainage water, and are capable of crystallising together. In the works attributed to Basil Valentine the fact is recognised that both iron and copper vitriol can occur together, for he says: "Venus and Mars can be brought back into a virtuous vitriol." The alchemists frequently experimented on such mixed vitriols, as they believed that they contained the *materia prima* employed for the preparation of the philosopher's stone. Thus, in the above-mentioned work we read, "where copper and iron are found together gold will not be far distant."

The artificial production of copper sulphate is first described by Van Helmont in 1644, who obtained it by heating together copper and sulphur, and moistening the residue with rain-water. Glauber in 1648 proved that it might be readily obtained by boiling copper with oil of vitriol.

[1] Faraday, *Quart. Journ. Sci.*, **21**, 183.
[2] Bodroux, *Compt. rend.*, 1900, **130**, 1397
[3] Rossing, *Zeit. anorg. Chem*, 1900, **25**, 407.

Copper sulphate is obtained on the large scale chiefly from copper pyrites, which is carefully roasted, the copper under suitable conditions being oxidised to copper sulphate, whilst the iron is chiefly converted into oxide. The residue is lixiviated and the copper sulphate separated by crystallisation. The mother-liquors contain both copper and iron sulphates, from which the copper may be precipitated by scrap iron. For agricultural use the presence of iron in the copper sulphate is not injurious, and for sulphate intended for this purpose the mother-liquor may be directly evaporated. The precipitated copper, as well as copper scale and metallic copper obtained by other processes or as scrap, is roasted in reverberatory furnaces, and the product is treated with dilute sulphuric acid. If the copper contains gold or silver it is treated with sulphuric acid mixed with its own volume of water, the silver and gold being left undissolved.

Where argentiferous copper mattes are used, the roasted material is added in small quantities to sulphuric acid and digested until the solution contains but little free acid. Lead and gold remain behind as an insoluble powder, and the clear liquor is run into wooden tanks lined with lead, and containing strips of copper on which the whole of the silver and part of the arsenic and antimony are deposited, whilst the greater portion of the bismuth separates as a basic sulphate. The purified copper sulphate solution is then crystallised in large lead-lined coolers on strips of lead hung up in the liquid.

The commercial sulphate always contains small quantities of iron; this may be removed by boiling the solution with a little nitric acid, the ferrous sulphate being thus converted into ferric sulphate, which remains in the mother-liquor on recrystallisation.

Cupric sulphate is also obtained as a secondary product in the refining of silver; the original metal frequently contains copper which passes into solution with the silver on treatment with sulphuric acid. The silver is then precipitated in the metallic form by strips of copper, and pure sulphate remains behind.

Copper sulphate crystallises from warm saturated solutions on cooling in transparent blue triclinic crystals having the formula $CuSO_4,5H_2O$ and a specific gravity of 2·28. One hundred parts of water dissolve, according to Poggiale, as follows:

At	10°	20°	30°	50°	70°	90°	100°
$CuSO_4,5H_2O$	36·95	42·31	48·81	65·83	94·60	156·44	203·32

The salt is insoluble in absolute alcohol and only slightly soluble in dilute spirits. The dehydration of copper sulphate pentahydrate takes place in stages, a trihydrate, $CuSO_4,3H_2O$, being known. When it is heated for some time to 100°, the hydrate $CuSO_4,H_2O$ remains as a bluish-white powder, which at a temperature of from 220° to 260° loses nearly all its water. Even at 360°, however, a small amount of water (0·04 per cent.) is retained; this is lost only at a temperature at which the salt begins to lose sulphur trioxide (Richards). The residue at 260° forms a white mass which is extremely hygroscopic, becoming blue on absorption of water. This reaction is sometimes used for the purpose of ascertaining the presence of water in organic liquids, and also for dehydrating them. The anhydrous compound may be obtained in the form of grey prismatic needles by heating the hydrated sulphate with ammonium sulphate out of contact with the flame gases.[1] A period of induction,[2] interpreted in terms of the relatively high vapour pressure of small crystal particles, has been observed in the dehydration of the pentahydrate.

The anhydrous salt is stable up to 341°, but above this temperature evolution of sulphur dioxide begins.[3] Between 341° and 621° small quantities of a brown oxy-salt, $8CuO,3SO_3$, are formed. Between 621° and 670° sulphur dioxide and sulphur trioxide are evolved and an orange-coloured oxy-salt, $2CuO,SO_3$, is formed. This orange-coloured salt begins to decompose at 704°, the decomposition being incomplete at 850°.

The anhydrous as well as the hydrated sulphate absorbs two molecules of hydrogen chloride with evolution of heat and formation of cupric chloride and sulphuric acid. The same decomposition takes place when copper sulphate is treated with an excess of aqueous hydrochloric acid; the temperature falls and the salts dissolve with formation of a green liquid which on concentration yields crystals of cupric chloride. This reaction of copper sulphate is employed for separating hydrochloric acid from mixtures of gases, as, for instance, from chlorine, or from carbon dioxide which has been prepared by means of hydrochloric acid. Copper sulphate is largely used in calico-printing, and in the preparation of the pigments of copper, as Scheele's green and emerald green. It is also used in very large quantity in the process of electro-metallurgy. A crude copper sulphate con-

[1] Klobb, *Compt. rend.*, 1892, **114**, 836.
[2] Partington, *Journ. Chem. Soc.*, 1911, **99**, 466.
[3] Vanjukoff, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 688.

taining ferrous sulphate is used in agriculture for preventing "smut" in seeds.

Copper forms a series of basic sulphates. When the normal sulphate is kept for several hours at a dark-red heat, an amorphous orange-yellow powder remains behind having the composition $SO_2<\begin{matrix}O—Cu\\O—Cu\end{matrix}>O$, which is decomposed in contact with cold water into copper sulphate and an insoluble green basic sulphate, $CuSO_4,3Cu(OH)_2$. By the action of boiling water a salt having the composition $CuSO_4,2Cu(OH)_2$ is formed. These as well as other basic salts are also obtained when a solution of copper sulphate is treated under certain conditions with potash or ammonia. Some occur as minerals; thus brochantite is a native basic sulphate having the formula $CuSO_4,3Cu(OH)_2$, and occurring in bright green rhombic tablets, whilst a basic sulphate of composition $CuSO_4,2Cu(OH)_2$ has also been found occurring in nature as a mass of small green crystals.[1] The former can be artificially prepared by allowing a piece of porous limestone to lie in a solution of copper sulphate. No acid sulphates of copper are known, the only effect of addition of sulphuric acid to the system $CuSO_4$–H_2O being to dehydrate the pentahydrate progressively to the trihydrate, the monohydrate, and the anhydrous salt.[2]

When a solution of copper sulphate containing sulphuric acid is shaken with metallic copper, some cuprous sulphate is formed [3] and equilibrium is set up according to the equation:

$$CuSO_4 + Cu \rightleftharpoons Cu_2SO_4.$$

The amount of cuprous sulphate produced increases with the temperature and the concentration; thus at 100° in a solution containing originally one gram-molecule per litre of cupric sulphate, the concentration of the cuprous sulphate is 1/82 of that of the cupric salt, when equilibrium has been attained.

A double sulphate of copper and sodium, $Na_2SO_4,CuSO_4,2H_2O$, is known (Foote).

Cupric Selenate, $CuSeO_4$, closely resembles the sulphate, and crystallises from aqueous solution as the pentahydrate, which is converted to the trihydrate on treatment with acetone and loses

[1] Cesaro and Buttgenbach, *Ann Soc. Geol. Belgique*, 1897, **24**, *Bull.*, p. xli. See also Ermen, *J. Soc. Chem. Ind.*, 1912, **31**, 312; Young and Stearn, *J. Amer. Chem. Soc.*, 1916, **38**, 1947.

[2] Foote, *J. Ind. Eng. Chem.*, 1919, **11**, 629.

[3] Abel, *Zeit. anorg. Chem.*, 1901, **26**, 361.

$4H_2O$ at 104° to form the monohydrate. The salt is completely dehydrated at 230–235° and is then stable up to 280°.[1] It forms with the alkali selenates a series of double salts of the type $R_2SeO_4,CuSeO_4,6H_2O$.[2]

Cupric Nitrate, $Cu(NO_3)_2$.—In his *De furnis novis philosophicis*, published in 1648, Glauber mentions the fact that the solution of copper in nitric acid on evaporation leaves a green residue, and Boyle in 1664 observed that crystals could be obtained from the solution, and that these had the power of colouring the flame of a spirit-lamp green. In order to prepare copper nitrate, copper scale or copper oxide is dissolved in dilute nitric acid and the solution evaporated to crystallisation. In this way fine blue prismatic crystals, having the composition $Cu(NO_3)_2,3H_2O$, are obtained which melt at 114·5°, possess a caustic metallic taste, and cauterise the skin. This hydrate is stable in contact with its solution from its melting point to 24·5°, when it forms the hexahydrate, which in its turn passes at about -- 20° into a hydrate with $9H_2O$. The hydrated salt when heated loses nitric acid, a basic salt of the composition $Cu(NO_3)_2,3Cu(OH)_2$ being formed. Copper nitrate is deliquescent and very soluble in water, and is deposited as a fine crystalline powder when its concentrated solution is mixed with nitric acid of specific gravity 1·522.[3] This salt, owing to the ease with which it is decomposed, possesses strong oxidising properties. If some crystals of it are wrapped up in tinfoil and rubbed, decomposition begins, often accompanied by a rise of temperature sufficient to cause emission of sparks. If a solution of copper nitrate is evaporated with one of ammonium nitrate, decomposition takes place at a certain degree of concentration attended with violent detonations. Copper nitrate is used as an oxidising agent in the processes of dyeing and calico-printing, especially in the production of catechu-browns and of some steam colours containing logwood.

Anhydrous copper nitrate[4] is prepared by the action of nitric anhydride, or a solution of this in nitric acid, on hydrated salts of copper. It is a white powder, is very deliquescent, and decomposes at 155°.

Cupric Nitrite, $Cu(NO_2)_2$, is prepared in solution by double decomposition between (*a*) cupric sulphate and barium nitrite

[1] Dennis and Koller, *J. Amer. Chem. Soc*, 1919, **41**, 949.
[2] Tutton, *Proc. Roy. Soc.*, 1920, **98**, [*A*], 67.
[3] Cumming and Gemmell, *Proc. Roy. Soc. Edin.*, 1912, **32**, 4.
[4] Guntz and Martin, *Bull. Soc. chim.*, 1909, [4], **5**, 1004.

or (*b*) between cupric chloride and silver nitrite. The solution obtained in this manner is bright grass green in colour. According to Hampe,[1] it evolves nitric oxide even in the cold, whilst Berzelius states that it absorbs oxygen from the air and is slowly converted into nitrate. When the solution is evaporated under diminished pressure over sulphuric acid, nitric oxide is evolved; the residue is insoluble in water, is bluish-green in colour, and consists of a mixture of nitrite and nitrate.[2]

Cupric Phosphide, Cu_3P_2, is formed when phosphine is passed over cupric chloride or when phosphorus is boiled with a cupric salt. It is a black powder, or, when prepared at a high temperature, a greenish-black metallic mass, which, when ignited in hydrogen, is converted into cuprous phosphide.

Normal Cupric Phosphate, $Cu_3(PO_4)_2,3H_2O$, is best obtained by dissolving the carbonate in dilute phosphoric acid and heating the solution to 70°, when a fine blue crystalline powder is deposited. On heating this with water in closed tubes it decomposes into phosphoric acid and a *basic salt*, $CuPO_4,CuOH$ (Debray), or $Cu_3(PO_4)_2,CuO,H_2O$,[3] which latter occurs in nature as libethenite. The artificial compound crystallises in rhombic prisms, and libethenite in dark olive-green prisms having a waxy lustre. The same compound also occurs in the massive state. Another basic copper phosphate is the mineral phosphochalcite, or pseudomalachite; this occurs in triclinic emerald-green crystals having the composition $PO_4(CuOH)_3$. Other basic phosphates of copper are known.

Copper Arsenides. -Copper and arsenic combine in several proportions, whilst certain copper arsenides are found as minerals; thus whitneyite, Cu_9As, occurs as a bluish-red or greenish-white amorphous or crystalline malleable substance found in Michigan, and also in California and Arizona. Algodonite, Cu_6As, found in Chili and Lake Superior, possesses a silver-white or steel-grey lustre; and domeykite, Cu_3As, found at Portage Lake, has a tin-white to steel-grey colour. According to Reinsch, the grey deposit obtained when metallic copper is placed in a solution of arsenious oxide in hydrochloric acid has the composition Cu_5As_2, and this on heating is converted into Cu_3As. When arsenic vapour mixed with carbon dioxide or some other inert gas is passed over copper heated to the boiling point of

[1] *Annalen*, 1863, **125**, 345.
[2] Rây, *Journ. Chem. Soc.*, 1907, **91**, 1405
[3] Caven and Hill, *J. Soc. Chem. Ind.*, 1897, **16**, 29.

sulphur, the arsenide Cu_5As_2 is formed and this, when the temperature is raised, is transformed into Cu_3As.[1] The freezing point curve of copper and arsenic also points to the formation of these two arsenides.[2] When arsine is passed over dry cupric chloride the compound Cu_3As_2 is formed.

Cupric Arsenite, $CuHAsO_3$, was first obtained by Scheele by precipitating a solution of potassium arsenite with copper sulphate, and is still prepared by the same process. It is a siskin-green precipitate, which is known as a pigment under the name of *Scheele's green*. The salt forms a blue-coloured solution in caustic potash which is quickly decomposed on heating, with separation of copper oxide.

Arsenates of Copper.—These salts correspond closely to the phosphates and several basic salts occur in the mineral kingdom. The *ortharsenate*, $Cu_3(AsO_4)_2,2H_2O$, is obtained as a blue amorphous powder by heating together copper nitrate and calcium arsenate. Olivenite, $CuAsO_4,CuHO$, crystallises in olive-green or brown rhombic prisms, and can be obtained artificially by heating a solution of the ortharsenate to 100°.

Clinoclasite, $AsO_4(CuHO)_3$, forms dark green monoclinic prisms possessing a pearly or vitreous to resinous lustre.

Carbonates of Copper.—We are only acquainted with basic copper carbonates. Of these, two occur in large quantity in the mineral kingdom. Malachite, $CuCO_3,Cu(OH)_2$, forms monoclinic, frequently twin, crystals which are rarely perfectly developed, simple crystals being seldom found. It also occurs massive with botryoidal or stalactitic surface, often fibrous and frequently granular or earthy. Its colour is a bright green, and its specific gravity varies from 3·7 to 4·01. Green malachite accompanies other ores of copper, occurring especially in the Urals, at Chessy in France, in Cornwall and Cumberland in England, and at the copper mines of Nischne-Tagilsk. The fibrous varieties are frequently deposited in different coloured layers which take a high polish, and from these masses vases and other ornamental articles are manufactured. Crystals of malachite can be obtained artificially by allowing a piece of porous limestone to lie in a solution of copper nitrate having a specific gravity of 1·1, until the stone becomes covered with basic nitrate, and then bringing it into a solution of sodium carbonate

[1] Granger, *Compt. rend.*, 1903, **136**, 1397.

[2] Richards, *Ber.*, 1898, **31**, 3163. See also Friedrich, *Metallurgie*, 1908, **5**, 529.

having a specific gravity of 1·04, when after a few days malachite crystals are formed (Becquerel).

Verdigris, or copper rust, formed by the joint action of air and water on copper, possesses the same composition as malachite.

Azurite or Azure Copper Ore, $2CuCO_3,Cu(OH)_2$, occurs together with malachite and other copper ores in shining monoclinic tablets or short prisms, and also as an amorphous or earthy mass having a dark azure-blue colour. It possesses a specific gravity of 3·5 to 3·83. If crystallised copper nitrate be heated with pieces of chalk under a pressure of from 3 to 4 atmospheres a crystalline warty mass of azurite is formed (Debray). Azurite dissolves in a hot solution of sodium bicarbonate and the solution on boiling deposits a green powder of malachite.

Commercial basic carbonates of copper contain from 65—80 per cent. CuO and in this respect approximate to the composition of azurite: they contain, however, much less carbon dioxide than either malachite or azurite. It is apparently impossible to prepare basic carbonates of definite composition by simple treatment of copper sulphate solution with sodium carbonate or sodium hydrogen carbonate. By using both precipitants and subjecting the precipitate to special treatment a definite basic salt is obtained of the composition $2CuCO_3,5Cu(OH)_2$.[1]

Silicates of Copper.—Two silicates of copper occur as minerals. *Dioptase* or *emerald copper*, H_2CuSiO_3, is found in compact limestone in the Kirghese Steppes and also in Siberian gold-washings. It forms emerald-green hexagonal crystals (class 17, p. 209), having a specific gravity of 3·3.

Chrysocolla, H_2CuSiO_4,H_2O, exists as a bluish botryoidal mass occurring with other copper ores. The name of chrysocolla occurs in old writers and serves to describe the most diverse bodies. The word originally was used to signify the substance employed for soldering gold (χρυσός, gold, and κολλάω, to cement); this, being prepared from urine, was probably microcosmic salt, which became coloured blue in the act of soldering gold to copper or brass. The word then came to be used for any green or blue substance, especially such as contained copper; the confusion thus created was that all blue or green minerals, such as emerald and malachite, as well as substances which were employed for soldering, were termed chrysocolla. Brochant, in

[1] Dunnicliff and Lal, *Journ. Chem. Soc.*, 1918, **113**, 718; cf. Pickering, *Proc. Chem. Soc.*, 1909, **25**, 188; Groger, *Zeit. anorg. Chem.*, 1900, **24**, 127; Ermen, *J. Soc. Chem. Ind.*, 1912, **31**, 312.

the year 1808, first proposed to confine the use of the name to this particular mineral.

When copper oxides are heated with silica, silicates are formed. These are found in various slags obtained during the treatment of copper ores, especially in converter and refinery slags. They are readily reduced by carbon in the presence of oxide of iron and are decomposed by iron sulphide and by metallic iron at furnace temperatures.

Ammoniacal Compounds of Copper.

211 By the action of ammonia on both cuprous and cupric salts, a large number of compounds have been obtained the empirical formulæ of which show that combination has taken place between the copper salt and a varying number of molecules of ammonia. As to the manner in which the combination takes place, and the exact constitution of the products, very little is at present known, and they are usually formulated as additive compounds or in accordance with Werner's co-ordination theory. Many other metals form similar series of ammoniacal derivatives, these being often more complex than in the case of copper, as for example those of cobalt and platinum. The compounds appear to be formed chiefly by the metals occurring in the middle of Mendeléev's double periods (p. 54).

The ammoniacal cuprous compounds are colourless when pure, but very readily undergo oxidation, yielding the corresponding ammoniacal cupric salts, which usually have a deep blue colour and yield solutions of the same colour. The most important of these are the derivatives of cupric chloride and sulphate.

Cuprous Ammonium Sulphate.—Colourless crystals of the composition $Cu_2SO_4,4NH_3,H_2O$ have been obtained by passing a weak electric current through a strongly ammoniacal solution of cupric sulphate.[1] In moist air this substance changes rapidly to copper and a cupric compound.

The compound $Cu_2SO_4,4NH_3$ is precipitated as a white crystalline powder on the addition of alcohol to a solution of cuprous oxide and ammonium sulphate in aqueous ammonia at 50° in an atmosphere of hydrogen.[2]

Cupric Chloride and Ammonia.—Anhydrous cupric chloride absorbs ammonia, increasing in bulk and forming a blue powder

[1] Foerster and Blankenberg, *Ber.*, 1906, **39**, 4428.

[2] Bouzat, *Compt. rend.*, 1908, **146**, 75.

having the composition $CuCl_2,6NH_3$; this gradually dissociates first into $CuCl_2,4NH_3$, and then further to $CuCl_2,2NH_3$.[1]

When ammonia is passed into a hot saturated solution of cupric chloride a dark blue solution is formed, which, on cooling, deposits small dark blue octahedra or pointed tetragonal prisms of *cuprammonium chloride*, $CuCl_2,4NH_3,2H_2O$.[2] It is converted at 150° into $CuCl_2,2NH_3$, which is a green powder, and on further heating decomposes as follows:

$$6(CuCl_2 2NH_3) = 6CuCl + 6NH_4Cl + 4NH_3 + N_2.$$

Water converts it into cuprammonium chloride, ammonium chloride, and a basic cupric chloride having the composition $CuCl_2,4CuO,6H_2O$.

Cupric Sulphate and Ammonia.—When a solution of copper sulphate is treated with ammonia a basic sulphate is first thrown down. On further addition of ammonia this dissolves to a deep pure blue liquid containing *cuprammonium sulphate*, $CuSO_4,4NH_3,H_2O$, which was first described by Stisser in 1693 as an *arcanum epilepticum*, and afterwards termed *cuprum ammoniacale*. In order to obtain this compound in fine crystals a layer of strong alcohol is poured on to the concentrated aqueous solution and the whole allowed to stand: in this way very long and thin transparent azure-blue rhombic prisms are deposited. These on exposure to the air lose ammonia and are gradually transformed into ammonium sulphate and basic copper sulphate. Heated gently to 150° an apple-green powder of the composition $CuSO_4,2NH_3$ is obtained. Anhydrous copper sulphate absorbs dry ammonia gas with evolution of heat, forming a fine blue powder consisting of $CuSO_4,5NH_3$, which, like the foregoing compound, on heating to 200° forms the compound $CuSO_4,NH_3$ (Graham).

Detection and Estimation of Copper.

212 The halogen compounds and nitrate of copper colour the non-luminous gas flame green, and the same coloration is obtained from the other salts when mixed with a chloride or moistened with hydrochloric acid.

The spectrum of this flame is a banded one containing a large

[1] Bouzat, *Compt. rend.*, 1902, **135**, 292; *Ann. Chim. Phys*, 1903, [7], **29**, 305.

[2] Sabbatani, *Ann. Chim. Farm.*, 1897, **26**, 337.

number of lines, of which two in the violet, lying between the rubidium and cæsium lines, are the most characteristic. The spark spectrum of cupric chloride is also rich in lines and contains very bright lines in the green (Lecoq de Boisbaudran). When borax is moistened with any copper salt and heated in the oxidising flame a bead is obtained which, when hot, is green, and when cold possesses a blue colour; in the reducing flame, especially with the addition of a small quantity of tin or a tin compound, the bead becomes red and opaque with separation of cuprous oxide or metallic copper. Copper salts are thrown down by sulphuretted hydrogen in the form of a brownish-black precipitate of cupric sulphide, CuS, which is slightly soluble in ammonium sulphide, but not in freshly prepared potassium or sodium sulphide. The precipitated sulphide dissolves readily in warm dilute nitric acid, forming a clear blue solution which assumes a fine dark blue colour on the addition of ammonia. Copper can also easily be detected by the reduction to the red metallic bead on charcoal before the blowpipe, or upon the charred end of a match (Bunsen's test).

Copper is estimated quantitatively either as oxide, sulphide, or metal. For the purpose of estimating it as oxide, the boiling solution of the copper salt is treated with a slight excess of pure potash or soda, the precipitate repeatedly washed by decantation with boiling water, then thrown on to a filter, again washed, dried, and ignited.

Very satisfactory results are obtained by the electrolytic deposition of the metal, this method being especially advantageous where a large number of determinations have to be made daily, as is the case in a copper works. The copper solution may be electrolysed in a platinum basin, which acts as the cathode, the anode being a platinum wire. The copper is thus deposited on the basin; it is washed by decantation with water, then with a little alcohol, dried, and weighed together with the tared basin. By using revolving electrodes stronger currents may be employed and the copper obtained as a coherent deposit in a shorter time.

Copper is often estimated volumetrically by adding potassium iodide to a solution of the sulphate, and estimating the iodine liberated by titration with standard sodium thiosulphate, or by the titration of the ammoniacal solutions of the copper salts with potassium cyanide solution.

Atomic Weight of Copper.—By the reduction of precipitated

copper oxide with hydrogen Berzelius[1] obtained the number 63·30, whilst Erdmann and Marchand[2] by the same method obtained the number 63·46. Hampe,[3] by the reduction of the oxide and by the electrolysis of pure copper sulphate, obtained a number almost identical with that of Berzelius, viz., 63·31. The careful experiments of Richards have shown that all these numbers are too low, the error being due to the fact that copper oxide contains occluded nitrogen and oxygen, and that copper sulphate cannot, as previously supposed, be completely dehydrated at 255°. Richards therefore determined the atomic weight by the analysis of pure cupric bromide, the amount of silver required for complete decomposition of the bromide and also the weight of the silver bromide formed being ascertained. The average of the results gave the number 63·57 for the atomic weight of copper. From the sulphate he obtained the number 63·55.[4] Shrimpton[5] has determined electrolytically the atomic weight of copper relative to silver (107·88), obtaining a final mean value of 63·563, which agrees well with the number 63·57 now accepted (1922).

SILVER (ARGENTUM). Ag = 107·88. At. No. 47.

213 Silver has been known from the earliest times, and the oldest names by which it was designated referred to its bright white colour; thus in the Hebrew, Késeph, the root signifies to be pale, whilst the Greek word ἄργυρος, is derived from ἀργός, shining. The alchemists termed silver Luna or Diana, and it is often represented by the symbol of the crescent moon.

Silver occurs frequently in the native state, and is sometimes found in considerable quantity; thus, in the museum at Copenhagen there is a mass of native silver found at Kongsberg in Norway which weighs a quarter of a ton, and in South Peru masses have been found which weigh more than 8 cwt., whilst at Idaho, at the " poor man's lode," large masses of native silver have also been obtained. Native silver usually contains gold, copper, and sometimes mercury and other metals.

The most important silver minerals are: argentite or silver-

[1] *Pogg. Ann*, 1826, **8**, 177.
[2] *Journ. pr. Chem.*, 1844, **31**, 380.
[3] *Zeit. anal. Chem.*, 1873, **13**, 352.
[4] Numerous papers in *Chem. News*, 1891–2, **63**, **65**, **66**.
[5] *Proc. Physical Soc.*, London, 1914, **26**, 292.

glance, Ag_2S; pyrargyrite, ruby-silver, or dark-red silver, Ag_3SbS_3; stromeyerite or silver-copper glance, $(Ag,Cu)_2S$; stephanite, Ag_5SbS_4; polybasite, $(Ag,Cu)_9(Sb,As)S_6$; chlorargyrite or horn-silver, AgCl. Of less importance are proustite or light-red silver ore, Ag_3AsS_3, dyscrasite, Ag_4Sb, silver bromide, AgBr, silver iodide, AgI, and others. Silver also occurs in sea-water, a fact which was known to Proust in the year 1787.

214 *Metallurgy of Silver.*—Metallic silver is obtained from its ores by four different processes; either it is alloyed with lead, and then the lead is removed by oxidation, or it is amalgamated with mercury and this removed by distillation, or it is brought into combination with copper sulphide by smelting with pyritic copper ores, and the argentiferous matte produced is treated by a wet method, or reduced to metallic copper which is refined by the electrolytic process, or lastly it is brought into solution as a salt and precipitated. The adoption of one or other of these processes depends upon the nature of the ore, the position of the mine, and the cost of labour, fuel, etc.

It was by the first of these methods that the ancients extracted silver from its ores, and this remained for long the only known process. Strabo describes the method adopted in Spain for this purpose. The washed ore was melted with lead, and after this was got rid of (*ἀποχυθέντος τοῦ μολύβδου*), the pure silver remained behind. Pliny also, though he did not understand the nature of the operation, states that in order to obtain pure silver the ore must be cupelled together with lead; concerning the silver ore he says, "excoqui non potest, nisi cum plumbo nigro aut cum vena plumbi—et eodem opere ignium descendit pars in plumbum, argentum autem innatat, ut oleum aquis," this being an indistinct statement of the mode in which metallic silver separates from the oxidised slag. This process was termed in the works attributed to Basil Valentine "saigern" or "eliquation."

The Cupellation Process.—In this process the silver ores are first converted into an alloy of lead and silver by smelting with lead ores, which reduces the silver to the metallic state, the lead combining with it to form an alloy. The metallic lead obtained from galena always contains silver in small quantities, and from this a quantity of lead rich in silver is obtained by the Pattinson or Parkes process (see under Lead). To obtain the silver free from lead in both cases the alloy is subjected to the process of cupellation, the lead being oxidised to litharge,

which is removed, leaving the silver in the metallic state. For this purpose there are two distinct methods employed, viz.: (1) the English, and (2) the German system.

(1) *The English Process.*—The peculiarity of this system is

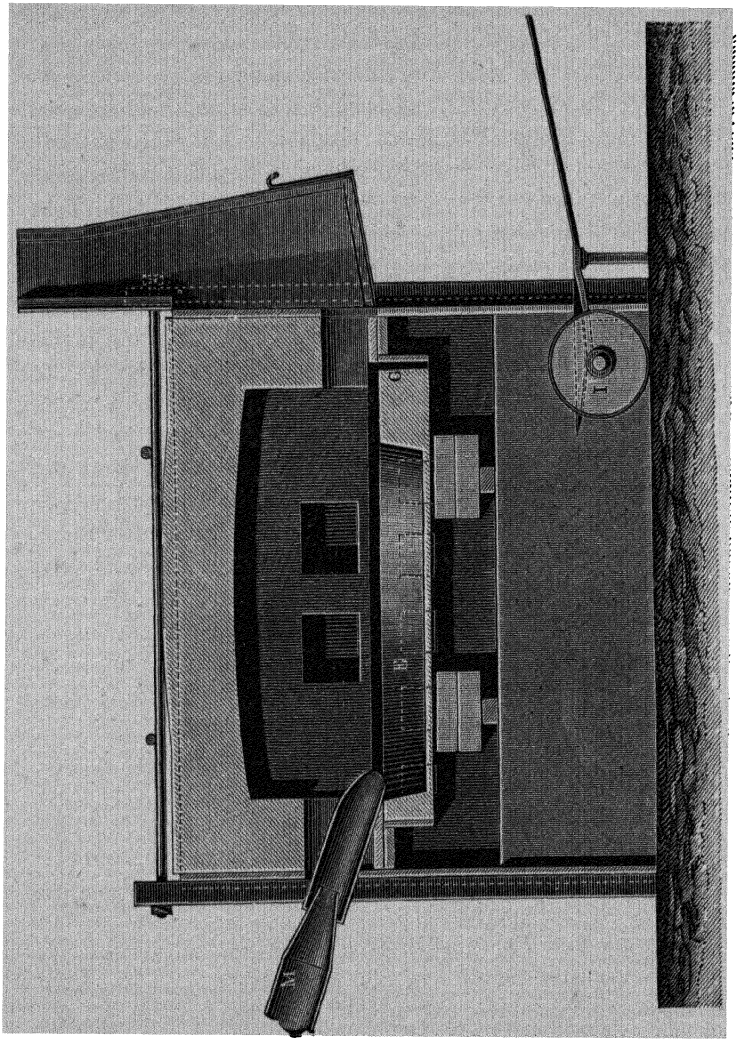


Fig. 121.

that the cupel or test upon which the oxidation takes place is movable, and the lead is added at intervals.

Fig. 121 shows a transverse section through the test, and Fig. 122 a plan and sections of the test and test frame of the English cupellation furnace.

The metal to be refined is placed upon the hearth, or cupel, or test (E), which consists of an oval wrought-iron frame (AA', Fig. 122) about five feet long and two and a half feet wide, crossed by five iron bars (*a*).

Formerly this frame was filled with finely-powdered bone-ash moistened with a little water in which a small quantity of potassium carbonate had been dissolved. This was well solidified by beating, and scooped out until it was an inch thick and had the form shown in the figure. At the present time, barytes and cement, or various mixtures of cement and fireclay, are used.

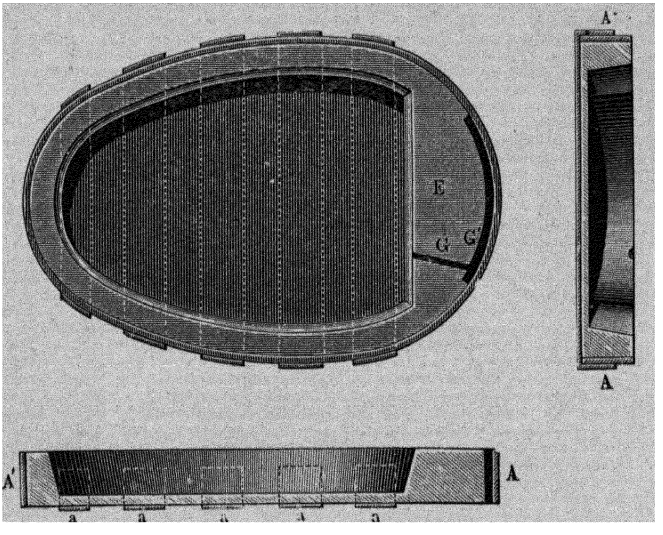


FIG. 122.

In forming the test, a flat rim is left all round about two inches wide, except at one end (E, Fig. 122), called the front or breast of the cupel, where it is five inches wide, and through this a channel (G) connecting the bed of the cupel with the slot (G') is cut to allow the melted oxide of lead to flow out into the waggon (I) beneath. The cupel thus arranged is wedged up into its place in the furnace, of which it forms the hearth (E, Fig. 121), and where it is so arranged that the flame from a coal or oil fire plays over its surface, and the products of combustion escape through two flues. A blast of air from the nozzle or tuyere (M, Fig. 121) enters the furnace at the side opposite that against which the breast of the cupel is placed, a current of air being thus blown over the surface of the lead at the rate of about

200 cubic feet per minute. Opposite the door is a hood for carrying the fumes into the chimney. The temperature is gradually raised to redness, and the cupel is almost filled with the lead to be treated. Fresh lead is added from time to time to supply the place of that which is oxidised, until at length a quantity of lead originally amounting to about five tons is reduced to between two and three cwt. This metal is withdrawn by making a hole through the bottom of the cupel; the aperture is afterwards closed and another charge is proceeded with. When a quantity of rich lead sufficient to yield from 3,000

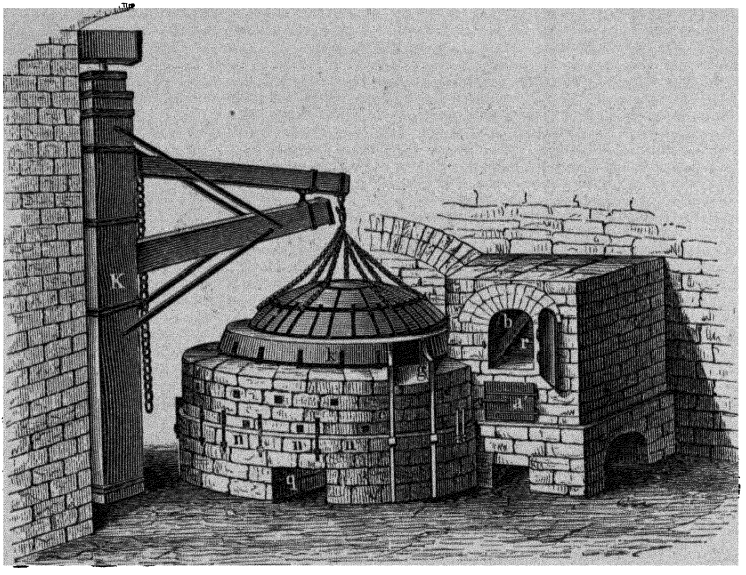


Fig. 123.

to 5,000 ounces of silver has been thus obtained, it is again placed in a cupel, and the last portions of lead are removed. It is found advantageous to effect this final purification of the concentrated silver-lead separately, because in the last stages of the operation the litharge carries a good deal of silver with it; these portions of litharge, therefore, after being reduced, are again subjected to the desilverising process.

(2) *The German Cupellation Process.*—This differs from the English process inasmuch as the treatment is completed in one operation. The natural marl used for the hearth consists of about 65 per cent. of limestone and 30 per cent. of clay, together with 5 per cent. of magnesium carbonate and oxide of iron.

The hearth is made of large dimensions, and the whole of the charge is placed on the cupel at once. The furnace used for this purpose is shown in Fig. 123. The circular cover (*k*) is movable for the purpose of renewing the cupel. When all is ready, straw is thrown upon the hearth, on to which the pigs of rich lead are placed; the cover (*k*) is then lowered and the joints made good with clay; the fire is lighted, and as soon as the lead is melted its surface becomes covered with a dark crust termed "abzug," consisting of the oxides of foreign oxidisable metals and other impurities in the lead; this crust is skimmed off through the working door (*g*); the heating is regulated so as to maintain the lead at a dark red heat, until the impurities cease to separate in the form of scum. The next product which appears is known as "abstich," or impure litharge, and at the end of two hours the formation of the pure litharge begins, the temperature being kept up at a cherry-red heat until the operation is complete. Just before the last portions of lead are removed a beautiful appearance, known as the fulguration of the metal, is noticed. During the early stages of the operation the film of lead oxide is constantly being formed, and this is renewed as rapidly as it is removed; but when the lead has all been oxidised, the film of litharge becomes thinner and thinner, and as it flows off a succession of beautiful iridescent tints due to the colour of thin films (Newton's rings) is observed, and after a few moments the film of oxide suddenly disappears and the brilliant surface of the metallic silver is seen beneath.

The Mexican Amalgamation Process.—Although the ancients were well acquainted with the fact that mercury dissolves gold and silver, it does not appear that they applied this knowledge to the extraction of silver from its ores. This was first done in Mexico in the year 1557 by Bartholomeo de Medina, and applied on the large scale in the year 1566. The same process was employed at Potosi in Peru in 1574, and fully described in 1590 by Joseph Acosta, in his *Historia natural y moral de las Indias*. The identical method is still carried on to some extent in Mexico, Peru, and Southern Chili, but is being rapidly displaced by the cyanide process. The ores which are worked by this process contain metallic silver, sulphide of silver, chloride of silver, etc., these substances being distributed in small masses through large quantities of gangue.

The first operation in the process is the fine division of the ore, which is effected by stamping and grinding mills worked by

horse or mule power, and termed *arrastra*. Into these water and ore are brought and ground together to a fine mud between blocks of porphyry fastened to an axis which is turned by the mules; the wet and powdered ore is then brought on to a paved floor termed a *patio*, and mixed with from 3 to 5 per cent. of common salt, and the salt thoroughly incorporated with the mass by the treading of mules. After standing for a day, mercury is added together with a substance termed *magistral*, an impure mixture of copper and iron sulphates. As soon as the magistral has been added, more mercury is poured on, and the heap or *torta* is again trodden by mules to bring about a thorough incorporation of the ingredients and thus to effect the chemical decomposition which their contact entails. The time necessary for working a torta varies from fifteen to forty-five days, according to circumstances.

As soon as the amalgamation is found to be complete, the slimy mass is washed in buddles worked by mules, the lighter particles of mud washed away, and the heavier amalgam deposited. The amalgam is next filtered through canvas bags to remove excess of mercury, and is then distilled by being placed under a large iron bell luted at the bottom with water, round the upper part of which a charcoal fire is lighted. The silver which is left behind, termed *plata piña*, possesses a white frosted appearance, and is fused into bars in the usual way.

The chemical reactions which occur in the process have been investigated by Boussingault, Karsten, and other chemists, but in spite of their investigations there still remains some degree of doubt respecting their exact nature.

The following is the probable explanation of the chemical changes which occur. The first reaction is a double decomposition between the sulphates of iron and copper and chloride of sodium with formation of the chlorides of the metals. These decompose silver sulphide with the formation of silver chloride:

$$2CuCl_2 + Ag_2S = 2CuCl + 2AgCl + S.$$

The cuprous chloride thus formed dissolves in common salt and acts further upon the sulphide:

$$2CuCl + Ag_2S = Cu_2S + 2AgCl.$$

The solution of the silver chloride in common salt is then decomposed by the metallic mercury with formation of calomel and metallic silver. All the mercury which is thus converted

into calomel is lost, and it amounts to about double the weight of the silver obtained.

Since 1904, the Mexican process has been largely displaced by the introduction of fine-grinding in tube-mills in conjunction with a modification of the cyanide process.

The American or *Washoe Amalgamation Process.*—Owing to the scarcity of fuel and labour in the Nevada districts, where large quantities of both rich and poor silver ores occur, it is found impossible to work the ordinary methods, because a process necessitating the preliminary roasting of the ore cannot be carried on, and the loss of mercury in the Mexican process is too great to render that method applicable to the large quantity of poor ore which the district yields.

This necessity has led to the invention of a process of amalgamation in iron pans, which is called, from the name of the district, the Washoe process. The richer ores of the Nevada mines are roasted with common salt in reverberatory furnaces and then amalgamated in barrels. The poor ore, on the other hand, after having been stamped to powder, is ground in cast-iron pans together with mercury and hot water, with or without the addition of common salt and copper sulphate. The amalgam is next washed, strained in bags, and distilled in cast-iron retorts and the silver which remains melted and cast into ingots. The chemical changes which occur in this process of amalgamation are similar to those taking place in the Mexican operation, but as the ore contains a considerable proportion of native silver, the presence of a copper salt is not so necessary, as under the influence of heat and friction mercury and iron alone are capable of extracting the silver. The loss of mercury in this method is much less than in the older amalgamation operations, as it is mechanical, no mercury salt being formed.

A third amalgamation process is known as the Boss continuous process, in which the ore is first crushed in a stamp-mill and the pulp finely ground in pans. After this, it is caused to pass through a series of amalgamating pans, often ten in number, placed side by side, each pan having an overflow pipe, through which the pulp flows into the next one of the series. From these it is passed through a series of settlers arranged in the same manner, in which any mercury or amalgam passing over settles and is collected. By this process the labour of conveying the pulp to the pans is avoided, and the ore is kept in contact with mercury for a longer period.

215 *Extraction of Silver in the Wet Way.*—Of the processes described below, the application of cyanide solutions to the treatment of silver ores is the most important at the present time. It has been largely developed in Mexico, where it has practically displaced the amalgamation process and it has been used on an extensive scale in Nevada, Cobalt, and other places. The Ziervogel and Augustin processes were formerly largely used for the treatment of argentiferous copper mattes and ores, but are now used only in a few places and on a small scale, as the method of producing argentiferous copper from which the silver is obtained by electrolysis is more suitable. The Patera, Russell, and Kiss processes are also rapidly becoming obsolete.

The Cyanide Process.—That metallic silver and various silver compounds are soluble in dilute solutions of potassium or sodium cyanide has been known for many years, but it is only within recent years that the process has been applied on a large scale to the treatment of silver ores. It is especially suitable for ores containing chloride, bromide, iodide, or sulphide of silver, also for native silver, provided this is present in a finely divided state, and also for ores containing sulph-arsenides and sulph-antimonides of silver.

In the process, the ore is first broken down in rock breakers and then crushed in stamp batteries (see p. 513), with sufficient lime to render the pulp strongly alkaline, to pass a 4- to 16-mesh screen. If argentiferous or auriferous pyrites be present, the pulp is passed over concentrating tables for the separation of this material, which may be smelted or cyanided separately. The pulp is then finely ground or slimed to 200-mesh size in tube mills and the slime thickened by the separation of a certain amount of water. The thickened slime is then agitated in some form of tank by mechanical or aerial agitation for thirty-six hours or more with solution containing 0·3–0·6 per cent. of potassium cyanide, passed to vacuum filters or filter presses, and the solution treated with metallic zinc for the precipitation of the silver. The proper aeration of the solution is very important. Any gold which may be present in the ore is extracted at the same time. The solution of the silver and silver sulphide present takes place according to the following reactions:

$$4Ag + 8KCN + 2H_2O + O_2 = 4KAg(CN)_2 + 4KOH$$
$$Ag_2S + 4KCN = 2KAg(CN)_2 + K_2S.$$

From the second equation it will be seen that the amount of

silver sulphide which can be dissolved and remain in solution will depend upon the amount of free cyanide present, which reacts with the sulphide formed as follows:

$$2K_2S + 2KCN + O = 2KCNS + 2K_2O.$$

For the precipitation of the silver, the solution is either passed through suitable boxes containing zinc shavings, or is agitated with zinc dust or aluminium powder, when the following reaction takes place:

$$2KAg(CN)_2 + Zn = K_2Zn(CN)_4 + 2Ag.$$

The silver precipitate thus obtained is dried in shallow pans, heated in a muffle furnace and melted down in crucibles with suitable fluxes and the silver bullion obtained is refined.

Ziervogel's process depends upon the fact that the silver in mattes containing silver, copper, and iron sulphides may be converted into silver sulphate by careful roasting, while the iron and copper are converted into oxides. The silver sulphate is readily soluble in hot water and is extracted by lixiviation in wooden vats, the silver being precipitated from this solution in the metallic state by treatment with metallic copper. The mattes obtained from the smelting of argentiferous pyrites are first ground and then subjected to a preliminary roast, during which ferric sulphate is first formed, together with copper and iron oxides. When the temperature is raised the ferric sulphate is decomposed, sulphuric anhydride being evolved, which brings about the formation of copper sulphate. After about five hours the charge is withdrawn, and consists of a mixture of ferric oxide, cuprous and cupric oxides, silver sulphide, and copper sulphate. This charge is prepared for the "final" or "sulphating" roast by fine grinding, and is charged into a gas-fired, double-hearthed reverberatory furnace. The temperature is carefully regulated so that copper sulphate is decomposed, silver sulphate formed, and any cuprous oxide present converted into cupric oxide; the charge is then withdrawn and allowed to cool, and is ready for lixiviation.

Augustin's Process.—This method was formerly employed for argentiferous copper regulus and for argentiferous ores. These are roasted to remove excess of sulphur, and then re-roasted with 5 per cent. of common salt, the silver chloride thus formed extracted by a hot saturated solution of salt, and the silver deposited from the solution by the action of metallic copper.

As silver chloride is much more easily dissolved by a solution of sodium thiosulphate than by brine, the Augustin process is only used in conjunction with the Patera process (see below), and is not as a rule used for working up argentiferous mattes or other products.

Percy-Patera Process.—This process depends upon the following reactions, first suggested by Percy, and afterwards carried out by von Patera. The argentiferous ore is first roasted with common salt, by which the silver is converted into the chloride as in the Augustin process; this is then dissolved out by a cold dilute solution of sodium thiosulphate:

$$2AgCl + 3Na_2S_2O_3 = Ag_2S_2O_3,2Na_2S_2O_3 + 2NaCl.$$

The silver in solution is precipitated by means of a solution of sodium sulphide, whereby silver sulphide is formed and sodium thiosulphate regenerated:

$$Ag_2S_2O_3,2Na_2S_2O_3 + Na_2S = Ag_2S + 3Na_2S_2O_3.$$

Gold, copper, and any other heavy metals in solution are precipitated with the silver. Only sufficient sodium sulphide to precipitate the metals is added, as the liquors are used over and over again for the extraction of fresh ore. The sulphide precipitate is collected in a filter press, dried, roasted in a muffle, and charged into a bath of hot lead, the rich argentiferous lead thus obtained being afterwards cupelled.

Kiss Process.—This is a modification of the Patera process, in which calcium hyposulphite is used as the solvent and calcium polysulphide as the precipitant.

Russell Process.—This consists in leaching the ores by a solution of sodium–copper thiosulphate, which dissolves any gold or silver in the metallic state, and any sulphide, arsenate, or antimonate of silver which is not readily attacked by sodium thiosulphate alone. It is therefore chiefly used as an auxiliary to the Patera process, the extraction with the thiosulphate of sodium solution being followed by an extraction with the double thiosulphate. The metals in solution are precipitated by means of sodium sulphide, and the precipitate treated with hot concentrated sulphuric acid in cast-iron vessels. This dissolves the silver and copper present, leaving any gold behind. From the solution the silver is precipitated by means of copper, and the resulting copper sulphate used for making fresh leaching liquors.

Claudet's Process.—The burnt pyrites of the sulphuric acid makers contains, as we have seen, not only copper, but also a small quantity of silver, which occurs in the cupreous liquors in the form of chloride dissolved in the excess of common salt. Although the quantity of silver in the burnt ore does not often exceed 12 dwt. to the ton, it is found possible to obtain this economically in the form of insoluble silver iodide by adding a solution of iodide of potassium, sodium, or zinc to the tank liquor, a small trace of gold being at the same time precipitated. The precipitate is reduced to the metallic state by means of zinc in the presence of hydrochloric acid, metallic silver being formed together with zinc iodide, which may be used to precipitate a further quantity of silver. The results obtained at the Widnes metal-works show that between 150 and 300 grains of silver and between 1½ and 3 grains of gold may be extracted from each ton of ordinary Spanish pyrites.

Argentiferous Copper.—Much silver is also obtained by the treatment of argentiferous copper by an electrolytic refining process, the copper having been reduced from argentiferous copper pyrites, or obtained by Bessemerising the copper mattes obtained from the pyritic smelting of mixtures of pyritic copper ores and argentiferous materials (see Copper).

Electrolytic Refining of Silver.—Large quantities of silver are refined by the Moebius process, in which the electrolyte consists of a silver nitrate solution containing about 1 per cent. of free nitric acid. Silver is deposited on the cathode and gold is left insoluble. Copper is not allowed to accumulate in the electrolyte to more than 4 or 5 per cent.

The total production of silver during 1918 throughout the world is given in the following table, expressed in ounces.[1]

United States of America	67,810,100	China	97,900
Canada	21,284,600	Dutch East Indies	400,000
Mexico	62,517,000	Transvaal	877,500
Central America	2,900,000	Rhodesia	175,700
South America	15,561,000	Congo	32,500
British India	270,000	Spain and other European Countries	6,871,700
Burma	1,970,500	Australasia	10,000,000
Japan	6,626,400		
TOTAL	197,394,900		

[1] *Mineral Industry*, 1919, **28**, 248.

The decline in the world's production of silver since 1912, when it amounted to 233,000,000 ounces, has been serious. In 1916 it had fallen to 166,250,000 ounces, a decrease of nearly 30 per cent. in five years. Since then it has risen somewhat, mainly due to an increased production in Mexico.

216 *Preparation of Pure Silver.*—The purest silver which occurs in commerce contains traces of other metals. Stas's classical researches on atomic weight determinations have shown how difficult it is to obtain any substance chemically pure, and this fact is especially well illustrated in the case of silver, a metal which possesses such characteristic reactions that one might suppose its separation in a state of chemical purity to be an easy task.

Silver was obtained by Stas in a highly pure state by the reduction of carefully purified silver chloride by boiling with sodium hydroxide solution and sugar, by reducing silver nitrate solution with ammonium formate and acetate, and in several other ways. The precipitated silver was then dried by fusion with borax or lime. Stas's silver, however, probably contained a little occluded oxygen (Richards and Wells).

Samples of silver in a still purer state than those obtained by Stas have been prepared by Richards and Wells [1] for use in determinations of the atomic weights of chlorine and sodium. These investigators started with silver nitrate, which was purified by repeated crystallisation from water; in one preparation as many as fifteen recrystallisations were performed. This was converted into silver chloride with pure hydrochloric acid, and the well-washed chloride reduced to metallic silver by warming with a solution of chemically pure caustic soda and invert-sugar. The precipitate of silver was then washed with water, dried, and fused on pure lime. In this way a button of extremely pure silver was obtained. This was then further purified by making it the anode of an electrolytic cell containing a concentrated solution of silver nitrate obtained from the same preparation of silver. The cathode was a wire of pure silver and upon this crystals of electrolytic silver were deposited. These crystals were dried and fused on a boat of pure lime in an atmosphere of hydrogen to remove any occluded oxygen. The bars of silver so formed were freed from lime by rubbing with sand, and washed, first with dilute nitric acid, then with ammonia

[1] A revision of the atomic weights of sodium and chlorine; *J. Amer. Chem. Soc.*, 1905, **27**, 459.

to remove any silver nitrate, and finally with water. They were then dried by heating in a vacuum at 400°, in a hard glass tube.

Richards and Wells also prepared pure silver by dissolving commercial fine silver in dilute nitric acid, and reducing the nitrate, after recrystallising several times, by boiling with ammonium formate. The white precipitate of silver was washed repeatedly with water until the washings showed no Nessler test, and was then fused in hydrogen, rubbed with sand and acid, and treated as above. In all this work vessels of silver were used whenever possible in order to prevent contamination with other metals, and in other cases vessels of platinum, Jena glass, and fused quartz were employed.

Pure silver is used in the laboratory for volumetric analysis and for cupellation assays. It is not necessary for this purpose to have it as pure as the metal employed for atomic weight determinations, and it may be obtained sufficiently so by boiling well-washed silver chloride with caustic potash and sugar. The metal is then melted in a crucible together with some pure sodium carbonate or borax. Pure silver chloride may also be reduced by fusion with excess of sodium carbonate or by means of zinc, as described below, followed by fusion.

Molecular silver, employed in organic chemistry, is obtained, according to Wislicenus, by bringing zinc into contact with finely-divided silver chloride which has been precipitated in the cold and washed until nearly free from acid. In a few hours the chloride is completely reduced, and the precipitated silver may be separated from the sheet zinc by washing, and then treated with diluted hydrochloric acid to remove every trace of zinc. It is then brought on to paper and dried in the air, and afterwards gently heated to 150°. Thus prepared it is a grey powder, possessing no metallic lustre, which, however, it assumes when rubbed under a burnisher or heated to redness.

217 *Properties.*—Silver possesses a pure white colour, and takes a high polish. Of all the metals it is the best conductor of heat and electricity; it is very tough and malleable, since 0·1 gram can be drawn out into a wire 180 m. in length, and silver leaf can be beaten out to a thickness of 0·00025 mm. In the finely-divided state, as obtained by the reduction of the chloride and other salts, silver presents the appearance a dull dark-grey powder.

Silver is precipitated in very thin films in the form of a

lustrous metallic mirror-like deposit on glass from ammoniacal solution in presence of many reducing agents, especially organic substances; it then adheres to the glass and transmits blue light.

Metallic silver is found native in regular octahedra, which frequently occur twinned, and also in dendritic forms. It is also often found in the crystalline form in silver smelting furnaces. Another crystalline variety of silver has been obtained, in long needles belonging to the cubic system, by preparing spongy silver by ignition of the tartrate and digesting this with nitric acid freed from lower oxides of nitrogen by boiling with urea.[1]

Silver fuses at a temperature of 962° in the absence of air, and at 956° in the presence of air. In the liquid state it possesses the power of absorbing oxygen from the air, which it gives up on solidification. When a mass of the metal is rapidly cooled the silver solidifies before the oxygen has escaped from the interior; this gas then bursts through the crusts, and drives out part of the fused silver in globular masses and excrescences; this peculiar phenomenon is known as the "spitting" of silver. When charcoal powder is thrown on the surface of the metal the charcoal withdraws the absorbed oxygen, and consequently prevents silver from spitting. The same preventive effect is noticed when silver is fused under common salt, but when fused under nitre the spitting takes place. The presence of small quantities of copper or lead prevents the spitting of silver.

When silver is heated, and then allowed to cool while ozone is impinging on the suface, a black stain is formed, due to partial oxidation.[2] The maximum effect is produced at 220° to 240°, and no stain is produced above 450°.

Silver begins to volatilise at a white heat, and when heated in a lime crucible by means of the oxy-hydrogen blowpipe it may readily be made to boil. By this process Stas was able to distil fifty grams of pure silver in from ten to fifteen minutes; no residue whatever was left behind, and a portion of the vapour, which has a bright blue colour, was carried out by the current of oxygen gas, and rendered the air of the laboratory hazy, imparting to it a metallic taste. Distilled silver has a specific gravity of 10·4923 (Kahlbaum, Roth, and Siedler); fused silver has a specific gravity of from 10·424 to 10·511 (Holzmann); whilst silver which has been exposed to pressure under the coining press has a specific gravity of 10·57 (G. Rose).

[1] Choudhri, *J. Amer. Chem. Soc.*, 1915, **37**, 2037.

[2] Manchot and Kampschulte, *Ber.*, 1907, **40**, 2891.

Silver foil becomes slightly transparent in air at 240°, and more so at higher temperatures;[1] heating, however, to 500° in hydrogen or charcoal powder does not produce transparency, showing that the presence of oxygen is necessary although the quantity of oxygen absorbed is very minute.

The vapour density of silver at 2,000° has been determined by Nernst's[2] adaptation for high temperatures of Victor Meyer's displacement method, the bulb in which the heating takes place being made of iridium coated inside with a mixture of zirconia and yttria, and heated by means of an electric current. In this way the molecular weight was found to be 107 and 111; silver therefore at this temperature is monatomic.[3]

Silver is often used in the laboratory for the preparation of chemical utensils, as this metal is not, like glass or platinum, attacked by fused caustic alkali.

Colloidal Silver.—By the action of different reducing agents such as sodium tartrate and citrate, ferrous sulphate, dextrin, and tannin, on solutions of silver salts, Carey Lea[4] obtained a number of different precipitates which he regarded as allotropic forms of silver. This view has, however, proved incorrect, and the differences between these bodies and metallic silver are readily explained by their fine state of division and by their invariably containing small amounts of the other products of the reactions. The precipitates readily dissolve in water to form colloidal *silver solutions*, or silver "sols," which are coagulated or reprecipitated by the addition of small amounts of electrolytes.

Solutions of colloidal silver may also be prepared by Bredig's method, which consists in passing an electric arc between poles of silver under water. In this way a brown solution is obtained which will rapidly decompose hydrogen peroxide.[5]

By heating silver nitrate with an alkaline solution of sodium lysalbate or protalbate, Paal[6] obtained a yellow solution of

[1] Turner, *Proc. Roy Soc*, 1908, [A], **91**, 301.

[2] *Zeit. Elektrochem*, 1903, **9**, 622.

[3] von Wartenberg, *Ber*, 1906, **39**, 381.

[4] *Amer. J. Sci.*, 1889, [3], **37**, 476; **38**, 47, 129: *Phil. Mag.*, 1891, [5], **31**, 238, 320, 497; **32**, 337; *Amer. J. Sci*, 1894, [3], **48**, 343. See also Schneider, *Ber.*, 1891, **24**, 3370; 1892, **25**, 1164, 1281, 1440; Barus and Schneider, *Zeit. physikal. Chem.*, 1891, **8**, 278; *Ann. Phys. Chem.*, 1893, **48**, 327; Oberbeck, *ibid.*, 1892, **46**, 265, 353; 1893, **48**, 745; Blake, *Amer. J. Sci.*, 1903, [4], **16**, 282.

[5] Bredig, *Anorganische Fermente* (Engelmann, Leipzig, 1901).

[6] *Ber.*, 1902, **35**, 2206.

colloidal silver, and this on dialysing and concentrating on the water-bath yielded a deep brownish-black powder, readily soluble in water. This product, sometimes termed *collargol*, has been prepared containing as much as 93 per cent. of silver.

Colloidal silver may also be obtained by heating silver nitrate solution with formaldehyde and sodium silicate, and concentrating the mixture on the water-bath;[1] also by boiling ammoniacal silver nitrate solution with acraldehyde and a small quantity of gelatin solution. By this latter method, concentrated solutions of colloidal silver, having the colour of bromine, may be prepared which may be kept for years without losing their properties or changing colour;[2] and several other methods of preparing colloidal silver have been published.[3] A simple one[4] is to mix solutions of silver nitrate and pyrogallol in dry pyridine. A pale yellow solution is thus obtained which gives colloidal silver on treatment with water. The colour of the solutions varies from yellow to orange and violet by transmitted light.

All the colloidal solutions described contain small amounts of other substances resulting from the original reactions, which are " adsorbed," *i.e.*, condensed on the silver particles, and cannot be completely removed. Even Bredig's solutions, which are not produced by a reaction but by disintegration of solid silver, are not pure, as they always contain oxides.

Investigation by *X*-ray methods has proved that the particles of colloidal silver are actually crystalline though of ultra-microscopic size.[5]

Silvering and Plating.

218 Objects made of copper, or of brass, bronze, German silver, or similar alloy, are frequently silvered to give a bright and permanent surface to these metals. If the covering of silver be thick the goods are said to be plated; if thin, they are said to be silvered. Silvering may be effected in several

[1] Kuspert, *Ber*, 1902, **35**, 2815, 4066, and 4070.

[2] N. Castoro, *Gazz.*, 1907, **37**, 391.

[3] Lottermoser and von Meyer, *J. pr. Chem*, 1897, **56**, 241; 1898, [2], **57**, 540; Lottermoser, *ibid.*, 1905, [2], **71**, 296; Gutbier and Hofmeier, *Zeit. anorg. Chem.*, 1905, **45**, 77. See also an "Introduction to the Physics and Chemistry of Colloids," by Emil Hatschek (J. and A. Churchill).

[4] Pieroni, *Gazz.*, 1913, **43**, i, 197.

[5] Scherrer, *Nachr. Ges. Wiss. Göttingen*, 1918, 96.

ways, the following process, for example, being employed for silvering small articles such as pins, buttons, etc. For this purpose a solution of silver chloride in sodium sulphite or thiosulphate, or in common salt, or cream of tartar, is employed; a warm solution is used, and the silver is instantly deposited upon the metallic object.

The *plating* of copper is effected by polishing the surface of the ingot which is to be plated, and then placing upon it a strip of bright silver, the area of which is somewhat smaller than that of the copper; the compound ingot is then exposed to a temperature slightly below the fusing point of silver, and by hammering or rolling at this temperature the two metals are sweated together, as it is termed; no soldering is employed in this process; the ingot is then rolled until it is reduced to the required thickness.

Electro-deposition of Silver.—The process of electro-plating in silver was discovered by Wright and Parkes, of Birmingham, in the year 1840. They were employed during that year in making experiments with the view of obtaining a bright and firm deposit of metallic silver by an electro-process similar to that by which Jacobi, Jordan, and Spencer had succeeded in obtaining the deposition of copper. Their attempts, however, were not completely successful, inasmuch as they either obtained only a very thin coherent film or else the whole of the silver was thrown down in the form of a grey powder. At this juncture Wright met with a passage in Scheele's *Chemical Essays* (pp. 404–406), which soon proved of the highest importance to the commercial success of this undertaking, by enabling him to obtain suitable deposits of silver and gold. Speaking of the solubility of the oxides and cyanides of gold, silver, and copper, Scheele says that, "if these calces (that is, the cyanides of gold and silver) have been precipitated, and a sufficient quantity of the precipitating liquor be added in order to redissolve them, the solution remains clear in the open air, and in this state the aerial acid (that is, the carbonic acid of the air) does not precipitate the metallic calx."[1] Working with this idea, Wright first employed a solution of chloride of silver in potassium ferrocyanide, and quickly got a thick deposit of firm and white silver, a result which had never previously been obtained. Soon afterwards he found that the solution of silver cyanide in cyanide of potassium gave still better results; and,

[1] Gore, *Electro-Metallurgy*, p. 19.

submitting his results to the well-known firm of G. R. and H. Elkington, a patent was taken out, and this patent process proved to be the foundation of all electro-plating of gold and silver, because it included the solutions of the alkali cyanides, the only liquids which fulfil all the necessary conditions. The silver-plating solution consists of a solution of cyanide of silver in cyanide of potassium, an excess of the cyanide of potassium being added in order that no cyanide of silver shall separate out on the positive pole, which always consists of silver. The action which takes place in this electrolysis is the same as that described under copper electro-plating. The negative pole is connected with the object to be silvered, and upon this the silver is deposited, whilst at the positive pole the radical CN combines with the silver which forms the pole, and the cyanide of silver thus formed dissolves in the excess of potassium cyanide.[1]

Silvering of Glass Specula and Mirrors.—Many organic bodies such as milk-sugar possess the power of precipitating silver in the form of a highly coherent mirror when brought into contact with an alkaline silver solution.

219 *Alloys of silver.*—The presence of small quantities of other metals, such as antimony, arsenic, bismuth, tin, or zinc, renders silver brittle and liable to crack when rolled. The alloys of silver and copper are the only ones which are largely used in the arts. Almost all commercial silver is alloyed with copper, as pure silver is too soft for ordinary purposes such as coining and jewellery work. The addition of a small quantity of copper imparts to it a sufficient degree of hardness, and makes it tougher as well as more easily fusible. Thus, for instance, a wire of pure silver having a sectional area of 1 sq. cm. breaks with a weight of about 2,800 kilos., whereas if it be alloyed with 25 per cent. of copper and drawn cold, it will sustain a weight of from 6,000 to 9,000 kilos.; after annealing it becomes soft, and breaks with a weight of from 3,800 to 4,800 kilos. It has been found that alloys of copper and silver, however perfectly the metals may be mixed and melted together, undergo on solidification a process of segregation, the upper and the lower portions of the ingot differing in fineness from 0·002 to 0·015. Levol[2] has shown that the only alloy of these metals which does not exhibit this

[1] Further particulars respecting this interesting process will be found in Gore's *Electro-Metallurgy*.

[2] *Ann. Chim. Phys.*, 1849, [3], **26**, 220.

peculiarity is one having the specific gravity 9·9045, and containing 28 per cent. of copper; this is now recognised as the the eutectic alloy of the series. The fineness of silver alloy is generally calculated upon a thousand parts; thus, for instance, the one above mentioned will have a fineness of 720. The colour of the silver–copper alloys becomes more and more red as the percentage of copper is increased, but an alloy of 1 part of silver and 4 parts of copper does not possess the true copper colour.

Silver Coin.—The proportion of copper in the standard silver used in different countries varies considerably. The English standard coinage silver until recently contained 7·5 per cent. of copper, or had a fineness of 925, the specific gravity being 10·30. In France three standard alloys are employed; one containing 900 per mille for coin; and a third containing 800 per mille for jewellery work. In Germany and Austria the standard for coin contains 900 per mille of silver. The German alloy used for silver-plating contains from 700 to 810 per mille of silver.

The composition of British silver coin up to 1920 was the same as that issued in the time of Edward I., the alloy in this reign containing 925 of fine silver and being described as "the old standard of England."

Up to the year 1851 the manufacture of coin was entrusted to a private company termed the moneyers, who had to produce coin varying within very narrow limits, the alloy thus produced being compared with plates of standard silver termed "standard trial plates." Since the above year, the business of coining has devolved upon the Government, the Chancellor of the Exchequer being Master of the Mint. The ancient ceremony of the "trial of the pyx" is, however, still carried on every year. This consists in a public trial by competent assayers appointed by the freemen of the Goldsmiths' Company of the coin (both gold and silver) issued during the year. By this means the accuracy of the coin both as to fineness and as to weight is ascertained, and this trial served in former days as the only safeguard against debasement of the coinage. The fineness of the coins is ascertained at the trial of the pyx by reference to the trial plates the composition of which has been determined with the greatest accuracy.

The following table gives the accurate composition of trial plates of various dates, portions of which have been preserved and analysed [1] in the Royal Mint. The plates made in former

[1] Roberts, *Journ. Chem. Soc.*, 1874, **27**, 197.

times, when no accurate means of analysis existed, show considerable variation in the composition of the silver standard plates, the standard prescribed by law being in each case the same, viz., 925 :

Date	Fineness
1477	923·5
1560	930·2
1660	924·2
1728	928·9
1829	925·0
1873	924·96

Owing to the high price of silver during recent years it became necessary to reduce the standard of the British silver coinage and in 1920 a coinage was minted containing silver 500, copper 400, nickel 100.

COMPOUNDS OF SILVER.

Silver and Oxygen.

220 Silver forms two oxides : —

Silver oxide, Ag_2O.
Silver peroxide, AgO, or Ag_2O_2.

A third oxide, known as silver suboxide, was described by Wöhler,[1] who obtained it by acting on different silver salts with hydrogen, and by heating silver citrate in hydrogen, and treating the solution of the residue, which he supposed to contain silver subcitrate, with caustic potash. Further investigations by Bailey and Fowler[2] and by Muthmann have shown that such an oxide does not exist, the substance thus described being a mixture of silver and silver oxide.[3] The peculiar red colour of the supposed solution of silver subcitrate is due to very finely divided silver.

Silver Oxide, Ag_2O.—This is the best defined oxide of silver and is obtained by precipitating silver nitrate with pure potash or soda. Thus prepared it forms a brown precipitate, which when dried at a temperature of from 60° to 80°, becomes almost

[1] *Annalen*, 1839, **30**, 1.
[2] *Journ. Chem. Soc.*, 1887, **51**, 416.
[3] See also Lewis, *J. Amer. Chem. Soc.*, 1906, **28**, 139; Luther and Pokorny, *Zeit. anorg. Chem.*, 1908, **57**, 290.

black. When freshly precipitated silver chloride is boiled with an excess of caustic potash the same oxide is obtained in the form of a finely divided bluish-black powder. It is soluble in 15,360 parts of water at ordinary temperatures,[1] imparting to the solution a metallic taste and an alkaline reaction. In the moist condition it absorbs carbon dioxide from the air, whilst carbonic oxide reduces the dried oxide at the ordinary temperatures with formation of silver and carbon dioxide.[2]

It decomposes soluble chlorides with formation of silver chloride, and precipitates the corresponding oxides from solutions of many metallic salts. When heated to 250° it begins to decompose, and it loses the whole of its oxygen at 300°. It is reduced by hydrogen at the ordinary temperature in the presence of a trace of water,[3] but large quantities of water retard this reaction. When rubbed in a mortar with antimony sulphide, arsenic sulphide, milk of sulphur, amorphous phosphorus, tannic acid, or other easily oxidisable substances, ignition takes place. It is dissolved by ammonia, the solution on exposure to air yielding fulminating silver, a black explosive compound which has the composition NAg_3 (p. 494).[4]

Silver oxide corresponds to the only well-defined series of silver salts, which may frequently be obtained from it by the action of the corresponding acid, but are usually formed by double decompositions, as most of them are insoluble in water, the principal exceptions being the nitrate and fluoride, which are readily soluble, and the sulphate and nitrite, which are sparingly soluble. The salts with colourless acids are usually colourless, but a few, such as the bromide, iodide, phosphate, and arsenate, are coloured. The soluble salts have a neutral reaction and an unpleasant metallic taste, and are poisonous. Many silver salts, such as the sulphate and thiosulphate, are isomorphous with the corresponding salts of sodium and lithium.

Silver Peroxide, Ag_2O_2.—In 1804 Ritter obtained a black crystalline powder by passing an electric current between platinum electrodes through an aqueous solution of silver nitrate. This substance, which separated out at the anode in small octahedra, was found to give off oxygen when heated, and was for a long time considered to be silver peroxide.

[1] Levi, *Gazz.*, 1901, **31**, ii, 1.
[2] Dejust, *Compt. rend.*, 1905, **140**, 1250.
[3] Kohlschütter, *Zeit. Elektrochem.*, 1908, **14**, 49.
[4] See also Matignon, *Bull. Soc. chim.*, 1908, [4], **3**, 618.

Subsequent analyses,[1] however, have shown that it contains nitrogen and has the constant composition represented by the formula Ag_7NO_{11}, and the name of *silver peroxynitrate* is generally given to it. It has been pointed out, however, that when the assumption is made that the nitrate in the precipitate is present as silver nitrate, the results indicate that the oxide present has the formula Ag_3O_4,[2] and the compound is best represented as $2Ag_3O_4,AgNO_3$.[3] Black powders are also obtained by the electrolysis of solutions of other salts of silver; thus the sulphate yields *silver peroxysulphate*,[4] $5Ag_2O_2,2Ag_2SO_7$, whilst silver fluoride gives the *peroxyfluorides*,[5] $Ag_{15}F_3O_{16}$, and Ag_7FO_8.

Silver peroxide has also been obtained as a black precipitate by the action of potassium persulphate solution on silver nitrate or silver sulphate,[6] whilst it is stated to be formed when ozone acts on silver oxide and on silver (see p. 474).

The black substance, stated by Wöhler to be prepared by the electrolysis of dilute sulphuric acid, using a silver anode, is probably not the peroxide, but the peroxysulphate.

Silver peroxide, as prepared from the peroxynitrate, is a grey powder of specific gravity 7·44 (Watson). It may be heated to 100° without decomposition, but at higher temperatures is decomposed into its elements, whilst when heated with dilute sulphuric acid it evolves half its oxygen, silver sulphate being formed. When treated with ammonia, nitrogen is liberated,[7] in an amount corresponding with the equation:

$$6Ag_2O_2 + 2NH_3 = 3Ag_4O_3 + N_2 + 3H_2O.$$

The oxide Ag_4O_3 has, however, not yet been isolated.

[1] Mulder and Heringa, *Rec. trav. chim.*, 1896, **15**, 1 and 235; Mulder, *Rec. trav. chim.*, 1896, **16**, 57; 1903, **22**, 235 and 405; Šulc, *Zeit. anorg. Chem.*, 1896, **12**, 89 and 180; 1900, **24**, 305; Watson, *Journ. Chem. Soc*, 1906, **89**, 578; Barbieri, *Atti R. Accad. Lincei*, 1906, [5], **15**, i, 500.

[2] Baborovský and Kuzma, *Zeit. physikal. Chem.*, 1909, **67**, 48 See also *Zeit. Elektrochem.*, 1908, **14**, 196.

[3] Brown, *J. Physical Chem.*, 1916, **20**, 680.

[4] Mulder, *Proc. K. Akad. Wetensch. Amsterdam*, 1898; *Rec. trav. chim.*, 1900, **19**, 115.

[5] Tanatar, *Zeit. anorg. Chem.*, 1901, **29**, 331.

[6] Marshall, *Proc. Roy. Soc. Edin.*, 1900, **23**, 163; 1902, **24**, 88; *Journ. Chem. Soc.*, 1891, **59**, 771.

[7] Watson, *Journ. Chem. Soc.*, 1906, **89**, 578.

Silver and the Halogens.

221 *Silver Subfluoride*, Ag_2F, is obtained as a bronze-like crystalline powder by heating a saturated solution of silver fluoride with metallic silver, and is reconverted into these by the addition of an excess of water.[1] According to Vanino and Sachs,[2] however, it is not a true compound, but a mixture of silver fluoride, silver, and silver oxide in varying proportions.

Silver Fluoride, AgF.—Hydrofluoric acid does not act upon metallic silver, but the fluoride is obtained by dissolving silver oxide or carbonate in aqueous hydrofluoric acid and evaporating to dryness. If the solution be allowed to evaporate in a vacuum, colourless, lustrous, deliquescent, tetragonal pyramids are deposited, having the composition AgF,H_2O (Marignac), whilst the concentrated solution when allowed to stand exposed to the air deposits hard transparent prisms of the compound $AgF,2H_2O$, which are nearly as deliquescent as calcium chloride. Under the influence of light, solutions of silver fluoride are decomposed with the formation of silver subfluoride and silver peroxide.[3] It is extremely difficult to obtain silver fluoride in the anhydrous state. The hydrate, AgF,H_2O, decomposes when dried in a vacuum, and yields a brown amorphous mass which still contains 1·5 per cent. of water, and dissolves in 0·85 part of water at 15·5°. When heated to the melting point of lead in a covered crucible, 0·5 per cent. less than the calculated quantity of water is given off, together with some hydrofluoric acid and oxygen:

$$4AgF + 2H_2O = 4Ag + 4HF + O_2.$$

This decomposition goes on until all the water is driven off and the salt melted, and from this point it can be heated in absence of air up to the melting point of silver without any further decomposition taking place.[4] The fused salt solidifies to a black mass which is elastic and may be cut with scissors. In the fused state it conducts electricity without decomposition. The dry powder absorbs 844 times its volume of ammonia.

It has been proposed to employ silver fluoride, under the name of tachyol, for the disinfection of drinking water.[5]

[1] Guntz, *Compt. rend*, 1890, **110**, 1337.
[2] *Zeit. anal. Chem.*, 1911, **50**, 623.
[3] Eisenreich, *Zeit. physikal. Chem.*, 1911, **76**, 643.
[4] Gore, *Phil. Trans.*, 1871, **161**, 321.
[5] Paternò and Cingolani, *Gazz.*, 1907, **37**, 1313.

Silver Chloride, AgCl, occurs as the mineral *chlorargyrite* or *horn-silver*, which crystallises in octahedra and other forms of the regular system, but is more frequently found as a massive wax-like mass, which generally has a pearl-grey colour, though sometimes it possesses a whitish and sometimes a violet-blue colour. It occurs at Andreasberg, mixed with alumina, as an earthy mass which is called butter-milk ore, and this ore was known to the older mineralogists. Gesner, in 1565, terms horn-silver *Argentum cornu pellucido simile*, and Matthesius, in his *Berg-Postilla*, published in 1585, terms it "glass-ore, transparent like horn in a lantern." The largest masses are brought from Peru, Chili, and Mexico, and the mineral also occurs in Cornwall, in Nevada, where it is abundant, in Arizona, and other localities. The method of preparing silver chloride artificially was probably known to the old alchemists, but it is first distinctly mentioned in the works of "Basil Valentine," who says: "Common salt throws down ☽." This precipitate was afterwards termed *Lac argenti*, and when it was found that it was fusible, and solidified to a transparent horn-like mass, the name *Luna cornea*, first mentioned by Croll in 1608, was given to it. Libavius stated that the substance obtained by precipitating silver solution with common salt weighed less than the silver itself, but this statement was contradicted by Boyle; and Kunkel, in his *Laboratorium Chymicum*, speaking of this, says that many substances are difficult to separate from one another: "Such is seen in ☽ cornea, as 12 loth ☽ retain out of the common salt, 4 loth terra and salt." This determination is in fact nearly correct, for 12 parts of silver form 15·94 parts of silver chloride.

Silver chloride is formed, without the phenomenon of incandescence, when chlorine is passed over silver at a dull red heat (Stas). It is also formed by the action of hydrochloric acid on the ignited metal, whilst on the other hand hydrogen is able to reduce silver chloride to the metal (Boussingault). Aqueous hydrochloric acid converts the surface of metallic silver into chloride of silver, and common salt solution acts in a similar way. Proust examined some piasters which had for many years lain at the bottom of the sea, and he found that the whole of the silver was converted into chloride. In order to prepare pure chloride of silver a solution of the nitrate is precipitated by hydrochloric acid or common salt; in this way a white curdy precipitate is obtained which, on standing, or more quickly on

agitation, becomes powdery. This precipitate must be washed and dried in absence of light. It has a specific gravity of 5·5. On heating, silver chloride assumes a yellow colour and melts at 460°, forming a dark yellow liquid. This solidifies on cooling, forming a botryoidal, colourless, tough, solid mass which refracts light strongly, and is so soft as to take impressions of the nail.

Silver chloride and sodium chloride when melted together and cooled, form brittle, crystalline masses which are homogeneous[1]; the melting points vary from 460° (AgCl) to 792° (NaCl), showing that the salts form an unbroken series of mixed crystals.

Silver chloride volatilises at a white heat, the vapour density[2] agreeing approximately with the formula AgCl.

According to Stas,[3] fused chloride of silver is absolutely insoluble in water at the ordinary temperature, or at any rate its solubility does not reach the limit of our present tests for chlorine, which Stas places at 1 in 10,000,000. In boiling water, on the other hand, it is appreciably soluble.

The freshly precipitated curdy chloride is slightly soluble in cold water, but the solubility becomes less when the precipitate has become powdery by standing or shaking, measurements of the electrical conductivity showing that this form dissolves to the extent of 0·00152 gram[4] at 18°, and 0·0218 gram[5] at 100° in 1 litre of water. The solution becomes opalescent on the addition of either silver nitrate or hydrochloric acid. The presence of nitric acid does not affect the solubility of the curdy chloride, whereas the solubility of the powdery form increases proportionally to the amount of nitric acid added : 100,000 parts of concentrated nitric acid dissolve 2 parts of the freshly prepared silver chloride (Thorpe); on boiling, it is decomposed into nitrate with evolution of chlorine. One part of silver chloride dissolves in about 200 parts of concentrated hydrochloric acid, and in 600 parts of the acid diluted with an equal bulk of water. Soluble chlorides, such as sal-ammoniac and common salt, dissolve silver chloride tolerably easily, and it is very soluble in ammonia, 12·88 parts of aqueous ammonia of specific gravity 0·89 dissolving 1 part of silver chloride (Wallace and

[1] Botta, *Centr. Min.*, 1911, 138.
[2] Biltz and Meyer, *Berichte*, 1889, **22**, 725.
[3] *Compt. rend.* 1871, **73**, 998.
[4] Kohlrausch and Rose, *Zeit. physikal. Chem.*, 1893, **12**, 242.
[5] Böttger, *Zeit. physikal. Chem.*, 1906, **56**, 83.

Lamont). It is likewise dissolved in quantity by mercuric nitrate, sodium thiosulphate, and potassium cyanide.

Various metals, such as iron and zinc, reduce the chloride to the state of metal in the presence of water, more rapidly in presence of hydrochloric acid and sulphuric acid. It is also decomposed by mercury when a solution of common salt is present. Cold sulphuric acid does not act upon it, but it is decomposed slowly, though completely, by the boiling acid with evolution of hydrochloric acid.[1] Concentrated hydriodic acid converts it with evolution of heat into silver iodide (Deville), and if moist, freshly precipitated chloride be treated with a solution of bromide of potassium, or iodide of potassium, it is completely converted into silver bromide or iodide.[2]

White silver chloride, obtained by precipitation, when exposed to light, is first coloured violet, then brownish-grey, and afterwards black. This alteration in colour was known to Boyle,[3] who, however, ascribed it to the action of the air. Scheele[4] afterwards proved that it was only discoloured on exposure to light, and he also showed that in this reaction hydrochloric acid was liberated and that on treating the residue with ammonia, black flakes of silver remained behind.

It has been shown by Abney and by Baker that the pure dry chloride does not blacken when exposed to light in a vacuous tube, in perfectly dry oxygen, or under pure carbon tetrachloride in the absence of oxygen. Baker[5] has also shown that not only is chlorine lost when the chloride blackens, but that oxygen is at the same time absorbed, an oxychloride of silver, Ag_2ClO, being probably formed. The amount of silver chloride which undergoes this change is, however, extremely small, even when a large quantity is exposed for a long period. The blackening is accelerated by the presence of substances which are capable of taking up chlorine, such as water, silver nitrate, stannous chloride, &c., and retarded by such as readily give up chlorine, such as chlorine water and ferric chloride.

Sonstadt[6] states that hydrogen peroxide is always formed when light acts on silver chloride. The same chemist finds that if silver chloride be sealed up in a tube and blackened by expo-

[1] Sauer, *Zeit. anal. Chem.*, 1873, 376.
[2] Field, *Journ. Chem. Soc.*, 1858, 234.
[3] *Op.* **1**, 756.
[4] *Von der Luft und dem Feuer*, Leipzig, 1784, p. 64.
[5] *Journ. Chem. Soc.*, 1892, **41**, 728. See also Hartung, *ibid.*, 1922, **121**, 688.
[6] *Proc. Chem. Soc.*, 1898, 371.

sure to light, a reversion to white silver chloride takes place when the tube is kept in the dark: whereas if the products of decomposition of the chloride by light are removed by sealing up calcium chloride and ammonia in another part of the tube containing the silver chloride, no bleaching of the blackened compound takes place in the dark.

Silver Chloride and Ammonia.—Glauber states that a calx is formed when silver solution is precipitated by common salt, and he adds that the calx "readily dissolves in *spiritu urinæ, salis armoniaci, cornu Cervi, succini, fuliginis et capillorum,* and may be used to form a good medicament." Faraday [1] first obtained a compound by the direct union of ammonia and silver chloride by saturating dry precipitated silver chloride with ammonia; 100 grains or 6·48 grams absorbed 130 cubic inches or 2·13 litres of the gas. The absorbed ammonia is again given off at 37·7° (Faraday). When heated in a closed tube for the purpose of obtaining liquid ammonia, the compound fuses between 88° and 95°, swells up, and begins to boil at 99°, losing ammonia and gradually becoming white. Two compounds are formed by the direct union of ammonia with silver chloride; $AgCl,3NH_3$, which has a dissociation pressure of 618 mm. at 15°, and $2AgCl,3NH_3$, the dissociation pressure of which is 38·3 at the same temperature.[2]

When a solution of silver chloride in concentrated ammonia is rapidly evaporated, silver chloride crystallises out in glittering octahedra, but if it be allowed to evaporate at ordinary temperatures over quicklime, the compound $2AgCl,3NH_3$ separates out in colourless, birefractive prisms which are not affected by light.[3] On the other hand,[4] a solution of silver chloride in liquid ammonia, when evaporated at $-40°$ to $-20°$, deposits long colourless needles of the composition $AgCl,3NH_3$.

Bodländer and Fittig [5] have shown that solutions of silver chloride in ammonia contain the silver almost exclusively as the complex $Ag(NH_3)_2Cl$, although the solid in contact with the solution has the formula $2AgCl,3NH_3$.

Silver Bromide, AgBr, occurs in Chili and Mexico as the mineral bromargyrite, being usually found in small yellow or

[1] *Quart. Journ. of Science,* 1818, **5**, 74.
[2] Horstmann, *Ber.*, 1876, **9**, 756.
[3] Jarry, *Ann. Chim. Phys.*, 1899, [4], **17**, 327.
[4] Jarry, *Compt. rend.*, 1897, **124**, 288.
[5] *Zeit. physikal. Chem.*, 1902, **39**, 597. See also Straub, *ibid.*, 1911, **77**, 331.

greenish masses, rarely crystalline. The mineral embolite is a mixture of silver chloride and bromide, varying from 25 to 75 molecular percentage of silver bromide. It likewise occurs in Chili and Mexico, and is very similar to the foregoing mineral. When an excess of silver nitrate is precipitated in the dark with hydrobromic acid, a white curdy precipitate is obtained which in contact with potassium bromide, or on heating, becomes yellow. It melts at 426°, and is soluble in a hot solution of hydrobromic acid, and in a solution of mercuric nitrate, separating out in octahedra from these solutions on cooling. The solubility of silver bromide in water has been determined by electrical conductivity measurements, and has been found to be 0·107 mgrm. per litre at 21°,[1] and 3·7 mgrm. at 100°.[2]

Silver bromide is scarcely soluble in dilute ammonia, but easily soluble in concentrated ammonia; it melts, on heating, to a reddish liquid which solidifies to a yellow lustrous mass, and the latter, when heated in a current of chlorine, is slowly converted into chloride. The finely divided precipitate suspended in water is instantly decomposed by chlorine, and hydrochloric acid gas also decomposes it at 700° with evolution of hydrogen bromide. It is soluble in sodium thiosulphate, the saturated solution corresponding to a double salt containing five molecules of silver bromide to nine molecules of crystallised thiosulphate. This salt exists only in solution, and on evaporation, or when precipitated with alcohol, yields [3]

$$2Na_2S_2O_3,Ag_2S_2O_3,2H_2O.$$

Whilst the fused bromide is hardly acted upon by light, the precipitated salt is soon coloured a greyish-violet on exposure to light; if, however, it contains a trace of free bromine, it is unacted on. The action is also lessened by the presence of nitric acid, whilst it is increased by the presence of silver nitrate. The darkening on exposure to light is accompanied by loss of bromine and formation of metallic silver.[4]

Stas [5] described several varieties of this salt which differ in their behaviour towards light.

[1] Kohlrausch and Dolezalek, *Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 1018.

[2] Bottger, *Zeit. physikal. Chem.*, 1906, **56**, 83.

[3] Lumière and Seyewetz, *Bull. Soc. chim.*, 1907, [4], **1**, 946.

[4] Hartung, *Journ. Chem. Soc.*, 1922, **121**, 682.

[5] *Ann. Chim. Phys.*, 1874, [5], **3**, 289.

Dry silver bromide absorbs no gaseous ammonia[1]; on the other hand, the ammoniacal solution deposits on standing white glistening crystals, and these on heating lose ammonia,[2] whilst liquid ammonia below 4° converts silver bromide into a white substance, $AgBr,3NH_3$. This loses ammonia at 4°, yielding another white substance of the composition $2AgBr,3NH_3$, which gives off ammonia at 35°, silver bromide being left.[3]

Silver Iodide, AgI.—This salt occurs as iodargyrite in Mexico, Chili, Spain, and in the Cerro Colorado Mine in Arizona, in the form of slightly elastic hexagonal tablets. Silver combines directly with iodine on heating. The metal also dissolves in hydriodic acid, with violent evolution of hydrogen, and if the liquid be warmed as soon as the action becomes lessened, the evolution again increases, and, on cooling, colourless crystalline scales separate out. These on exposure to air decompose quickly, and probably possess the formula AgI,HI. The mother-liquor on standing deposits thick hexagonal prisms of silver iodide.[4] The same compound is formed by the action of concentrated hydriodic acid on silver chloride, and the iodide is also produced by the treatment of silver chloride or bromide with aqueous potassium iodide or other soluble iodides, silver iodide being deposited as a light yellowish powder. It is dimorphous and melts at 556°, forming a yellow liquid, which on further heating becomes red and then dark reddish-brown, and on cooling solidifies to a soft yellow mass having a specific gravity of 5·687 at 0° (Deville), whilst the crystalline variety has at 14° a specific gravity of 5·669, that of the precipitated salt being 5·596 (Damour). An interesting fact with reference to the abnormal expansion and contraction of silver iodide by heat has been observed by Fizeau[5]; it contracts when heated from − 10° to + 70°, and expands on cooling. This is explained by Rodwell,[6] by the fact that silver iodide exists in two modifications. Fizeau, however, determined the coefficient of expansion of three different varieties of silver iodide and found it to be negative in each case, and G. Jones,[7] from a study of the free energy of formation of silver iodide, concluded that the affinity of the

[1] Rammelsberg, *Pogg. Ann.*, 1842, **55**, 246.
[2] Liebig, *Schweiggers Journ.*, **48**, 103.
[3] Jarry, *Compt. rend.*, 1898, **126**, 1138.
[4] Deville, *Compt. rend.*, 1851, **32**, 894.
[5] *Compt. rend.*, 1867, **64**, 304.
[6] *Chem. News*, 1875, **31**, 4.
[7] *J. Amer. Chem. Soc.*, 1909, **31**, 191.

silver and iodine increases with rising temperature, which tends to cause a diminution in volume.

Measurements of the electrical conductivity of the solution show that silver iodide dissolves in water to the extent of 0·0035 mgrm. in a litre.[1]

Pure silver iodide is left unaltered by the action of direct sunlight. If, however, it be precipitated from an excess of silver nitrate so that traces of this salt are carried down with it, it becomes coloured green on exposure to light, and in presence of more silver nitrate a deep greyish-black colour is attained although no loss of iodine is observed (Stas). Iodide of potassium, and nitric acid (specific gravity 1·2) have the power of reproducing the yellow colour. The changes effected by light upon silver iodide are brought about chiefly in the presence of substances which have the power of combining with a portion of the iodine. Ammonia changes the yellow colour of silver iodide to white and dissolves it very sparingly; it differs from the chloride and bromide of silver, inasmuch as it is only sparingly soluble even in concentrated ammonia, one part of the iodide dissolving, according to Wallace and Lamont, in 2493 parts of ammonia of specific gravity 0·89; its solubility in aqueous ammonia, however, increases appreciably with rise of temperature.[2]

It is readily soluble in liquid ammonia, and if the solution be allowed to evaporate at $-40°$ to $-10°$, white crystals of AgI,NH_3 separate out.[3] This substance evolves ammonia at 4°, yielding the white compound, $2AgI,NH_3$, which is also formed by the action of ammonia gas on dry precipitated silver iodide,[4] and on exposure to air gives off its ammonia.

Silver iodide is tolerably soluble in a strong solution of potassium iodide, from which solution it is precipitated by the addition of water, whilst a hot solution of potassium iodide, saturated with silver iodide, deposits, on standing, white needles of a salt having the composition AgI,KI. When silver iodide is gently heated in chlorine gas it decomposes into silver chloride, and the same reaction takes place when it is treated with dry hydrogen chloride at 700° (Hautfeuille). It is only

[1] Kohlrausch and Dolezalek, *Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 1018.

[2] Baubigny, *Compt. rend.*, 1908, **146**, 1263.

[3] Jarry, *Ann. Chim. Phys.*, 1899, [7], **17**, 327.

[4] Rammelsberg, *Pogg. Ann.*, 1839, **48**, 170.

incompletely reduced in a current of hydrogen even when exposed to a white heat (Vogel).

Silver Chlorite, $AgClO_2$, is obtained by precipitating a weak alkaline solution of a chlorite with silver nitrate. If forms a crystalline substance which separates from a solution in hot water in crystalline scales. These deflagrate when moistened with concentrated hydrochloric acid, or when heated to 105°; they also take fire when mixed with sulphur (Millon).

Silver Chlorate, $AgClO_3$.—This salt is obtained when chlorine is passed into water through which silver oxide is diffused, until bubbles of oxygen are evolved; the chloride of silver is filtered off and the liquor evaporated to its crystallising point. Silver chloride and hypochlorite are first formed; part of the latter, according to Forster and Jorre,[1] is then hydrolysed to hypochlorous acid, and this reacts with the silver hypochlorite to form silver chlorate and chloride.

The chlorate may also be obtained by dissolving silver oxide in chloric acid, the action being accompanied by evolution of heat. It crystallises in white, opaque, tetragonal prisms, having a specific gravity of 4·43. These dissolve in about 10 parts of cold water, and melt at 230°; when further heated to 270°, they give off oxygen and a trace of chlorine. When mixed with sulphur it detonates with the utmost violence on friction.

Silver and Sulphur.

222 *Silver Sulphide*, Ag_2S, occurs as argentite, or vitreous silver. The occurrence of this ore was known to Agricola: "Argentum rude plumbei coloris et galenæ simile." This important silver ore, occurring in blackish-grey crystals belonging to the regular system, occurs widely distributed, but is found especially in the Erzgebirge, in Hungary, in Norway near Kongsberg, in the Altai, in the Urals, in Cornwall, Bolivia, Peru, Chili, Mexico, and in Nevada, at the Comstock lode. This compound occurs in the Erzgebirge in two distinct forms; one of these is termed daleminzite, and the other acanthite, the first of these being isomorphous with chalcocite. Argentite can be obtained artificially by igniting silver chloride in a current of sulphuretted hydrogen. Silver sulphide is also formed when silver is heated with sulphur or sulphuretted hydrogen, and forms the yellow or brownish stains which are

[1] *J. pr. Chem.*, 1899, [2], **59**, 537; see also Vol. I., p. 350.

formed on articles of silver on exposure to the air (Proust). Sulphuretted hydrogen produces in solutions of silver a blackish-brown flocculent precipitate of silver sulphide which is soluble in hot nitric acid, and is converted into silver chloride when a solution of copper chloride in the presence of common salt is added to it.

Silver Disulphide, Ag_2S_2, has been prepared by adding a solution of sulphur in carbon disulphide to a solution of silver nitrate in benzonitrile. It is a brown amorphous powder which oxidises very rapidly when moist, and is converted into silver sulphate by shaking with water and air. When heated in the air it melts to a red liquid and gives off sulphur and sulphur dioxide, metallic silver being left.[1]

Silver Sulphite, Ag_2SO_3, is a white curdy precipitate almost insoluble in water or sulphurous acid. It was supposed to decompose when heated to 100° into silver, silver sulphate, and sulphur dioxide, but Baubigny[2] has shown that only a small proportion is decomposed in this manner, more than 80 per cent. being converted into dithionate, thus :

$$2Ag_2SO_3 = Ag_2S_2O_6 + 2Ag,$$

and that it is only at a much higher temperature that silver sulphate and sulphur dioxide are produced from the dithionate.

Normal Silver Sulphate, Ag_2SO_4.—This substance was obtained in solution by Glauber, for he states in this *De furnis novis philosophicis* (1648) : " Dissolve *rasuram* ☽ in a rectified oil of vitriol, with the addition of a sufficiency of water, but not so much as in the case of Mars or Venus. Or, still better, dissolve a calx of ☽ which is precipitated from aqua fortis, either by copper or by spirits of salt."

It is best obtained by heating the reduced metal with sulphuric acid, or by dissolving the carbonate in dilute sulphuric acid. It forms small, lustrous rhombic crystals, which are anhydrous, and isomorphous with anhydrous sodium sulphate;[3] it has a specific gravity of 5·4, and dissolves to the extent of 0·77 part at 17°, 1·46 parts at 100°, in 100 parts of water. In consequence of the sparing solubility of the salt, it is obtained as a precipitate when sulphuric acid or a soluble sulphate is added to a silver solution, and this fact was known to Boyle.[4] It is easily soluble

[1] Hantzsch, *Zeit. anorg. Chem.*, 1898, **19**, 104.

[2] *Compt. rend.*, 1909, **149**, 735, 858.

[3] Mitscherlich, *Pogg. Ann.*, 1827, **12**, 138.

[4] " Considerations and Experiments touching the Origin of Qualities and Forms," Boyle, *Op.* **3**, 66.

in water containing sulphuric acid, and still more soluble in nitric acid, and also dissolves readily in strong sulphuric acid, being precipitated from this solution on the addition of water. It fuses at a dark-red heat and decomposes at a very high temperature into metal, oxygen, and sulphur dioxide. When dissolved in less than three parts of sulphuric acid, light yellow prisms of *hydrogen silver sulphate*, $HAgSO_4$, are obtained.

According to Carey Lea,[1] a double salt of silver sulphate and a lower sulphate, having the formula Ag_4SO_4,Ag_2SO_4,H_2O, is obtained by the reduction of silver nitrate, phosphate, or carbonate with hypophosphorous acid in presence of sulphuric acid; it forms a pale brown powder which is permanent in the air and does not evolve sulphuric acid even at a dull red heat. It always contains about 2 per cent. of phosphoric anhydride, which cannot be removed even by treatment with strong sulphuric acid.

Silver Thiosulphate, $Ag_2S_2O_3$, is obtained by gradually adding a moderately dilute solution of silver nitrate to an excess of concentrated solution of sodium thiosulphate, washing the precipitated grey mixture of thiosulphate and sulphide with cold water, extracting the thiosulphate with ammonia, precipitating it as quickly as possible by exact neutralisation with nitric acid, and quickly drying it by pressure between filter paper.[2] It forms a snow-white powder, having a sweet taste; it is slightly soluble in water, and when moist easily decomposes into sulphuric acid and silver sulphide (Rose):

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4.$$

Silver Sodium Thiosulphate, $AgNaS_2O_3$, was discovered by Herschel, and may be obtained by evaporating a solution of silver chloride in aqueous sodium thiosulphate until it crystallises. It is, however, best prepared by adding a neutral solution of silver nitrate to a solution of sodium thiosulphate, until a permanent precipitate is produced. The solution is then filtered and alcohol added, when the salt is precipitated in silky laminæ (Lenz). Its solution, evaporated in a vacuum, deposits tabular crystals of the salt. It is soluble in water and possesses a sweet taste (Herschel). A saturated solution of silver chloride in sodium thiosulphate corresponds to the formula $2Na_2S_2O_3,Ag_2S_2O_3,2H_2O$, and this solution deposits a salt

[1] *Amer. J. Sci.*, 1892, [3], **44**, 322.

[2] Herschel, *Edin. Phil. Journ.*, 1819, **1**, 26; **2**, 154.

corresponding to the formula $Na_2S_2O_3,Ag_2S_2O_3,2H_2O$.[1] A number of double thiosulphates of silver and potassium are also known.[2]

Silver and the Elements of the Nitrogen Group.

223 *Silver Nitride*, NAg_3.—This compound, usually known as Berthollet's fulminating silver, was first obtained by this chemist in 1788 by the action of ammonia on the silver oxide prepared by precipitating a silver solution with lime water. It is a black powder which, especially in the dry state, explodes most violently on the slightest percussion, or even on touching with a feather. Great care is necessary in working with ammoniacal solutions of silver oxide, and such solutions should not be kept.[3] Raschig[4] has shown that the compound has the composition NAg_3, but it is usually mixed with a certain quantity of metallic silver. In some cases the powder was also found to contain hydrogen, and had then the formulæ $NHAg_2$. A yellow nitride of silver is stated to be formed when magnesium nitride and silver nitrate are gently heated together in a sealed tube. It is decomposed by water with formation of silver oxide and ammonia.[5]

Silver Amide, $AgNH_2$, is formed as a white precipitate when a solution of potassamide in liquid ammonia is added to excess of silver nitrate dissolved in the same solvent. It is soluble in solutions of ammonium salts in liquid ammonia, darkens on exposure to light, and when dry readily explodes.[6] The amide dissolves readily in a solution of potassamide in liquid ammonia to form *potassium ammonoargentate*, $AgNH{\cdot}K$, which crystallises with one molecule of ammonia.[7]

Silver Azoimide, AgN_3, is obtained by the addition of silver nitrate to a solution of azoimide or one of its soluble salts. It forms minute prisms, which are insoluble in water and readily explode with extreme violence.

Silver Hyponitrite, $Ag_2N_2O_2$, is a yellow precipitate which is

[1] Lumière and Seyewetz, *Bull. Soc. chim.*, 1907, [4], **1**, 946.

[2] Rosenheim and Steinhauser, *Zeit. anorg Chem.*, 1900, **25**, 72.

[3] See Matignon, *Bull. Soc. chim.*, 1908, [4], **3**, 618; also Sieverts, *Zeit. angew. Chem.*, 1909, **22**, 6.

[4] *Annalen*, 1886, **233**, 93.

[5] Smits, *Rec. trav. chim.*, 1896, **15**, 135.

[6] Franklin, *J. Amer. Chem. Soc.*, 1903, **27**, 820.

[7] Franklin, *J. Amer. Chem. Soc.*, 1915, **37**, 847, 852.

deposited from ammonia in small yellow crystals.[1] It is sparingly soluble in water, and when moist slowly decomposes at ordinary temperatures. When pure it does not explode when heated, but decomposes into nitrogen, oxides of nitrogen, silver nitrate, and silver.[2]

Silver Nitrite, $AgNO_2$.—This substance was first obtained by Proust, who regarded it as the nitrate of silver suboxide, having obtained it by boiling a solution of silver nitrate with the powdered metal. It is best prepared by mixing lukewarm solutions of 24 parts of silver nitrate and 15 parts of potassium nitrite. On cooling, silver nitrite separates as a white crystalline powder which may be readily filtered. It is less soluble in cold water than silver sulphate, but dissolves more readily in hot water with partial decomposition. When slowly deposited, it forms long, acicular, rhombic crystals.

When heated, silver nitrite decomposes without fusion at 180°,[3] according to the following equations:—$AgNO_2 = Ag + NO_2$; $Ag + 2NO_2 = AgNO_3 + NO$; $AgNO_2 + NO_2 = AgNO_3 + NO$.

The double nitrites, $Na_2Ag_2(NO_2)_4$; $K_2Ag_2(NO_2)_4,H_2O$; and $BaAg_2(NO_2)_4,H_2O$, have been described.[4]

Silver Nitrate, $AgNO_3$.—This salt was obtained in the crystalline form by Geber: "Dissolve ☽ calcinatam in aqua dissolutiva, quo facto, eoque eam in phyala, cum longe collo, non obturato ori per diem solum, usque quo consumetur ad ejus tertiam partem aquæ, quo peracto pone in loco frigido, et devenient lapilli ad modum crystalli fusibiles." At the end of the seventeenth century, Angelus Sala directed the attention of the iatrochemists to this salt, known as *crystalli dianae* or *magisterium argenti*, to which, when cast into sticks, the name of *lapis infernalis* or *lunar caustic* was given.

Silver nitrate is obtained on the large scale by dissolving silver in dilute nitric acid, and occurs in commerce both in crystals and cast into sticks (lunar caustic). It crystallises in transparent rhombic plates (Fig. 124), having a specific gravity of 4·328 (Schröder) and melting at 209°, solidifying on cooling to a white, fibrous, crystalline mass. It is dimorphous, passing into a hexagonal modification at 159°.[5] It possesses an acrid, metallic

[1] Krischner, *Zeit. anorg. Chem.*, 1898, **16**, 424.

[2] Divers, *Journ. Chem. Soc.*, 1899, **75**, 95.

[3] Divers, *Proc. Chem. Soc.*, 1905, 281; see also Oswald, *Compt. rend.*, 1911, **152**, 381.

[4] Oswald, *Ann. Chim.*, 1914, [9], **1**, 32.

[5] Compare Guinchant, *Compt. rend.*, 1909, **149**, 569.

taste, and acts as a violent poison, blackening and destroying organic matter, but it does not blacken in the air except in contact with organic substances. When it is wrapped up in paper for some time it gradually decomposes, leaving a residue of metallic silver, and at a red heat it yields nitrogen peroxide, oxygen, and metallic silver.[1]

One hundred parts of water dissolve as follows:[2]

At	0°	20°	50°	80°	100°	110°
$AgNO_3$	115	215	400	650	910	1110 parts.

The aqueous solution has a neutral reaction. If ammonia be added to a solution of silver nitrate until the precipitate first formed redissolves, and this solution be then allowed to evaporate fine bright rhombic prismatic crystals having the composition $AgNO_3,2NH_3$ are deposited. These do not give off ammonia at 100°, but when more strongly heated they melt, evolving nitrogen and ammonia, whilst ammonium nitrate and a metallic mirror of silver are left behind. When a current of dry ammonia is passed over dry silver nitrate, this substance absorbs 29·55 per cent. of the gas, enough heat being developed to produce fusion of the mass. The product of this reaction, $AgNO_3,3NH_3$, is a white solid soluble in water (Rose).

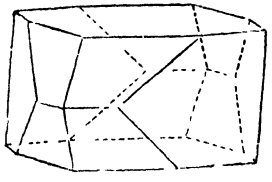


FIG. 124.

Silver nitrate is largely used in chemical analysis and especially in photography. It is also employed in medicine both externally and internally. In external application it acts as a powerful cautery, inasmuch as it unites with the albuminoid substances to form insoluble compounds. Large doses given internally act corrosively upon the mucous membrane, producing serious inflammation. Experiments on animals have shown that it produces paralysis of the nerve-centres, difficulty of breathing, and coma. It is given in doses of from 0·02 gram in chronic stomach diseases, epilepsy, and other nervous affections. When administered for some length of time, it produces a peculiar bronze colour of the skin, caused by the deposition of metallic silver under the cuticle.

[1] Divers, *Journ. Chem. Soc.*, 1899, **75**, 83.

[2] Kremers, *Pogg. Ann.*, 1854, **92**, 497; see also Étard, *Ann. Chim. Phys.*, 1894, [7], **2**, 526; Meyerhoffer, *Landolt-Börnstein Physikalisch-Chemische Tabellen* (Berlin, Springer).

Ammoniates of many silver salts have been described,[1] *e.g.*, $AgF,2NH_3,2H_2O$; $AgClO_3,3NH_3$; $AgCl_4,2NH_3$; $AgBrO_3,3NH_3$; $AgMnO_4,3NH_3$; $Ag_2SO_3,4NH_3$; $Ag_2SeO_3,4NH_3$, etc.

224 *Silver Diphosphide*, AgP_2, may be prepared by passing phosphorus vapour over finely divided silver or silver chloride heated at 400°. The product must be cooled in an atmosphere of phosphorus vapour, as it decomposes at the temperature of formation when heated in an inert gas.[2]

Phosphates of Silver.—The *normal phosphate*, Ag_3PO_4, is formed as a yellow precipitate when a silver salt is added to a solution of any one of the sodium orthophosphates. On heating, its colour changes to brown, and it melts at a red heat. It is soluble in aqueous phosphoric acid, yielding the *mono-hydrogen salt*, HAg_2PO_4, which is deposited in the form of white crystals. The *pyrophosphate*, $Ag_4P_2O_7$, is a white compound melting below a red heat to form a dark brown liquid which solidifies to a colourless fibrous mass. When heated for some time with aqueous phosphoric acid, the *dihydrogen pyrophosphate*, $H_2Ag_2P_2O_7$, is formed as a crystalline powder, which is decomposed by the addition of water. The same compound may also be formed by heating silver pyrophosphate with pyrophosphoric acid until a clear fused mass is obtained, dissolving the cooled product in a small quantity of water at 0°, and adding alcohol, when it is precipitated as a white crystalline powder melting at 240°.[3] The *metaphosphates* of silver are white compounds.

Arsenites and Arsenates of Silver.—The *normal arsenite*, Ag_3AsO_3, is a canary-yellow powder easily soluble in nitric acid and ammonia. When the ammoniacal solution is boiled, metallic silver separates out. The *normal arsenate*, Ag_3AsO_4, is a dark reddish-brown crystalline powder, formed by precipitating a concentrated solution of arsenic acid with a boiling solution of silver nitrate. The same substance is precipitated as a brownish-red powder if a solution of an arsenate be added to silver nitrate.

Silver Acetylide or Silver Carbide, C_2Ag_2.—When acetylene is passed into aqueous silver nitrate a white precipitate is first formed of composition $C_2Ag_2,AgNO_3$, which with more acetylene changes to white silver acetylide. It may also be obtained by passing acetylene into ammoniacal silver nitrate.[4]

[1] Bruni and Levi, *Gazz.*, 1916, **46**, ii, 17, 235.
[2] Granger, *Compt. rend.*, 1897, **124**, 896; *Chem. News*, 1898, **77**, 227.
[3] Cavalier, *Compt. rend.*, 1904, **139**, 284.
[4] Arth, *Compt. rend.*, 1897, **124**, 1534; Chavastelon, *ibid.*, 1564.

Silver Carbonate, Ag_2CO_3, is a light yellow powder of a paler colour than the phosphate, which readily becomes black on exposure to light, or on heating, and loses all its carbon dioxide at 200°. When a mixture of ammonio-nitrate of silver and caustic potash is exposed to the air, silver oxide separates out, and after a time lemon-yellow needles of the carbonate.

When silver nitrate is added to a concentrated solution of potassium carbonate a yellow precipitate separates out, and this quickly changes to the white compound, *silver potassium carbonate*, $AgKCO_3$.[1]

Silver Cyanide, AgCN, is a white curdy precipitate easily soluble in ammonia. On heating with water or with caustic potash solution it is reduced to metallic silver.[2] It is insoluble in cold dilute nitric acid, but dissolves in the hot acid, forming silver nitrate and hydrocyanic acid, which may be removed by distillation.[3] It forms soluble double salts with the cyanides of the metals of the alkalis and alkaline earths.

Potassium Silver Cyanide, $KAg(CN)_2$, crystallises in feathery tufts or six-sided prisms, and is soluble in 4 parts of water at 20°.[4] It does not undergo alteration on exposure to light.

Silver Cyanamide, Ag_2CN_2, may be obtained by precipitating an alkaline solution of sodium cyanamide with silver nitrate. On heating, it explodes more or less violently, the gases formed by the explosion being cyanogen and nitrogen.[5]

Silver Cyanate, AgCNO, is a white precipitate easily soluble in ammonia and nitric acid. On heating it explodes, a dull white mass of silver carbide remaining behind. This decomposes, on solution in nitric acid, leaving a finely-divided network of pure carbon.[6]

Silver Thiocyanate, AgCNS, is a white curdy precipitate easily soluble in ammonia and crystallising from the solution in glistening scales which do not contain any ammonia.

Potassium Silver Thiocyanate, $KAg(SCN)_2$, is formed when the foregoing salt is dissolved in a solution of potassium thiocyanate. It forms monoclinic crystals, melts at 140°, and is decomposed by water. Crystalline sodium and ammonium silver thiocyanates, NaSCN,AgSCN; 3NaSCN,AgSCN; NH_4SCN,AgSCN;

[1] Reynolds, *Journ. Chem. Soc.*, 1898, **73**, 265.
[2] Marsh and Struthers, *Proc. Chem. Soc.*, 1903, 249.
[3] Plimmer, *Journ. Chem. Soc.*, 1904, **85**, 12.
[4] Baup, *Ann. Chim. Phys.*, 1858, [3], **53**, 462.
[5] Ellis, *Chem. News*, 1909, **100**, 154.
[6] Liebig and Redtenbacher, *Annalen*, 1841, **38**, 129.

$5NH_4SCN,AgSCN$, are known, all being decomposed by excess of water.[1]

Photography.

225 The observation of Boyle that silver chloride and other silver salts undergo blackening on exposure to light, the chemical explanation of which was first given by Scheele, led to the foundation of the important art of photography. The first light-pictures were obtained by Thomas Wedgwood in the year 1802. These were simply prints of leaves or paintings on glass prepared by allowing the light to fall through a more or less transparent object on to white paper or leather which had been moistened with nitrate of silver. Davy, repeating these experiments, obtained fairly accurate copies of leaves, wings of insects, and similar objects, and even succeeded in preparing pictures of small objects which had been magnified by the solar microscope. The pictures thus obtained could not be exposed to daylight, but had to be examined by candle-light, as at that time no process was known by which that portion of the silver salt unacted upon by the light could be withdrawn, and the pictures thus rendered permanent. The first experiments which aimed at rendering the photographic image permanent were made by Niépce, who began his investigations in the year 1814. In 1826 he, together with Daguerre, investigated the same subject, and it is to the latter experimenter that we are indebted for the first process by which the image obtained in the camera can be fixed. In 1839 he discovered the process which now bears his name. This consists in allowing the vapour of iodine to act upon a polished surface of silver, which thus becomes coated with a film of silver iodide. The surface of the plate thus prepared is next exposed to light in the camera. After a short time the light has produced its action, although on the removal of the plate no change of the surface is perceptible. If the plate be now exposed to the action of the vapour of mercury, the picture makes its appearance, inasmuch as the mercury is deposited in extremely fine globules on those portions of the plate on which the light has fallen, whilst in the shadows the unaltered iodide remains. In order to remove those portions of the iodide which had been unacted upon by the light, Daguerre at first used a hot solution of common salt, but Herschel at once pointed out the

[1] Cernatescu, *Bull. Acad. Sci. Roumaine*, 1920, **6**, 53.

advantages of sodium thiosulphate for this purpose, and it was immediately adopted by Daguerre.[1]

The Daguerreotype process underwent many alterations, but it has now been altogether superseded by much more convenient methods. In the year 1839 Fox Talbot published his method of photogenic drawing, or photography on paper. This process, which was but an imperfect one, consisted in exposing in the camera a paper soaked in a weak solution of common salt and afterwards washed over with a solution of silver nitrate. The image obtained was a negative one; that is, the light portions of the landscape were dark, and *vice versâ*. These pictures were fixed by immersion in a solution of common salt. A great improvement was made in this process by Talbot in the year 1841, by coating the paper which was to be acted upon with a film of silver iodide by first dipping it into a solution of silver nitrate and then into one of potassium iodide. This paper does not exhibit any change after exposure in the camera, but on "development" with a mixture of silver nitrate, acetic acid, and gallic acid, the image becomes visible. The picture is a negative, but it may be rendered transparent by saturating it with white wax, and then a positive print may be prepared from it by placing it on a paper moistened with chloride of silver and exposing it to sunlight. This method was long known as the Talbotype or Calotype process.

A most important improvement in photography was made by Archer (1851), in the employment of a transparent film of iodised collodion spread upon glass as a sensitive film for the camera in place of the iodised paper used in the Talbotype process. Collodion is a solution of pyroxylin, consisting of the lower nitrates of cellulose, in a mixture of alcohol and ether, and to this is added a certain proportion of a soluble iodide or bromide, usually of zinc or cadmium. On pouring the solution on to the plate the ether and alcohol evaporate, and the plate becomes covered with a homogeneous film. The collodionised plate is next dipped into a bath of silver nitrate, and the plate thus "sensitised" is exposed, still wet with the silver nitrate solution, in the camera. The image produced on the film is in this case also latent, and requires to be developed or made visible by treating the surface with reducing agents, such as ferrous sulphate or pyrogallic acid, compounds which have the power of reducing it to the condition of metallic silver. The unaltered iodide may be removed by dissolving it in cyanide of

[1] Eder, *Geschichte der Photographie*, pp. 203, 209 (Knapp, Halle a.S. 1905).

potassium or sodium thiosulphate, and from the negative thus obtained any number of positive prints can be prepared, each of which is afterwards fixed in sodium thiosulphate. The application of collodion renders the process much more certain, shortens the necessary exposure to a few seconds, and admits of a far greater degree of precision in the reproduction of detail than was possible on the rougher surface of paper in the Talbotype.

Many attempts were made to lessen the inconvenience attaching to wet plate photography by washing the plate free from silver nitrate, covering it with a film of some substance such as tannin, albumin, etc., and then drying.

All these plates are, however, much surpassed in sensitiveness towards light by the modern dry plate, which consists of a glass plate coated with an emulsion in gelatin of silver bromide, sometimes accompanied by a little iodide. This emulsion is made by adding ammoniacal silver nitrate to a solution of an excess of potassium bromide and gelatin in hot water. The mixture is then heated at 45° for some time, a process termed "ripening," until the emulsion attains its most sensitive condition. During this operation a physical change appears to occur, the particles of bromide, which when first precipitated have a diameter of 0·0008–0·0015 mm., increasing during the process to 0·003–0·004 mm. in diameter. The emulsion is then washed, to remove the potassium bromide and nitrate, placed on the plate in a uniform film, and dried. When such a plate is exposed to light a latent image is produced which can be developed by many reducing agents which do not attack unexposed silver bromide. The reducing agents employed as developers include ferrous oxalate, which passes during the process into ferric oxalate, pyrogallic acid (trihydroxybenzene), hydroquinone (quinol, *para*-dihydroxybenzene) and metol (*para*-methylaminophenol); in presence of an alkali such as ammonia or potassium carbonate these hydroxy-compounds are converted by oxidation into quinones and similar substances. In order to prevent too vigorous development and consequent fogging of the plate, a *restrainer* or *retarder*, consisting of the bromide of the alkali used, is added to the developer.[1] The plates are then "fixed" by washing with sodium thiosulphate solution, which dissolves out the silver bromide unacted on by the developer, leaving the silver image.

The exact change in the sensitive salt that is effected by the

[1] See Lüppo-Cramer, *Zeit. Chem. Ind. Kolloide*, 1909, **4**, 92, and Sheppard, *ibid.*, 1909, **5**, 43.

light is not yet understood, the chief fact known being that the developer removes the bromine from the silver bromide where the light has fallen upon the film, whilst it is unable to bring about this change in those parts of the film where the light has not preceded it. If an exposed plate be treated with a halogen element or an oxidising agent such as nitric acid, potassium dichromate, etc., it is found that the image can no longer be developed.

Several theories have been advanced as to the nature of this change, all of which may be classed into two groups; the one attributing it to a chemical and the other to a physical change in the silver bromide. According to the first of these views, the light causes a very small amount of bromine to be lost by the silver bromide, a sub-bromide being formed. This bromine is taken up by the gelatin, which thus acts as a sensitiser and replaces the silver nitrate of the wet collodion plate and the tannin of the dry collodion plate. Many hold that the sub-bromide thus formed has the composition Ag_2Br, whilst Eder,[1] from the alteration in the action of certain reagents on plates exposed to light for varying periods, concludes that several sub-bromides are obtained depending on the length of the exposure. Another view is that an oxybromide of silver is formed with loss of bromine, and not a sub-bromide. During development the altered silver bromide is first reduced and the reducing action becomes extended to the silver bromide in the immediate proximity of this reduced silver. It will be seen that according to this theory the density of the silver image which can be obtained by development is limited only by the thickness of the film, the amount of silver produced increasing steadily with the duration of the development. It has, however, been shown by Hurter and Driffield[2] that the maximum density attainable depends entirely on the length of the exposure and the intensity of the light, and is not altered by prolonging the development beyond a certain necessary time. The same chemists have further proved that when a plate is exposed so long that the whole of its silver bromide can be reduced to metallic silver by development, no evidence of the formation of hydrobromic acid, which would accompany the action of bromine on gelatin,

[1] Eder, Address to the Viennese Academy of Sciences, *British Journ. Phot.*, 1905, **52**, 950 and 968; see also Trivelli, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, **11**, 730.

[2] *J. Soc. Chem. Ind.*, 1890, **9**, 455; Sheppard and Mees, *Proc. Roy. Soc.*, 1905, **74**, 44.

can be detected, and that the whole of the bromine in the plate is given up to the developing liquid.

It has, moreover, been found by Dewar that gelatin emulsions of silver bromide remain sensitive to light, although to a somewhat smaller extent, even at a temperature of −252·5° C., at which nearly all chemical reactions proceed extremely slowly.

These results, therefore, have given rise to the view that no chemical decomposition is brought about by the light, but that the silver bromide molecule undergoes a physical alteration which renders it capable of being reduced by the developer.

Joly,[1] who supports the physical hypothesis, considers that the light causes an electronisation of the silver bromide.

It is well known, from the experiments of Hertz and others, that light has the power of discharging negative electrification from the surface of many bodies; that is, of bringing about the escape of negatively charged electrons (p. 40); and such bodies are termed "photo-electric." It has also been found that the halogen salts of silver are vigorously photo-electric, and possess an activity in the descending order, bromide, chloride, and iodide, which is the same order as their photographic sensitiveness.

Moreover, an image capable of development is also formed by the action of cathode rays, or the electronic discharge from radium. Joly, therefore, considers that the latent image is made up of atoms or molecules electronised by the action of light on the silver halide salt, and that it is upon these that the developer acts. A number of experiments, in which the rate of action of developers upon the silver bromide of exposed plates was measured, have been carried out by Sheppard and Mees,[2] and their results point to the conclusion that the reducing agent in the development acts upon ionised silver bromide with formation of metallic silver.

H. Weitz[3] considers the latent image to consist of a solid solution of silver sub-halide and possibly silver in silver halide, but Lüppo-Cramer[4] considers that the assumption of the formation of sub-chloride or sub-bromide is unnecessary and that the latent image is a colloidal compound. He also explains the peculiarities of the silver deposits obtained with different

[1] Address to the Photographic Convention of the United Kingdom, Dublin, 905; *British Journ. Phot.*, 1905, **52**, 551.

[2] *Proc. Roy. Soc.*, 1905, **74**, 447; 1905, **76**, [*A*], 226; 1907, **78**, [*A*], 461.

[3] *Zeit. physikal. Chem.*, 1906, **54**, 305.

[4] *Zeit. Chem. Ind. Kolloide*, 1907, **2**, 135.

developers, and with gelatin and collodion films, by the more or less colloidal nature of the silver and by adsorption of different substances from the developers.[1]

The question cannot, however, as yet be considered as settled.

226 *Action of Light of Different Degrees of Refrangibility on the Salts of Silver.*—Scheele observed that the violet rays of the solar spectrum are those which affect silver chloride most strongly, and to these the name of chemical rays has frequently been given. It has, however, been shown that all the rays of the solar spectrum are able, under certain circumstances, to effect chemical change, each particular chemical compound being decomposed by the rays upon which it is most capable of exerting an absorbent action. Not only is this the case, but an addition to the sensitive compound of certain coloured, but chemically inactive, substances has the effect of altering the position of the maximum of chemical action for that particular compound. Thus, for example, it is possible by the addition of a yellowish-red colouring matter, such as aurin, to the bromide film to prepare a plate which is more affected by the yellow rays than the untreated plate, whilst the addition of erythrosin confers increased sensitiveness to the yellow and orange rays, and of cyanin to the red rays.

These dyes cause the bromide film with which they are mixed to be specially sensitive to the rays corresponding roughly to their absorption spectra. In this way Draper,[2] Vogel,[3] and Abney[4] have succeeded in photographing the lines of the visible solar spectrum from *b* downwards, and have not only secured pictures of the portions included between the lines *E* and *A*, but have obtained photographic action even in the infra-red regions. Orthochromatic plates are now made by means of which the relative intensity of the various colours to the eye is much more truly represented.[5] The exact function of the dyes in producing this effect is not understood, but they are known to be photo-electric, and it has been suggested by Joly that the electron-producing power for that particular ray absorbed by the dye is responsible for the special sensitiveness it produces in the film.

For a full account of the theory and practice of photography,

[1] *Zeit. Chem. Ind. Kolloide*, 1908, **3**, 33, 135.
[2] *Phil. Mag.*, 1877, [5], **3**, 86.
[3] *Ann. Phys. Chem.*, 1885, **26**, 527.
[4] *Phil. Mag.*, 1878, [5], **5**, 61.
[5] See Bothamley, *Brit. Assoc. Rep.*, 1895, 661.

the reader is referred to Abney's "Instruction in Photography," Chapman Jones's "Science and Practice of Photography," and to Meldola's "Chemistry of Photography."

Detection and Estimation of Silver.

227 There is probably no element whose presence can be more readily detected by chemical methods than silver, owing to its chloride being insoluble in water and easily soluble in ammonia. In order to detect silver in an insoluble compound, it may be melted with sodium carbonate on charcoal before the blowpipe or simply heated on charcoal in the reducing flame of the blowpipe. Silver is then obtained in the metallic state as a bright shining bead, which easily dissolves in warm nitric acid, the solution giving on the addition of hydrochloric acid a curdy precipitate of silver chloride, or, if only a trace of silver be present, a mere opalescence. This disappears on the addition of ammonia, but is reproduced when the ammonia is neutralised with nitric acid.

The spark spectrum of silver is obtained by the use of poles of the metal with a powerful discharge. It may also be seen when platinum poles are moistened with silver nitrate solution. Two bright green lines are the most characteristic in its spectrum, and several weaker lines occur in both the blue and the violet.

Silver is estimated gravimetrically as the chloride. The precipitate after washing and drying is heated in a porcelain crucible until it begins to melt, and then its weight is obtained. This method is used in the Indian mint. In some few cases the silver is determined as the cyanide or sulphide, and, in the case of organic silver salts, the metal which remains behind on heating the salt is weighed.

Silver can also be easily determined volumetrically with standard hydrochloric acid, common salt solution, or potassium thiocyanate. In the mints, where a large number of silver assays has to be made daily, a method proposed by Gay Lussac[1] is often adopted. In this process the alloy is dissolved in nitric acid, and the silver precipitated from solution in the form of chloride, the volume of the standard solution necessary for the complete precipitation of the silver being ascertained. Chemically pure silver is required for standardisation; this is best used in

[1] *Instruct. sur l'Essai des Matières d'Argent par la Voie Humide.* Paris, 1833.

the form of thin foil; then a standard solution of common salt is needed of such a strength that 100 c.c. correspond exactly to one gram of silver; thirdly a salt solution 1–10th of this strength, prepared by diluting one volume of the standard solution to ten volumes.

Sufficient of the alloy (of which the composition must be known approximately) to contain a little more than one gram of silver is accurately weighed, placed in a bottle, and dissolved in nitric acid. One hundred c.c. of the standard solution of salt are then added and the bottle well shaken. The titration is then continued with the 1–10th strength solution until precipitation is complete. Each c.c. of standard solution corresponds to 0·01 gram, and each c.c. of the second solution to 0·001 gram of silver.

Another method of assaying silver still used although not so accurate as the method just described, is the assaying of silver by cupellation. This process depends on the fact that the metals alloyed with silver oxidise in the presence of lead oxide at a high temperature, yielding an oxide which, together with the oxide of lead, is absorbed by the porous cupel, whilst any silver which the mixture contains is left behind in a bright globule which can be accurately weighed. The assay is usually made with 0·25 to 0·5 gram of silver and check alloys containing about the same amount of pure silver are cupelled at the same time to ascertain the cupellation loss, which is added to the assay results. The process of assaying by cupellation, even in experienced hands, may vary as much as two parts in 1,000, whilst Gay-Lussac's process admits of an accuracy of 0·5 in 1,000. The process of cupellation is, however, still in use in lead works, where it is required to determine the amount of silver which marketable lead contains, and it is also used for the estimation of silver in ores.

The electrolytic method has also been used for the determination of silver, a solution of the nitrate being used, and alcohol or potassium cyanide added to prevent the formation of the black compound described on page 481.[1]

The atomic weight of silver was determined with considerable accuracy by Stas, by the methods described on p. 12, the average of the numbers obtained by the different methods being 107·93. Guye and Ter Gazarian[2] have found that potassium chlorate

[1] Kuster and von Steinwehr, *Zeit. Elektrochem.*, 1898, **4**, 451; Wolman, *ibid.*, 1897, **3**, 537.

[2] *Compt. rend.*, 1906, **143**, 411; see also Richards and Wells, *J. Amer. Chem. Soc.*, 1905, **27**, 459.

crystallises with a small quantity of chloride as an impurity, the amount being nearly constant, about 2·7 parts in one thousand. Applying this correction to Stas's ratios, the atomic weight of silver is lowered from 107·93 to 107·89. The number now adopted (1922) is 107·88.

GOLD (AURUM). Au = 197·2. At. No. 79.

228 Of all the metals gold was probably the first to attract the attention of man, its occurrence in the native state, its brilliant lustre, and its permanence, rendering it an object of value from very early times.

Metallic gold is mentioned in the Old Testament and in Homer, and the various names by which it is designated denote lustre or fine colour. Thus in the Hebrew *zahâb*, the root signifies to glitter; whilst the Greek word χρυσός, probably derived from the Sanscrit *hiranya*, also signifies to glitter or flame. Our word "gold" probably is connected with *jvalita*, which also occurs in Sanscrit and is derived from *jval*, which means to shine. As being the most perfect of the metals gold was compared by the alchemists to the sun; to it were attributed the most singular virtues, and strenuous efforts were directed to the transmutation of the baser metals into ☉ (Sol).[1]

Gold is usually found in the native state, but never perfectly pure, being always alloyed with more or less silver. Native gold sometimes also contains small quantities of copper, and traces of iron, bismuth, platinum, palladium, or rhodium. Gold is likewise found in the following compounds: bismuth-aurite, Au_2Bi; calaverite, $AuTe_2$; sylvanite or graphic tellurium, $(Au,Ag)Te_4$; nagyagite or foliated tellurium, $(Pb,Au)_2(Te,S,Sb)_3$; white tellurium, $(Au,Ag,Pb)(Te,Sb)_3$. Small quantities of gold occur in many pyrites, blendes, and other ores. It has also been found in sea water.[2]

Native gold is generally found *in situ* in quartz veins or reefs which intersect metamorphic rocks, and to some extent also in the wall-rock of these veins. Metamorphic rocks which are thus intersected are generally chloritic, talcose, and argillaceous

[1] Those interested in the processes employed by the alchemists in the search after the philosopher's stone are referred to Thomson's *History of Chemistry*, and Berthelot, *Collection des Anciens Alchimistes Grecs*, and *La Chimie au Moyen Âge* (Paris, 1887–1893).

[2] Liversidge, *Trans. Roy. Soc. N.S.W.*, 1896.

schists; also, though less commonly, mica- and hornblende-schists; gneiss, diorite, and porphyry, and, still more rarely, granite. Gold is frequently found crystalline, the commonest forms being the octahedron and tetrahedron. The crystals are, however, sometimes acicular, through elongation of these two forms, passing into filiform, reticulated, and arborescent shapes, and occasionally exhibit a spongy form from the aggregation of filaments. It frequently occurs in masses termed nuggets, also in thin laminæ, and often in flattened grains or scales and in rolled masses in sand or gravel. Sometimes indeed it is so finely disseminated throughout the quartz that it is not visible, though present in quantities sufficient to pay for its extraction.

The occurrence of gold is not confined to the above-named rocks, the metal being found in many formations, even up to the chalk.

The sands, gravels, and clays formed by the disintegration of the gold-bearing rocks form an important source of the precious metal, and these alluvial deposits often occur of considerable thickness and of great extent.

229 Although gold occurs widely distributed in nature it is only found in certain places in quantities sufficient to repay the expenses of extraction. The most important European localities are Russia, Hungary, and Germany. Gold has been found in Cornwall, and has been worked to a small extent in Wales. Gold has also been found in Scotland, especially near Leadhills and in Glencoich and other parts of Perthshire, in Ireland in County Wicklow, in Sweden, and in Spain, where mines were worked by the Romans. In Asia, gold occurs chiefly on the eastern flanks of the Urals and in other parts of Siberia, but the metal has been found in almost all parts of this continent, especially in India, Japan, China, Korea, Borneo, and the Dutch East Indies. The vessels of gold in the possession of the ancient Scythians, which according to Herodotus were said to have fallen from the skies, were probably made from Uralian gold. The mines in the Urals were, however, not opened until the year 1819, but they soon became of such importance that they supplied the greater portion of the world's requirements until the discovery of Californian gold.

Africa also contains much gold. Thus a considerable quantity of gold dust has been found in Abyssinia, also on the coast opposite Madagascar, supposed by some to be the *Ophir* of Solomon, and in various parts of the interior of the western portion of the

continent whence it was formerly sent to the Gold Coast. Indeed this source, together with that of Hungary and the Brazils, yielded the chief supply of gold up to the beginning of last century. West Africa has a considerable gold-mining industry. Since the year 1884, the gold-fields of the Transvaal have become of great importance, the output having risen almost continuously since that date. In 1895 the amount of gold obtained from the Rand district was 2,549,036 ozs., whilst in 1905 it had increased to 4,897,221 ozs., and in 1918 to 8,419,100, surpassing the output from any other country.

In the year 1849 gold was discovered in California by Colonel Sutter, who having erected a saw-mill noticed that the water which was used to work the mill contained particles of gold. The attempt to keep this discovery secret naturally failed, and the few hundred inhabitants of the city of San Francisco rushed to the gold-diggings, and were soon followed by emigrants from all parts of the world. Considerable gold-fields exist in the western portion of the North American continent, reaching from Mexico up to British Columbia and the Klondyke district.

Australia is another country rich in gold-fields and occupied the premier position in the British Empire as a producer of gold until 1904. Important gold-mines occur in the table-lands of New South Wales and along the continuation of the Australian cordillera in Victoria, in Queensland and Western Australia, whilst smaller supplies are drawn from South Australia and Tasmania.

It is a matter of general notoriety that many years before anything was published respecting the existence of gold in Australia, gold was often brought into Sydney by shepherds and settlers in the bush. The actual occurrence of gold in Australia was, however, first discovered by Count Strzelecki in the year 1839, but this was not made known at the time, inasmuch as the Governor feared the consequences of such a statement in the existing conditions of the colony. In 1843–4 Count Strzelecki returned to England and exhibited his nuggets and gold specimens to Sir Roderick Murchison, who, arguing from the comparison of these with samples from the gold-bearing Urals, predicted that gold would be found widely distributed in the eastern chains of the Australian mountains. In the years 1841–3 gold was also found by the Rev. W. D. Clarke, an Australian geologist. To Mr. Hargreaves, an old Californian gold-digger, however, belongs the honour of proving, in 1851,

that gold existed in large quantities in various parts of the colony. The first discovery of workable gold-fields was made at Ophir, and this soon led to the finding of the precious metal in the soil and rocks of the colony over tracts many miles in extent. After a short time the proclaimed gold-fields extended, with a few intervals, the whole length of the colony, and westward about 200 miles, comprising an area of about 1,356 square miles, and numbering more than eighty distinct fields.[1]

Gold has also been found in New Zealand, where an average production of nearly £2,000,000 was maintained for several years prior to 1912: but the output has steadily declined since then. The Australian is, as a rule, much purer than the Californian gold, but it is a singular fact that the average fineness of the gold found in the several Australian colonies shows a regular depreciation as we advance northwards. Thus the average fineness of Victorian gold is about 960; that of the New South Wales gold is 935, while still further north in Queensland the average fineness is 872, and Maryborough gold contains only 85 per cent. of gold and as much as 14 per cent. of silver.[2] Very large nuggets occur in Australian fields; thus, for instance, one found at Ballarat weighed 184 pounds and was valued at £8,376 10*s.* 6*d.*

The total production of gold reached a very high mark in the fifties when the Australian discoveries followed on the opening of the Californian fields. During these years the annual production averaged £30,000,000, but afterwards gradually fell off, until in the period 1880–90 it averaged only about £20,000,000.

Since that date it constantly increased until 1915, with the exception of the years 1900–1902, when the production was affected seriously by the Boer War. Since 1915 it has shown a marked yearly falling off. In 1914 the value of the output amounted to slightly over £90,000,000, in 1915 it increased to £96,525,000. In 1916 the output decreased to £93,841,000, in 1917 to £86,980,000, and in 1918 it was only £78,221,700. The increases up to the year 1915 were largely due to the output from South Africa consequent upon the development of the Transvaal fields, but also to the improved methods of extraction adopted. The decreases since 1915 have been due to shortage of labour and the limitation of supplies caused by the European War.

The following figures give the production in ounces of fine gold

[1] Liversidge, *Trans. Roy. Soc. N.S.W.*, ix., 153.
[2] Miller, *Trans. Roy. Soc. N.S.W.*, 1870.

from each of the great gold-producing countries for the years 1895, 1905, and 1918,[1]

	1895.	1905.	1918.
Australasia	2,070,335	4,159,220	1,416,000
United States	2,261,612	4,260,504	3,321,000
Russia	1,537,584	1,063,883	580,000
Transvaal	1,811,391	4,897,221	8,419,000
Rest of Africa	257,806	580,620	—
India	218,186	576,889	485,000
Canada	92,448	700,863	710,590
Mexico	270,924	702,799	814,000
Other Countries	1,203,325	1,489,071	2,679,000
Total	9,723,612	18,431,073	18,424,690

Composition of Native Gold.—The following table gives the composition of several kinds of native gold.

Locality.	Barbara (Siebenbürgen).	Katharinenberg (Ural).	Senegal.	Bolivia.	California.	Australia.	Transvaal
Analyst.	Rose.	Rose.	Levol.	Forbes.	Hunt.	Northcote.	Cohen.
Gold	84 80	93 34	94·40	94·73	89·24	99 28	94 48
Silver	14 68	6 28	5 85	5 23	10·76	0 44	5·16
Iron	0 13	0 32	—	0 04	—	0 20	Trace
Copper	0 04	0·06	—	—	—	0·07	0·25
Platinum	—	—	0·15	—	—	—	—
Bismuth	—	—	—	—	—	0·01	—
	99·65	100 00	100·40	100·00	100 00	100·00	99 89

230 *Gold Extraction.*—The simplest method of extracting gold, namely, *alluvial-washing*, carried on from the simple pan-washing to hydraulic mining on a stupendous scale, necessarily requires a considerable quantity of running water. This or a similar process was in use amongst the ancients; thus Pliny describes the " bringing of rivers from the mountains, in many instances for a hundred miles, for washing the débris," etc.

The washing apparatus is simple, though frequently ingenious. The simplest of all these operations is that termed *pan-washing*, in which a shallow pan is used, of iron or zinc, sinking into a cavity in the middle in which the heavy particles collect, whilst the lighter dirt is washed away.

[1] *Mineral Industry*, 1897, **6**, 260; 1905, **14**, 236; 1911, **20**, 283.

The *cradle* is another simple apparatus for gold-washing, much used in the early days of the gold discoveries in California and Australia. It consists of a trough or cradle of wood or iron six or seven feet in length under which rockers are placed, so arranged that the cradle has a slanting position to allow the mud and water to run off. At the top of the cradle is a grating or sieve upon which the wash-stuff is thrown, and transverse bars of wood are placed across the bottom of the cradle to arrest the passage of the heavier particles of gold.

Other forms of apparatus used for washing gold-bearing deposits are the long tom and the sluice. The *long tom* consists of an inclined trough about 12 feet long, the lower end of which is closed by a screen inclined at an angle of about 45°. Below this screen is placed the upper end of a riffle-box, consisting of another trough 12 feet long fitted with riffles which are sometimes supplied with mercury. The gravel is shovelled into the upper trough and a stream of water is allowed to play upon it, washing down the fine gravel and gold into the riffle-box where the coarse gold is caught on the riffles.

The *sluice* consists of a number of boxes, hundreds sometimes being used, each resembling the upper box of the long tom; they are about 12 feet long and 4 inches wider at one end than at the other, the narrow end of each box fitting into the wide end of that next below it. Riffle boxes are placed at certain intervals in these boxes to intercept all heavy particles that pass down, such as gold, mercury, amalgam, pyrites, etc. The usual grade of the boxes varies from 8 inches to 20 inches in 12 feet, depending on the fall of the ground, on the nature of the material to be washed and on the amount of water available. A certain amount of mercury is added in sluicing to aid in the collection of the gold.

231 *Hydraulicing* consists in breaking down the auriferous gravel by the impact of powerful jets of water and allowing the disintegrated material to pass along a series of sluices. To carry out this process successfully, an immense amount of water is necessary under a good pressure, a head of from 100 to 300 feet generally being used. The nozzles for the discharge of the water vary in size up to 11 inches in diameter, and require special appliances to control them. The sluices used are similar to those described above, but are larger and made altogether stronger. A quantity of mercury is generally used to amalgamate and help to collect the gold.

232 *Extraction of Gold from Quartz, etc.*—The general method for the extraction of the gold from quartz consists in crushing the ore first to a moderate size in a rock-breaker, and then to a much finer state (usually with water) in a stamp battery.

A *stamp battery* (Fig. 125) consists of a number of stamps, which are heavy pestles made of iron or steel weighing from 400 to 2,000 lbs. each; these are raised by means of cams, keyed to a horizontal shaft, coming in contact with tappets fixed on to the upper portion of the stems, and are allowed to fall by

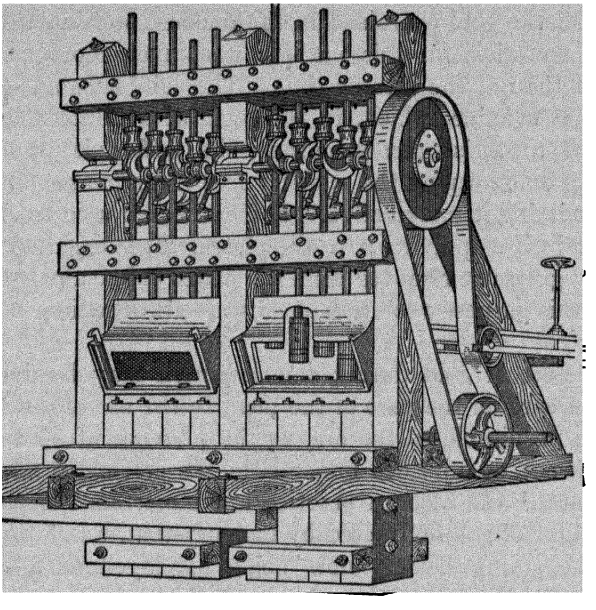


Fig. 125.

their own weight. These stamps work in mortars made of cast iron and weighing from $1\frac{1}{2}$ to 3 tons; as a general rule five stamps work in each mortar. Mercury is often placed inside the mortar, and the upper portions and sides of the latter are lined with amalgamated copper-plates. The pulp is discharged through screens of varying sizes according to the nature of the material under treatment, and then passes over a series of amalgamated plates, the tailing being generally treated by the cyanide process for the extraction of the remaining gold.

Very often the tailings from stamp batteries contain a certain proportion of heavy minerals, such as iron pyrites, copper pyrites, galena, etc., and as these contain gold which is

not collected on the amalgamated plates, they are extracted in some form of concentrating machine and are called concentrates. When these consist of copper pyrites or galena they are treated by smelting, but when they consist of iron pyrites they are treated by Plattner's chlorine process or by the cyanide process. The gold amalgam is scraped off the plates at certain intervals by means of rubber pads, cleaned, strained through wash-leather, and heated in iron retorts, the porous gold which remains being melted and cast into iron moulds.

Many methods have been proposed for promoting the amalgamation of the gold contained in the crushed ore, but the use of various materials for this purpose was much more general in the past than at the present time. The chief substance used is potassium cyanide, which, in the form of a dilute solution, is supposed to assist amalgamation; its action is probably a cleansing one, keeping the mercury free from grease and oil, and thus rendering it more active. Sodium is also used to clean the mercury before applying it to the plates. It is essential that all traces of grease be removed from the plates before amalgamation, and for this purpose a solution of caustic soda or sodium carbonate is used.

The losses of gold during amalgamation may be due to insufficient care on the part of the men, to the use of a method of working unsuitable to the ore, to the presence of float-gold, to the presence of injurious minerals in the ore, or to improperly kept plates.[1] In modern practice less importance is placed on the amount of gold extracted by mercury than was formerly the case, the stamp battery now being employed as a crushing machine and the bulk of the gold obtained by subsequent cyanidation of the slimed material.

233 *Gold Extraction by Chlorine.*—For the purpose of extracting gold from auriferous pyrites Plattner's chlorine method was formerly largely employed. In this process the pyrites is roasted, in order to remove the sulphur and arsenic and to render the ore porous, then moistened with water, and placed in vats furnished with false bottoms, beneath which chlorine is introduced. After all the air has been replaced by chlorine, and the whole mass has become impregnated with this gas, the vats are allowed to stand for about twenty-four hours, and the soluble gold chloride washed out with water.

[1] Full information concerning the metallurgy of gold may be found in *The Metallurgy of Gold*, by Rose (Griffin & Co.), 1902.

In some cases the chlorination is carried out in revolving lead-lined steel barrels or cylinders, the chlorine being produced by the action of sulphuric acid on bleaching powder placed inside the barrel. In this way a pressure of about two atmospheres is produced, and a charge of $3\frac{1}{2}$ tons is chlorinated in an hour and a half. The gold chloride solution is filtered through an asbestos cloth placed inside the barrel and passes directly into the precipitation tank. The metal may be precipitated from the solution by a number of different substances, the chief of which are ferrous sulphate, sulphuretted hydrogen, solid charcoal and sulphide of iron or copper; *e.g.*

$$AuCl_3 + 3FeSO_4 = Au + FeCl_3 + Fe_2(SO_4)_3.$$

Sulphuretted hydrogen and metallic sulphides precipitate a sulphide of the metal, whilst charcoal precipitates the metal. The precipitate is collected, dried, roasted if it consists of the sulphide, and the metal then fused with borax.[1]

At Mount Morgan a modification of the chlorination process is employed in which the crushed ore is leached with chlorine water, the gold being precipitated from solution by charcoal.

It has also been proposed to employ bromine for the extraction of gold, either as bromine water or by liberating nascent bromine by the action of sulphuric acid on a mixture of bromide and bromate of sodium or calcium.

234 *The MacArthur-Forrest Cyanide Process.*—Finely-divided gold dissolves readily in a weak solution of potassium cyanide in the presence of atmospheric oxygen, a soluble double cyanide being formed:

$$4Au + 8KCN + O_2 + 2H_2O = 4KAu(CN)_2 + 4KOH.$$

This reaction is now employed on a very large scale for the extraction of gold from the tailings obtained from the stamp batteries, which only contain a small amount of metal, and from such ores as are not readily treated by amalgamation. The process consists of four operations, viz. the preparation of the ore; treatment with solution of potassium cyanide; precipitation of the gold; and treatment of the precipitated gold.

In many cases the tailings from the stamp batteries only need sizing in order to be ready for the process, and this sizing consists of the separation of slimes or very finely-divided ore from the sandy portions, as these slimes tend to resist the percola-

[1] *J. Soc. Chem. Ind.*, 1896, **15**, 336.

tion of the cyanide solutions. In the case of low grade ores which are treated direct by the cyanide process these are crushed down by rock-breakers and rolls, care being taken to prevent the formation of slimes.

For the treatment with cyanide solution, large vats are used, made of wood, iron, or cement, and holding from 10 to 600 tons of material. These vats are provided with false bottoms which usually consist of frameworks of wood pierced with holes and covered with canvas or cocoanut matting, below this being placed a layer of coarse sand and pebbles. The vats are filled to within a few inches of the top and levelled.

It is often found advisable before treating with the cyanide solution to give a preliminary wash with water to remove soluble salts, or to use a solution of soda or lime to neutralise acids due to the decomposition of pyrites in the ore. In the Transvaal the material is first treated with a solution of cyanide containing about 0·3 per cent. of KCN, which is allowed to percolate for a period varying from 6 to 24 hours, according to the richness and nature of the ore; then a further treatment with a weak solution containing 0·05 to 0·15 per cent. is made, lasting from 24 to 48 hours. The amount of liquid used is generally about half a ton for every ton of ore. After the treatment with cyanide is finished, that is, when no more gold is being dissolved, the solution is drawn off as completely as possible, and the charge thoroughly washed with water and discharged. The tanks are emptied usually through doors in the bottom, either by hand labour or by sluicing out by means of water under pressure.

During the last few years large quantities of unleached slimes from previous working have been treated successfully at a very low cost by agitation in large tanks with cyanide solution for the extraction of the gold. After agitation the slimes are allowed to settle and the gold-bearing cyanide solution is drawn off, or else the slimes are pumped into large filter presses which separate the solution, leaving the solid matter in the form of cakes.

Fine grinding of the whole of the ore to pass through a 150 or 200 mesh sieve (40,000 holes to the square inch) in tube-mills, after partially pulverising in the stamp battery, followed by agitation and filter-pressing in pressure- or vacuum-filters, of which there are a number of successful forms on the market, has become the practice recently adopted on many of the great mines. In some cases of refractory ores, roasting is found necessary before cyanide treatment.

For the precipitation of the gold, the cyanide solutions from

the tanks are passed through wooden troughs divided by baffle boards into a series of compartments containing freshly-turned zinc shavings which effect the precipitation of the gold:

$$2KAu(CN)_2 + Zn = 2KCN,Zn(CN)_2 + 2Au.$$

A zinc-lead couple is found to be more effective for the precipitation of gold from solutions containing copper and from very weak cyanide solutions, and for this purpose the zinc shavings are pickled in a 10 per cent. solution of lead acetate until covered with a black coating. The gold-bearing cyanide solutions are sometimes agitated with zinc dust and the residues filter-pressed.

The precipitated gold, together with any silver in the ore, is separated as far as possible from the zinc, and then may be treated, after roasting, by smelting with suitable fluxes, such as sand, borax, and sodium bicarbonate. Plumbago crucibles are generally used for these charges, and the resulting bullion may be 800 fine, *i.e.* contain 800 parts of gold per 1,000.

Another method for treating the precipitated gold is to dissolve out the zinc with dilute sulphuric acid and then to wash and dry the insoluble residue and smelt down with suitable fluxes; this generally gives a bullion from 850 to 900 fine.

A more recent process, which is said to effect a saving in cost and to be attended by less loss of gold, is Tavener's lead-smelting method, in which the precipitate is melted with litharge, assay slags and sawdust in a reverberatory furnace for the production of a lead bullion containing about 10 per cent. of gold which is afterwards cupelled.

Aluminium powder and charcoal are also used as precipitants for gold from cyanide solutions.

In the Siemens-Halske process, the gold is deposited from solution by means of an electric current. The anodes are made of iron and the cathodes on which gold is deposited are of lead. These sheets of lead are afterwards melted down and cupelled for the extraction of the gold.

235 *Refining and Parting of Gold.*—The gold bullion obtained by the above processes varies very considerably in composition according to its origin and the treatment to which it has been subjected. It usually contains a considerable amount of silver along with copper, iron, lead, antimony, and other base metals. When the amount of these is at all considerable it is usual to submit the bullion to a preliminary refining process before removing the silver. This is done by melting the metal in a crucible

with borax and nitre, the base metals being thus oxidised and removed by skimming.

The parting of silver from gold was formerly carried out by means of nitric acid, this process having been first employed, it would appear, at Venice in the fifteenth century, for extracting the gold from Spanish silver. It remained in general use up to the beginning of last century, and is still frequently employed. It depends on the fact that nitric acid removes practically all the silver from an alloy of gold and silver, provided that a sufficient excess of silver be present. It was at first thought that the limiting proportion was 1 of gold to 3 of silver, and hence the process was termed *inquartation*, but it has been found that the method succeeds even when as much as 1 of gold is present to 2 of silver; the proportion most generally used is 1 of gold to $2\frac{1}{3}$ or $2\frac{1}{2}$ of silver.

For this process the bullion is first made up to the "parting" proportion, and then granulated. The granules are boiled for 5 or 6 hours in nitric acid of specific gravity 1·2, the gold is then allowed to settle and the supernatant liquor siphoned off. A second boiling for 2 to 3 hours, and a third for 1 or 2 hours follow, with nitric acid of specific gravity 1·4. The gold residue is then well washed with water, pressed and melted down; whilst the silver in solution is precipitated by means of common salt and reduced to metallic silver by means of zinc. It has now been shown, by careful investigation with a number of reagents, that in both the silver-gold and copper-gold series of alloys there are definite reaction-limits at metal concentrations expressed by simple multiples of $\frac{1}{8}$th. These limits are perfectly sharp for the well-annealed alloys, but not for cast metal or that which has been altered by cold work: for example, in the well-annealed silver-gold series the reaction-limit for solutions of gold chloride, chromic acid, permanganic acid and nitric acid lies quite sharply at the composition 50 molecular per cent. There are also relative resistance limits: if the gold content is less than $\frac{3}{8}$ molecular, boiling nitric acid will remove the whole of the silver or copper from the alloy; between $\frac{3}{8}$ and $\frac{4}{8}$ molecular of gold, only part of the baser metal is extracted; whilst above $\frac{4}{8}$ gold the alloy is completely resistant. These phenomena may be explained by geometrical considerations relating to the space lattice of the mixed crystals and are, therefore, of great theoretical importance.[1]

[1] Tammann, *Zeitsch. anorg. Chem.*, 1919, **107**, 1; see also for a condensed account, *Chem. Soc. Ann. Report*, 1919, **16**, 213.

Parting by Sulphuric Acid.—In 1753 Scheele discovered that sulphuric acid could be employed for this purpose. In a memoir on the subject, read before the Stockholm Academy, he says: "Sulphuric acid also dissolves silver when no water is amongst it, but gold is not in the least degree altered, so that silver and gold can be thus completely separated from one another; but such an oil of vitriol is much dearer than nitric acid, and for this reason it is not advisable to use it for this purpose, as there are other acids which cost less." Hence it was only when sulphuric acid became cheaper that the process of separation by its means could be carried out, and this was done by Darcet in 1802.

In order to separate the two metals by this method the alloy must not contain more than 33 per cent. of gold. If it be richer than this, it must be first melted with the necessary quantity of silver. The granulated alloy is heated in cast-iron boilers, together with two and a half times its weight of concentrated sulphuric acid of specific gravity 1·85. Each vessel is covered with a dome of lead, and the sulphur dioxide which is evolved during the solution of the silver is either allowed to escape into the air or utilised in some way. As soon as no further evolution of this gas takes place, sulphuric acid, of specific gravity 1·69, is added for the purpose of dissolving the copper sulphate. The clear liquid is then allowed to flow into leaden pans containing the mother-liquors of copper sulphate formed in the next operation, and the whole is heated by steam in order to keep the slightly soluble silver sulphate in solution. Here a further quantity of gold is deposited, the clear liquid is again drawn off, and the silver precipitated by means of metallic copper. The finely-divided gold is again treated with sulphuric acid in order to render it completely free from silver, and after having been well boiled, it is washed and fused in a plumbago crucible with sodium bicarbonate.

In a modified form of the process the sulphuric acid solution of the silver is diluted with steam, and the silver sulphate allowed to crystallise out. The crystals are then removed and reduced by heating in a furnace with charcoal.

Parting by Chlorine.—When gold does not contain more than 10 per cent. of silver, it may be purified by Miller's process with chlorine gas, first introduced by him in the Sydney Mint. This process consists in melting the gold in a clay crucible which has been glazed inside with borax, and passing chlorine gas through the molten metal by means of a clay pipe. The chlorine at once

combines with the silver to form silver chloride, which rises to the surface of the molten metal, whilst the chlorides of zinc, bismuth, antimony, and arsenic, should these metals be present, are volatilised, and the pure gold remains beneath. A layer of melted borax is placed on the top of the fused mass in order to prevent the silver chloride which is formed from being volatilised. The fineness of the gold thus prepared varies from 991 to 997 in 1,000 parts, whilst the metal obtained by other refining processes frequently contains a larger quantity of silver. This method of treatment may also be adopted with advantage for refining and toughening gold which is rendered brittle by the presence of small quantities of antimony, bismuth, tin, arsenic, etc.[1]

Electrolytic Refining and Parting of Gold.—For this purpose the Wohlwill process is used, which in its latest form[2] uses a combination of a direct and an alternating current, as by this means it is found that the difficulties presented when the amount of silver in the bullion exceeds 50 parts per 1,000 are lessened. The electrolyte contains from 2 to 5 per cent. of hydrochloric acid, and from 2·5 to 6 per cent. of gold chloride.

Refining Gold Bullion with Oxygen Gas.—Rose[3] has shown that impure bullion and zinc precipitates from the cyanide process may be refined and toughened by blowing a stream of oxygen or air through the molten metal contained in a crucible and covered with a slag, made by the addition of borax and silica to the crucible charge. The metals are oxidised in succession, each in turn partially protecting those which are less easily oxidised than itself.

236 *Preparation of Pure Gold.*—In order to prepare a gold containing less than one part of impurity in 10,000, gold cornets are dissolved in aqua regia, the liquid evaporated down, and traces of platinum removed by the addition of potassium chloride and alcohol. The clear solution of gold chloride is then allowed to stand, decanted from any precipitated chloride of silver, and reduced by warming with oxalic acid. The precipitate is repeatedly washed with hydrochloric acid, water, and ammonia, and is then fused in a clay crucible with potassium bisulphate and borax.

237 *Properties.*—Gold is distinguished from all the other metallic elements by its bright yellow colour. It crystallises in

[1] Roberts-Austen, *First Annual Report of the Mint*, 1870, 95.
[2] *Met. and Chem. Eng.*, 1910, **8**, 82.
[3] *Trans. Inst. Min. and Met.*, 1904–1905, 377.

the regular system, and in the native state is often found in distinct though small crystals. Some Australian gold worth about £1,100 consisted of grains from the size of a large pea to that of small grains of sand, all of which were more or less perfect dodecahedra.[1] Native gold has also been found crystallised in a very great variety of other forms of the regular system.[2] These small crystals are frequently connected together, so as to form hair-like filaments termed *moss-gold*. Liversidge[3] has obtained this form of gold artificially. He noticed the occurrence of crystallised gold in certain specimens of Australian auriferous pyrites, and he therefore roasted this mineral in a muffle, for the purpose of removing arsenic and sulphur, but at a temperature insufficient to bring about the fusion either of the mineral or of the gold. On removing the sample from the muffle, small cauliflower-like excrescences of metallic gold were observed on the surface of the mass, these excrescences being composed of fine filaments of the metal often wound round in spiral coils. This form of gold has also been obtained by Moissan[4] by distillation of gold in the electric furnace.

Gold precipitated from a concentrated solution by ferrous sulphate forms very small cubes, and that obtained by reduction with oxalic acid consists of minute octahedra, which are usually much distorted, whilst both forms are obtained when solutions of auric chloride or bromide are reduced with formaldehyde in the presence of nitric or hydrochloric acid.[5]

When an amalgam containing 5 per cent. of gold is heated for eight days to 80°, and then treated with hot nitric acid, an aggregate of crystals, some of which are 6 mm. in length, may be obtained. These, after heating to get rid of the mercury, have a bright lustrous appearance.

Gold is softer than silver, and is the most ductile of metals. This was known to Pliny, who says: "Superque omnia netur, ac texitur lanæ modo."[6]

Although the relation which the Roman weights and measures bear to those in use in the present day is still somewhat uncertain, the following statement may be of interest as showing the progress of the art of gold-beating. In the first place we read in Pliny, "nec aliud laxius dilatatur, aut numerosius

[1] Dana, *System of Mineralogy*, 5th ed., p. 8; see also Liversidge, *Journ. Chem. Soc.*, 1897, **71**, 1125.

[2] von Rath, *Zeit. Kryst. Min.*, 1877, **1**, 1.

[3] *Proc. Roy. Soc. N.S.W.*, 1876, 125. [4] *Compt. rend.*, 1905, **14**, 977.

[5] Awerkieff, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 828. [6] *N.H.*, **33**, 19.

dividitur, utpote cujus unciæ in septingenas et quinquagenas, pluresque bratteas, quat ernum utroque digitorum spargantur."[1] Then in 1621 Mersenne mentions that the Paris gold-beaters were in the habit of obtaining 1,600 leaves from one ounce of gold, which would cover 105 square feet. In 1680 Halley states that in his time a grain of gold could be drawn into a wire 98 ells in length, whilst Réaumur mentions in 1711 that one ounce of gold can be hammered out so as to cover 146½ square feet, and according to newer statements one grain may be made to cover 56·75 square inches, or one ounce to cover 189 square feet, whilst 280,000 leaves have to be placed one upon another to occupy the thickness of one inch. One grain of gold also serves to gild two miles of fine silver wire, whilst the thickness of such deposits of gold as, for example, that on gold lace is about 0·000002 mm. Gold is extremely ductile, and gold wire can be drawn so fine that 3,240 metres of it weigh only one gram. Gold leaf has usually a thickness of about 0·0001 mm., and allows green light to pass through it.

The relations of finely-divided gold to light have been carefully examined by Faraday.[2] By spreading a leaf of gold on a glass plate and then pouring on to it a solution of potassium cyanide, Faraday succeeded in obtaining films of gold of extreme tenuity. The green colour which ordinary gold leaf exhibits by transmitted light passes into a ruby-red when the highly attenuated film is heated to 316°. At 550°, gold leaf becomes apparently transparent,[3] due to the aggregation of the gold leaving spaces through which light passes, the metal itself becoming opaque. The red colour of ruby glass is due to the presence of metallic gold in an extreme state of division.[4] This is also the case with the above-mentioned film, the original green tint of which can be brought back by burnishing its surface.

The specific gravity of crystalline gold obtained by reduction of auric chloride[5] is 19·431 at 20°, whilst gold distilled *in vacuo* was found to have the specific gravity 18·884 at 20°/4°, which increased to 19·2685 when the metal was submitted to a pressure of 10,000 atmospheres.[6] It melts at 1064°, expanding considerably in the act of fusion and forming a bluish-green liquid. Gold loses

[1] *N.H.*, **33**, 19. An ounce of gold can be hammered into 750 leaves, each of which is 4 digits (about 3 inches) square.

[2] *Phil. Trans.*, 1857, **147**, 145.

[3] Turner, *Roy. Soc. Proc.*, 1908, [*A*], **81**, 301.

[4] Zsigmondy, "Zur Erkenntnis der Kolloide," Jena, 1905.

[5] Awerkieff, *Zeit. anorg. Chem.*, 1903, **35**, 329.

[6] Kahlbaum, Roth, and Siedler, *Zeit. anorg. Chem.*, 1902, **29**, 177.

weight perceptibly on heating even at temperatures only 100° above its melting point;[1] it may be distilled in the electric furnace, and condenses in yellow leaflets, in moss-like filaments, or in yellow cubes.[2]

Gold has the specific heat 0·0324; it is exceeded in conductivity for heat and electricity only by silver and copper, its electrical conductivity being 76·7 per cent. and its thermal conductivity 53·2 per cent. of that of silver.

Gold is not attacked at any temperature either by oxygen or by water, and it also remains unacted upon when fused with potassium chlorate. Alkalis and the nitrates, however, attack it. Gold does not dissolve in any single acid, with the exception of selenic (Mitscherlich), but it dissolves readily in aqua regia, or in any acid liquid in which chlorine, bromine, or iodine[3] is evolved, and in solutions of the easily decomposable perhalogen compounds of the metals, such as $FeBr_3$, $CoCl_3$, etc.

238 *Colloidal Gold.*—Solutions of colloidal gold, which are either red, purple, blue, or green, have been prepared in a number of ways. Red and blue solutions of colloidal gold were prepared by Faraday by reducing gold chloride by means of phosphorus. Bredig[4] obtained reddish-purple and blue solutions by passing an electric arc under water between gold wires (see p. 82); these solutions decomposed hydrogen peroxide, whilst freezing or the addition of electrolytes caused the separation of metallic gold. When aluminium foil is placed in an aqueous solution of auric chloride, colloidal gold is formed after some hours.[5] If aluminium chloride be added to the auric chloride solution, however, the gold is simply replaced by the aluminium, no colloidal gold being formed.[6] Colloidal gold has also been prepared by warming solutions of auric chloride with sodium lysalbate or protalbate,[7] formaldehyde, hydrazine hydrate, sugar solution, and other reducing agents,[8] and also by the action of

[1] Rose, *Journ. Chem. Soc.*, 1893, **63**, 714.

[2] Moissan, *Compt. rend.*, 1905, **141**, 977.

[3] Nickles, *Ann. Chim. Phys.*, 1867, [4], **10**, 318.

[4] *Zeit. angew. Chem.*, 1898, 951.

[5] Carnot, *Compt. rend.*, 1883, **97**, 105, 169.

[6] Dauve, *J. Pharm. Chim.*, 1909, [6], **29**, 241.

[7] Paal, *Ber.*, 1902, **35**, 2236.

[8] Zsigmondy, *Annalen*, 1898, **301**, 29; Kuspert, *Ber.*, 1902, **35**, 4070; Gutbier, *Zeit. anorg. Chem.*, 1902, **31**, 448; 1902, **32**, 347; 1904, **39**, 112; Henrich, *Ber.*, 1903, **36**, 609; Garbowski, *ibid.*, 1903, **36**, 1215; Hanriot, *Compt. rend.*, 1904, **138**, 1044; Vanino and Hartl, *Ber.*, 1905, **38**, 463; 1906, **39**, 1696; Donau, *Monatsh.*, 1905, **26**, 525; Vanino, *Zeit. Chem. Ind. Kolloide*, 1907, **2**, 51. See also *An Introduction to the Physics and Chemistry of Colloids*, Emil Hatschek. (J. and A. Churchill).

the mould *aspergillus oryzæ* on very dilute solutions of this salt.[1]

The different colours of colloidal gold solutions are due to differences in the forms of particles.[2] Distinct forms exist for the red and blue solutions, the violet is formed by a mixture of these, whilst the green is due to the condensation of the particles which give rise to the red and blue. By their action upon *X*-rays it has been shown that the particles of colloidal gold are actually crystalline.[3]

Hatschek and Simon have studied the reduction of gold in gels with a view of explaining the nature of gold in various ore deposits.[4]

When alcohol is added to the red solution obtained by the action of formaldehyde on auric chloride, the gold is precipitated in a form soluble in water (Zsigmondy).

239 *Purple of Cassius.*—This body, which is used in the preparation of ruby glass, was discovered by Andreas Cassius, who, however, did not publish anything on the subject, though his son of the same name published a pamphlet in 1685 entitled *De extremo illo et perfectissimo naturæ opificio ac principe terrenorum sidere, Auro, et admiranda ejus natura—cogitata, experimentis illustrata.* In the previous year, however, a Hessian mining official, Orschal, published a paper, *Sol Sine Vesta: or, Thirty Experiments to Draw out its Purple from Gold.* He declared that he had learned the process from Cassius, and that it consisted in precipitating gold with tin. After that time many investigations were made on this pigment without any satisfactory explanation of its chemical nature being arrived at. A variety of recipes was given for its preparation, in all of which gold chloride was precipitated by a mixture of stannous and stannic chlorides. This precipitate is, according to the mode of preparation, either of a dark purple-red or of a reddish-brown colour, but yields a brown powder on drying. The process by which the finest purple is obtained is, according to Fuchs, to add stannous chloride to a solution of ferric chloride until the yellow colour is changed to a pale green, and then to precipitate the gold solution with this mixture. The precipitate contains tin oxide in varying quantities, and some chemists have supposed that

[1] Vanino and Hartl, *Ber.*, 1904, **37**, 3620.
[2] Steubing, *Ann. Physik.*, 1908, [4], **26**, 329.
[3] Scherrer, *Nachr. Ges. Wiss. Göttingen*, 1918, **96**.
[4] *Trans. Inst. Min. and Met.*, 1912, **21**, 451.

the compound is a gold stannate, but this view is contradicted by the fact that when purple of Cassius is dried and then triturated, the powder assumes a metallic lustre, and on heating does not evolve oxygen. On the other hand, it is found that the freshly precipitated and moist pigment is soluble in ammonia forming a purple-coloured liquid which deposits gold when it is exposed to light or is heated;[1] the excess of ammonia can also be removed by dialysis leaving a colloidal solution of gold and stannic oxide.[2] Mercury does not extract gold from purple of Cassius. A similar purple colour is obtained by adding excess of mercurous chloride or a mixture of mercurous chloride with barium sulphate in suspension to a solution of auric chloride,[3] whilst Moissan[4] has obtained it by the distillation in air of an alloy of gold and tin, when the tin burns to tin oxide and purple of Cassius is deposited in the cool parts of the tube. This chemist has also obtained similar purple substances by distilling gold with alumina, magnesia, zirconia, silica, lime, or other oxides, and concludes that purple of Cassius is a lake of tin oxide coloured by very finely divided gold. The literature respecting the purple of Cassius up to 1866 has been collected by J. C. Fischer.[5]

240 *Gilding.*—The art of gilding is mentioned by Moses, and Pliny states that objects of wood and marble are gilt by means of gold leaf, whilst metallic surfaces are gilt by help of quicksilver. Gold leaf is obtained from gold foil by hammering pieces, each having an area of a square inch and weighing six grains, first between sheets of vellum or tough paper, and afterwards between leaves of gold-beater's skin—a material prepared from the cæcum of the ox. The small cuttings and waste leaf are employed for the preparation of the shell gold used by painters.

A variety of methods is employed for gilding metals. In gilding by immersion the well-cleaned objects are dipped into a boiling solution of gold chloride and potassium bicarbonate; whilst in wash-gilding a gold amalgam is rubbed on the surface, the mercury afterwards driven off by heating and the surface either burnished, or deadened by being heated with a fused mixture

[1] See also Muller, *J. pr. Chem.*, 1884, [2], **30**, 252.

[2] Schneider, *Zeit. anorg. Chem.*, 1893, **5**, 80.

[3] Antony and Lucchesi, *Gazz.*, 1896, **26**, ii., 195.

[4] *Compt. rend.*, 1905, **141**, 977. See also Debray, *ibid*, 1872, **75**, 1025, and Zsigmondy, *Annalen*, 1898, **301**, 361.

[5] *Dingl. Polyt. Journ.*, 1866, **182**, 39.

of common salt, saltpetre, and lime, when a small quantity of chlorine is liberated which etches the gold. These older methods have now, however, been almost completely supplanted by the *electro-deposition of gold.* For this purpose a solution of gold cyanide in potassium cyanide is employed, a gold plate being used as the positive electrode. The colour of the deposited gold can be modified by adding to the gold solution salts of silver or copper, or both, when alloys are deposited.

241 *Alloys of gold.*—Pure gold is very soft, and is soon worn away by use. Hence, for the purpose of coinage, and for the use of the goldsmith, it is alloyed with copper or silver, or with both together, the resulting alloys being much harder than pure gold. Copper imparts to the gold a red colour, and lowers its fusing-point. This alloy was formerly called red-carat gold, because the fineness of a gold alloy used to be universally expressed in carats, 24-carat gold being pure gold. In England at the present time five legal standards exist for gold ware; 22-carat or standard gold, 18, 15, 12, and 9-carat gold, the meaning of this being that 24 parts by weight of the alloy contain 22, 18, 15, 12, and 9 parts of gold respectively.

In the case of the coinage, however, the fineness of gold is generally expressed in parts per 1,000. Thus, for instance, English standard gold, being 22-carat gold, has a fineness of 916·67. In the German, American, and Italian coinage standard gold is of 21·6 carats, or has a fineness of 900. Red-carat ornaments are frequently covered with a thin coating of pure gold by heating them and then dipping them for a short time in dilute nitric acid.

The alloys of gold and silver are called white alloys, and have a greenish-yellow colour if they do not contain too small a quantity of silver, whilst when the latter metal is present in larger amount the alloy assumes a yellowish-white shade. A gold-silver alloy of varying composition occurs naturally as electrum, often found in crystals belonging to the regular system and containing from 15 to 35 per cent. of silver.

Trinket gold contains both copper and silver. It is hard, and, according to the proportion of its materials, possesses either a yellowish-red or a whitish colour.

Various other alloys have been examined and described. Of these the aluminium gold-alloys are distinguished by the richness and variety of their colours.[1]

[1] Roberts-Austen, *Proc. Roy. Soc.*, 1892, **50**, 367.

Gold combines with arsenic, antimony, and bismuth, when heated with these elements. The addition of one part of the last named metal to 1,920 parts of gold is sufficient to render the gold brittle.

Gold-amalgam.—Gold readily combines with mercury, the mixture becoming solid when 15 per cent. of gold is present. Crystalline amalgams of varying composition can be obtained artificially, whilst others occur naturally in California, Columbia, and Victoria. The mercury may be almost entirely removed from these amalgams by distillation at a red-heat, but the gold retains 0·1 per cent. practically up to its melting point.

COMPOUNDS OF GOLD.

242 Gold forms two chief series of compounds, the auric compounds in which it is trivalent, and the aurous compounds in which it is monovalent. The best known salts are those of the halogen acids, and hydrocyanic acid. These readily form double salts, as do aurous sulphite and thiosulphate. Auric oxide has well-marked acidic properties, as have also the various sulphides of the metal. The compounds with the halogens, oxygen and sulphur are all decomposed into their elements by heat, whilst reducing agents very readily precipitate the metal from the solutions of its salts.

Gold and Oxygen.

243 Gold does not combine directly with oxygen, and the two compounds, aurous oxide, Au_2O, and auric oxide, Au_2O_3, are obtained from the corresponding halogen compounds. A third compound, auro-auric oxide, $(AuO)_n$, is formed by the partial decomposition of auric hydroxide at 160°. The substance formerly known as purple oxide of gold appears to be nothing but finely-divided gold, and the oxides Au_2O_4 [1] and Au_2O_5 appear not to exist. All the oxides decompose into gold and oxygen when they are heated. Auric oxide acts towards strong bases as an acid-forming oxide, whilst it also forms salts with acids.

Gold Monoxide, Aurous Oxide, Au_2O.—The *hydroxide,* AuOH, is formed when the corresponding chloride is treated with cold dilute caustic potash (Berzelius), and when a solution of the trichloride is boiled with the potassium salt of acetic or

[1] Prat, *Compt. rend.*, 1870, **70**, 842.

another organic acid. It may be prepared pure by reducing potassium auribromide, $KAuBr_4$, with sulphurous acid, and then warming with dilute potash. It is a powder which when moist has a dark-violet colour, and becomes greyish-violet when dry. When freshly prepared it forms with cold water an indigo blue liquid [1] from which the oxide is removed when barium sulphate is precipitated in it.[2] It loses water at 200°, and is decomposed at 250° into gold and oxygen. When treated with hydrochloric acid, it yields gold and the trichloride, slowly in the cold, more rapidly on boiling. Sulphuric acid and nitric acid do not act on it, but it is easily dissolved by aqua regia.

Gold Trioxide, Auric Oxide, Au_2O_3.—The substance termed calx of gold by the early chemists was nothing more than the finely divided metal. Bergman was the first to state that the precipitate produced by alkalis in the gold solution was dephlogisticated gold; but the oxide was examined more carefully in 1806 by Proust, and in 1811 by Oberkampf. Gold trioxide is a brownish powder, obtained by carefully heating the hydroxide. If this be more strongly heated, it gives off oxygen, and is converted into a brown powder of metallic gold.

Gold Trihydroxide, Auric Hydroxide, $Au(OH)_3$, is best obtained by heating a solution of gold trichloride with an excess of magnesia, and well washing the precipitate with dilute nitric acid (Pelletier). The gold solution may also be treated with caustic potash until the precipitate which is formed is redissolved, and then the dark-brown solution boiled until its colour becomes light yellow, a slight excess of sulphuric acid added, and the precipitate washed. The hydroxide thus prepared always contains a little potash, and for this reason it is dissolved in concentrated nitric acid, again precipitated by water, and dried in a vacuum. According to Thomsen a better method is to precipitate the brown solution by Glauber's salt, when it is obtained in a form resembling precipitated ferric hydroxide. Gold trihydroxide when kept over phosphorus pentoxide is converted into a chestnut-brown powder of *auryl hydroxide,* AuO(OH), which at 140—150° yields auric oxide (Krüss).

When the hydroxide is warmed with alcoholic potash reduction occurs, and the metal is produced in the form of fine glistening scales, which are employed in miniature painting. It is a weak base, which dissolves slightly in concentrated sulphuric acid, and more readily in nitric acid, from which

[1] Krüss, *Ber.*, 1886, **19**, 2541. [2] Vanino, *Ber.*, 1905, **38**, 462.

solutions it is again precipitated by the addition of water. It forms the corresponding halogen salts with hydrochloric and hydrobromic acids. Gold trioxide is also an acid forming oxide, and its salts are termed aurates.

Potassium Aurate, $KAuO_2,3H_2O$, is obtained in the form of small yellow needles by evaporating in a vacuum a solution of auric hydroxide in caustic potash;[1] these are easily soluble in water and have a strong alkaline reaction. It is very unstable, and its solution is used for gilding copper and other metals.

The other aurates are less completely investigated. The solution of the potassium salt yields precipitates with many metallic salts.[2]

Auroauric Oxide, $(AuO)_n$, is formed when auric hydroxide is heated at 160°. It is a dark yellowish-brown hygroscopic powder which loses oxygen at 173°.[3]

Gold and the Halogens.

244 Gold unites with chlorine and bromine directly to form the auric compounds, $AuCl_3$, $AuBr_3$, which are easily soluble in water. These readily combine with the halogen acids and their salts with monovalent metals or radicles to form complex substances such as aurichloric acid, $HAuCl_4$, and the aurichlorides. The salts of this acid with the organic bases, such as methylamine aurichloride, $NH_3(CH_3)AuCl_4$, are often used for the characterisation of the latter. Both the halogen compounds themselves and their compounds with the corresponding acids decompose when heated, metallic gold being finally left.

The aurous compounds are unstable and readily decompose when heated. They are insoluble in water, like the corresponding silver and cuprous compounds.

The substances described as auroauric chloride and bromide,[4] Au_2Cl_4 and Au_2Br_4, have been proved to be nothing but mixtures of metallic gold with the corresponding auric salt.

Aurous Chloride, AuCl, is best obtained by carefully heating the trichloride to about 175°. It is a yellowish powder of specific gravity 7·4,[5] which decomposes gradually into gold and chlorine at 185°, more rapidly at a higher temperature.

[1] See also Meyer, *Compt. rend.*, 1907, **145**, 805.
[2] Fremy, *Ann. Chim. Phys.*, 1851, [3], **31**, 480.
[3] Kruss, *Ber.*, 1886, **19**, 2541.
[4] Kruss and Schmidt, *Ber.*, 1887, **20**, 2634; *J. pr. Chem.*, 1888, [2], **38**, 77.
[5] Rose, *Journ. Chem. Soc.*, 1895, **67**, 881, 905; see also Campbell, *Trans. Far. Soc.*, 1907, **3**, 103.

It is insoluble in water but is decomposed by it slowly in the cold, and more rapidly on heating, with formation of metallic gold and auric chloride. It dissolves in a solution of potassium bromide with formation of metallic gold and potassium aurichloride and auribromide.[1]

Liquid ammonia acts on aurous chloride at — 28° to form the compound $AuCl,12NH_3$, which loses ammonia on warming, yielding $AuCl,3NH_3$, and this above 180° is decomposed with formation of ammonium chloride and gold.[2]

Potassium Aurochloride, $KAuCl_2$, is formed when potassium aurichloride, $KAuCl_4$, is heated. It forms a yellow mass, which is decomposed by water into gold, potassium chloride, and auric chloride.

Auric Chloride, or *Gold Trichloride*, $AuCl_3$.—The Latin Geber and all the later chemists were acquainted with the fact that gold dissolves in aqua regia. When this solution is evaporated to dryness a portion of the chloride is decomposed with formation of aurous chloride (Berzelius). In order to prepare the pure anhydrous chloride the best process is that proposed by Thomsen. It consists in acting upon gold powder with chlorine and treating the mass with a small quantity of water. When gently heated, any aurous chloride decomposes as before described, the metallic gold is filtered off, the solution evaporated gently, and then heated to 150°, when anhydrous auric chloride remains as a brown crystalline mass which is soluble in ether. The anhydrous chloride is also formed by heating gold leaf in chlorine to 300°, or by heating gold with liquid chlorine in a sealed tube at 100°.[1] Gold chloride is also formed when gold is treated with fuming hydrochloric acid in the presence of a trace of manganese chloride and the mixture is exposed to light.[3] It melts at 288° when heated in a sealed tube, and has the sp. gr. 4·3. When the brownish-red aqueous solution is evaporated until a crystalline film is formed on the surface, large dark orange-red crystals of $AuCl_3,2H_2O$ are deposited. These deliquesce in moist air, whilst they effloresce in dry air.

The chloride dissociates very slowly below 100°, more rapidly at higher temperatures, with formation of aurous chloride, chlorine, and gold. The dissociation pressure of the chlorine is about 1 atmosphere at 251°, and 4 atmospheres at 330°. In

[1] Lengfeld, *Amer. Chem. J.*, 1901, **26**, 324.
[2] Meyer, *Compt. rend.*, 1906, **143**, 280.
[3] Berthelot, *Compt. rend.*, 1904, **138**, 1297.

spite of this dissociation the chloride can be sublimed in a stream of chlorine at all temperatures up to 1,100°, the most rapid volatilisation taking place at the melting point.[1]

Very dilute aqueous solutions of auric chloride are decomposed on heating for some time, or on continued exposure to direct sunlight, metallic gold being precipitated and hydrogen peroxide formed in the solution.[2]

Gold chloride in solution is decomposed by charcoal, and Avery [3] has quantitatively determined the hydrogen chloride and carbon dioxide produced by the reaction, and considers that the equation proposed by König [4] is substantiated, thus:

$$4AuCl_3 + 6H_2O + 3C = 4Au + 12HCl + 3CO_2.$$

Gases occluded by charcoal, such as hydrogen and carbon monoxide, will, however, also reduce gold chloride.

According to Brusson,[5] charcoal adsorbs gold either when shaken with a solution of gold chloride, or when a solution is filtered through charcoal. In all cases, the gold was completely withdrawn from solution, chlorine being left behind.

Gold chloride is largely used in photography for toning silver prints, a process which consists in the partial replacement of the silver by metallic gold.

Aurichloric Acid or *Chloro-auric Acid*, $HAuCl_4$.—When hydrochloric acid is added to a neutral solution of auric chloride it becomes yellow, and the liquid then contains the above compound in solution. The same substance is obtained when gold is dissolved in aqua regia containing an excess of hydrochloric acid. When either of the above solutions is evaporated and allowed to stand over quick lime, long yellow needles of $HAuCl_4,3H_2O$ are deposited,[6] which deliquesce on exposure. The solution has a bitter taste, is poisonous, and colours the skin, nails, ivory, etc., a purple-red tint when exposed to light. This fact was mentioned in 1663 by Boyle as being one then not generally known.

Gold is precipitated quantitatively in solutions containing

[1] Debray, *Compt. rend.*, 1869, **69**, 985; Kruss, *Annalen*, 1887, **238**, 249; *Ber.*, 1887, **20**, 2634; Rose, *Journ. Chem. Soc.*, 1895, **67**, 881; Meyer, *Compt. rend.*, 1901, **133**, 815.

[2] Sonstadt, *Chem. News*, 1898, **77**, 74; *Proc. Chem. Soc.*, 1898, 179.

[3] *J. Soc. Chem. Ind.*, 1908, **27**, 255. [4] *Chem. News*, 1882, **45**, 215.

[5] *Zeit. Chem. Ind. Kolloide*, 1909, **5**, 137.

[6] Weber, *Jahresber.*, 1867, 314; Schottländer, *Annalen*, 1883, **217**, 312; Schmidt, *Chem. Centr.*, 1906, ii., 855.

aurichloric acid by formaldehyde after neutralising with sodium hydrate.[1]

On adding silver nitrate to a solution of aurichloric acid, a brown precipitate is obtained thus :[2]

$$HAuCl_4 + 4AgNO_3 + 3H_2O = Au(OH)_3,AgCl + 4HNO_3.$$

By the action of ammonia this is converted into fulminating gold, $Au(OH)_2{\cdot}NH_2$.

Potassium Aurichloride, $KAuCl_4$.—When a strongly acid solution of auric chloride, to which the calculated quantity of potassium chloride has been added, is allowed to evaporate at a gentle heat, light-yellow monoclinic needles having the composition $2KAuCl_4,H_2O$ are deposited. On the other hand, when the neutral or slightly acid solution is employed, large transparent rhombic tablets of $KAuCl_4,2H_2O$ are formed, which easily effloresce on exposure. When heated these melt with evolution of chlorine, forming potassium aurochloride, $KAuCl_2$.

Sodium Aurichloride, $NaAuCl_4,2H_2O$, is obtained by dissolving common salt in a solution of auric chloride and concentrating the solution, when it is deposited in yellowish-red rhombic tablets or prisms, which do not alter on exposure.

Ammonium Aurichloride, NH_4AuCl_4, appears to have been prepared by the alchemists, who employed aqua regia containing sal-ammoniac for dissolving gold, and on cooling the solution obtained crystals which they considered to be a true gold vitriol. From the neutral solution large light-yellow rhombic tablets of the composition $2NH_4AuCl_4,5H_2O$ separate. These are tolerably permanent. From an acid solution, on the other hand, the salt $4NH_4AuCl_4,5H_2O$, crystallises in monoclinic plates. Both salts become anhydrous at 100°.

The chlorides of the calcium and magnesium groups, as well as those of manganese, nickel, cobalt, and thallium, also form crystalline aurichlorides.

Aurous Bromide, AuBr, is formed as a greenish-yellow micaceous powder when auribromic acid, $HAuBr_4$, is heated at 115°, but is decomposed at a higher temperature. It is insoluble in water, and hydrobromic acid decomposes it into gold and the compound from which it has been obtained. It dissolves in potassium cyanide solution without decomposition, and in ammonia with partial decomposition.[3]

[1] Vanino and Hartl, *Zeit. Chem. Ind. Kolloide*, 1907, **1**, 272.
[2] Jacobsen, *Compt. rend.*, 1908, **146**, 1213.
[3] Lengfeld, *Amer. Chem. J.*, 1901, **26**, 324.

Aurous bromide when acted on by dry ammonia gas at 18° yields the white compound $AuBr,2NH_3$, which is decomposed by heat into its elements, and by water with formation of ammonium bromide and gold.[1]

Auric Bromide, or *Gold Tribromide*, $AuBr_3$.—Finely-divided gold dissolves slowly in an aqueous solution of bromine (Balard). In order to obtain the anhydrous compound, bromine is allowed to act upon gold powder, and the tribromide is extracted from the product by ether. When the solution is evaporated at a low temperature, the tribromide remains behind as a black crystalline crust, which dissolves slowly in water. The concentrated solution is viscid and almost black (Thomsen).

When heated, auric bromide dissociates, forming a green mass of aurous bromide, and at higher temperatures this latter dissociates into its elements.[2]

Auribromic Acid, $HAuBr_4,5H_2O$, is formed when bromine is allowed to act upon gold powder, and as soon as the reaction is over, a quantity of hydrobromic acid, having a specific gravity of 1·38, equivalent to the quantity of gold present, is added, and then more bromine until the gold is completely dissolved. It crystallises in dark cinnabar-red flat needles, and melts at 77°.

Potassium Auribromide, $KAuBr_4,2H_2O$, is prepared by adding bromide to powdered gold in presence of the requisite amount of potassium bromide. It is also formed together with metallic gold when aurous bromide is dissolved in potassium bromide (Lengfeld). It forms reddish-purple monoclinic crystals. Similar compounds of the other soluble bromides are also known.[3]

Aurous Iodide, AuI, is formed when hydriodic acid acts upon gold oxide:

$$Au_2O_3 + 6HI = 2AuI + 3H_2O + 2I_2.$$

It is also formed when dry iodine is heated with metallic gold[4] between 50° and 114°, and also when the neutral trichloride is precipitated by a solution of three molecular proportions of potassium iodide, iodine being liberated. When finely-divided gold is boiled with hydriodic acid and a small quantity of nitric acid, and the filtrate allowed to run into hydriodic acid, a lemon-yellow coloured crystalline powder of aurous iodide is formed. It is when pure a very unstable white powder, which assumes a green colour when exposed to the air and deposits a bright surface

[1] Meyer, *Compt. rend.*, 1906, **143**, 280.
[2] *Ibid.*, 1909, **148**, 346.
[3] Thorpe and Laurie, *Journ. Chem. Soc.*, 1887, **51**, 576.
[4] Meyer, *Compt. rend.*, 1904, **139**, 733.

of metallic gold on the inside of the vessel in which it stands. The decomposition takes place more quickly on warming, and is complete at 190°. Aqueous acids decompose it only when heated.

Aurous iodide forms with either liquid or gaseous ammonia the compounds $AuI,6NH_3$ and AuI,NH_3, which are decomposed by heating or by addition of water.[1]

Auric Iodide, AuI_3.—When a neutral solution of auric chloride is added to one of excess of potassium iodide, the liquid becomes of a dark-green colour, and yields a green precipitate, which on agitation dissolves again, inasmuch as potassium auri-iodide is formed. If, however, more gold solution be added, a permanent precipitate is formed, and this, after washing, may be dried, but it evolves iodine, and is converted on standing into aurous iodide. It forms dark-coloured crystalline auri-iodides with the soluble iodides, but it is doubtful whether the free acid exists.[2]

Gold and Sulphur.

245 Gold does not combine directly with sulphur, but three sulphides corresponding in composition with the three oxides can be prepared indirectly. They are all dark-coloured powders which decompose into their elements when they are heated, and are soluble in the alkali sulphides.

Aurous Sulphide, Au_2S, is prepared by passing sulphuretted hydrogen into a solution of aurous cyanide in potassium cyanide and then acidifying. It forms a brownish-black powder which is soluble in water when it is freshly precipitated, but loses this property when it is dried. It is not attacked by hydrochloric or sulphuric acids, but dissolves readily in potassium cyanide. This sulphide is also formed, mixed with gold and sulphur, when sulphuretted hydrogen is passed into a hot solution of auric chloride.[3]

Sodium Aurosulphide, $NaAuS,4H_2O$, is obtained by heating metallic gold with sodium sulphide and sulphur, and treating the fused mass with water. The solution is filtered in an atmosphere of nitrogen and evaporated in a vacuum over sulphuric acid. Colourless, monoclinic prisms are then deposited which soon become brown on exposure to air. The same salt is formed

[1] Meyer, *Compt. rend.*, 1906, **143**, 280.
[2] Johnston, *Phil. Mag.*, 1836, [3], **9**, 266.
[3] Hoffmann and Kruss, *Ber.*, 1887, **20**, 2369.

when aurous or auro-auric sulphide is dissolved in sodium sulphide solution.[1]

That gold can be brought into solution by fusing it with liver of sulphur seems to have been known to Glauber, but Stahl, in his *Observationes Chymico-Physico-Medicæ*, is the first distinctly to mention this fact; and it may be added that he there explains that Moses burnt up the golden calf with alkali and sulphur, and gave the solution of liver of sulphur containing gold to the Israelites to drink.

Auro-auric Sulphide, AuS, is precipitated when sulphuretted hydrogen is passed into a cold neutral solution of auric chloride, this sulphuretted hydrogen being partially oxidised to sulphuric acid :[2]

$$8AuCl_3 + 9H_2S + 4H_2O = 8AuS + 24HCl + H_2SO_4.$$

It is a black powder which dissolves in sodium sulphide solution and is thereby reduced to aurous sulphide, the liquid being found to contain sodium aurosulphide and sodium disulphide.[1] It readily forms colloidal solutions in water and alcohol[3] and is dissolved by potassium cyanide. When left in contact with auric chloride it is reduced to metallic gold.[4]

Auric Sulphide, Au_2S_3, is a very unstable substance and cannot be prepared by passing sulphuretted hydrogen into a solution of auric chloride, nor by heating gold with sodium pentasulphide, as stated by Berzelius. It is formed when anhydrous lithium aurichloride is treated with dry sulphuretted hydrogen at $-10°$.[5] It is an amorphous, graphitic powder, has the specific gravity 8·754, and decomposes into gold and sulphur at 200°. It is decomposed by the sulphides of ammonium but dissolves in sodium sulphide forming sodium aurisulphide. Like the other sulphides it is soluble in potassium cyanide. Yellow crystals of the composition AuS_3,NH_4 have been prepared by allowing a mixture of aqueous auric chloride and ammonium polysulphide to stand for several days at 18°.[6]

Sodium Aurous Sulphite, $3Na_2SO_3,Au_2SO_3,3H_2O$, is formed when sodium hydrogen sulphite is added to a boiling alkaline

[1] Ditte, *Compt. rend.*, 1895, **120**, 320.

[2] Levol, *Ann. Chim. Phys.*, 1850, [3], **30**, 355; Hoffmann and Kruss, *Ber.* 1887, **20**, 2074.

[3] Schneider, *Ber.*, 1891, **24**, 2241; 1892, **25**, 1164.

[4] Antony and Lucchesi, *Gazz.*, 1889, **19**, 545.

[5] *Ibid.*, 1890, **20**, 601; 1891, **21**, ii., 209.

[6] Hofmann and Höchtlen, *Ber.*, 1904, **37**, 245.

solution of sodium aurate, or when this solution is saturated with sulphur dioxide at 50°. It is very easily oxidisable, but in presence of free sulphur dioxide the solution may be heated to boiling without decomposition occurring. When this solution is precipitated by alcohol the salt is obtained as a purple powder which appears yellow or green by reflected light. The corresponding ammonium salt, together with a compound of the formula $(NH_4)_2SO_3,3(NH_3Au)_2SO_3,3H_2O$, has also been described.[1]

Potassium Auric Sulphite, $5K_2SO_3,Au_2(SO_3)_3,5H_2O$, is formed when potassium sulphite solution is poured into a solution of potassium aurate, the above salt separating from the brown liquid in beautiful yellow needles. It is very unstable, and easily decomposes with separation of gold.

Sodium Auro-thiosulphate, $3Na_2S_2O_3,Au_2S_2O_3,4H_2O$, is formed by the gradual addition of a neutral 2 per cent. solution of auric chloride to a solution containing four molecular proportions of sodium thiosulphate. It is necessary to wait after each addition until the red liquid which is formed becomes colourless. The salt is formed according to the equation :

$$8Na_2S_2O_3 + 2AuCl_3 = (3Na_2S_2O_3 + Au_2S_2O_3) + 2Na_2S_4O_6 + 6NaCl$$

It is then precipitated with strong alcohol, and any sodium chloride and tetrathionate which may be present removed by repeated solution in water and precipitation with alcohol. It is also formed by the action of sodium thiosulphate on gold in the presence of oxygen. It crystallises in colourless needles, which have a sweet taste. Its solution is not reduced by ferrous sulphate or oxalic acid, nor is it at once decomposed by hydrochloric acid, or by dilute sulphuric acid, although this occurs on standing.

When barium chloride, and afterwards alcohol, are added to its solution a precipitate of the corresponding barium salt is obtained, from which a solution of the acid auro-thiosulphate, $3H_2S_2O_3,Au_2S_2O_3$, is obtained by addition of the requisite quantity of sulphuric acid. This salt is not known in the anhydrous state, but the solution can be evaporated in the air to a syrupy consistency.

The above compounds do not exhibit the reactions either of the aurous salts or of the thiosulphates, and hence it is assumed that they contain a compound radicle, whose hydrogen salt is

[1] See also Rosenheim, Hertzmann, and Pritze, *Zeit. anorg. Chem.*, 1908, **59**, 198.

the last-named compound. They may, therefore, be written $H_3S_4O_6Au$ and $Na_3S_4O_6Au,2H_2O$. The extraction of gold from auriferous silver ores by means of sodium thiosulphate depends on the formation of these compounds.

Gold Telluride, $AuTe_2$, has been found to occur associated with silver telluride in the minerals sylvanite, calaverite, and krennerite, in Kalgoorlie, Western Australia, and in Colorado and Dakota.[1]

Gold and Nitrogen and Phosphorus.

246 *Auro-diamine* or *Fulminating Gold*, $Au(NH)NH_2$.—The preparation of this compound was described with great accuracy in the *Last Testament* of Basil Valentine. He obtained it by dissolving gold in *aqua regia* mixed with *sal-ammoniac*, precipitating with *sal-tartari* (potashes), and subsequently washing with water. He then says: "Dry the gold calx in the air where no sun shines, and especially not over the fire, for as soon as this powder is exposed to a little warmth it ignites and does a great deal of damage, for it then explodes with such great power and might that no man can withstand." He then describes its properties, and, amongst others, that it loses its explosive power when heated with sulphur. The name of fulminating gold (aurum fulminans) was given to it by Beguin in 1608. It was, however, also known under other names, and was used as a medicine. Angelus Sala, writing in the first half of the seventeenth century, mentions that no fulminating gold can be prepared if aqua regia made with hydrochloric acid be employed instead of that made with sal-ammoniac, and Glauber says that the preparation obtained by means of volatile alkali (carbonate of ammonia) fulminates much more strongly than that made with *oleum tartari* (carbonate of potash). In spite of these observations, few chemists believed that the volatile alkali took part in the composition of the substance, and a great number of erroneous observations were made on the subject of the composition of fulminating gold.[2] Even Black in 1756 stated that the explosion was due to the sudden evolution of fixed air, although Kunkel, a very accurate observer, had already pointed out the true cause. For in his *Laboratorium Chymicum*,

[1] Frenzel, *Tsch. Min. Mitth.*, 1897, **17**, 288; Chester, *Amer. J. Sci.*, 1898, [iv], **5**, 375; Smith, *Trans. Amer. Inst. Mining Eng.*, 1897, **26**, 485; Pittman, *Records Geol. Survey N.S.W.*, 1898, **5**, 203, and others.

[2] Kopp, *Geschichte der Chemie*, **4**, 210.

which appeared in 1716, fourteen years after his death, he described the preparation of fulminating gold, and discussed the various reactions which took place. He then continued: "Once I precipitated the gold with *oleum tartari*, distilled the menstruum to dryness, and then edulcorated; and I thus obtained a fine gold calx which became brown but did not fulminate at all; when, however, the same substance was imbibed several times with *spiritus urinæ* and very gently dried, it exploded violently." He also said that when this substance was imbibed and afterward distilled with oil of vitriol, an acid sal-volatile sublimed in the neck of the retort. "Hence," he added, "thou canst see whence the power in the *aurum fulminans* comes, namely from the *sal-volatile concentratum*." This view was confirmed by the experiments of Bergman and Scheele, who considered fulminating gold to be a compound of ammonia and gold calx. Hence the Lavoisierians termed this compound *oxide d'or ammoniacal*. The composition of this body was subsequently more exactly investigated by Dumas,[1] and later by Raschig.[2]

When ammonia is added to a solution of auric chloride, a mixture of fulminating gold with *auric imidochloride*, Au(NH)Cl, is precipitated and cannot be obtained quite free from chlorine even by prolonged digestion with ammonia. Pure fulminating gold is therefore best prepared by the action of concentrated ammonia on auric hydroxide. When dried over phosphorus pentoxide it has the composition $2AuN_2H_3,3H_2O$, and is a dirty olive-green powder which explodes with great violence, either on percussion or when heated. When it is boiled with water a portion of the nitrogen is evolved in the form of ammonia, and the powder becomes so unstable that it can scarcely be touched without undergoing decomposition. It is decomposed by hydrochloric acid with formation of auric chloride and ammonium chloride:

$$AuN_2H_3 + 5HCl = AuCl_3 + 2NH_4Cl.$$

With sulphuric acid, on the other hand, it appears to unite, forming an extremely explosive *sulphate*, $(AuN_2H_3)_4H_2SO_4$. Both aurous and auroauric oxides are acted on by ammonia with formation of compounds analogous to fulminating gold. The aurous compound, *sesquiauramine*, has the formula NAu_3,NH_3, is not very explosive, and loses half its nitrogen when boiled with water, yielding *triauramine*, NAu_3. The derivative of

[1] *Ann. Chim. Phys.*, 1855, **44**, 167. [2] *Annalen*, 1886, **235**, 341.

auroauric oxide has the formula $N_2Au_3,5H_2O$, and is violently explosive.

When chloroauric acid in aqueous solution is treated with at least five molecules of ammonia,[1] the precipitate formed consists of a mixture of *sesquiammineauric oxide*, Au_2O_3, $3NH_3$, and *diamminoiminodiauric chloride*, $NH(AuCl,NH_2)_2$. Other compounds also containing gold and nitrogen in the ratio 1 : 1·5, *e.g.*, $2Au(OH)_3,3NH_3$, have been obtained.

If N/5 chloroauric acid is added to a cold saturated solution of ammonium chloride and ammonia, a dense yellow precipitate of the non-explosive *diamino-auric chloride*, $Au(NH_2)_2Cl,H_2O$, is obtained. Both the foregoing chlorides by treatment with aqueous ammonia give sesquiammineauric oxide, which on drying at 115° or treatment with hot water gives respectively *diamminetriaurous oxide*, $3Au_2O,2NH_3$ and *monoammineauric oxide*, $Au_2O_3,2NH_3$, both being highly explosive substances. By saturating *N*/5-chloroauric acid solution first with ammonium nitrate and then with ammonia colourless needles are precipitated of tetra-ammineauric nitrate, $[Au(NH_3)_4](NO_3)_3$, from which by double decomposition other salts of the radicle $Au(NH_3)_4$ may be obtained.

Phosphides of Gold.—Gold and phosphorus do not combine at a dull red heat, but the compound Au_3P_4 is formed by heating gold at 400° in phosphorus vapour, the tube being rapidly cooled while still full of vapour. It is a grey mass which decomposes on heating above the temperature at which it is formed, and is attacked by chlorine and aqua regia.[2] A phosphide of the formula AuP is formed by the action of phosphine on an ethereal solution of auric chloride.[3]

Gold and Carbon.

247 *Aurous Acetylide* or *Aurous Carbide*, Au_2C_2.—This compound is obtained as a yellow powder when acetylene is passed into a solution of aurous thiosulphate. It is very explosive when dry, and is decomposed by hydrochloric acid with formation of aurous chloride and acetylene, whilst it is decomposed into its elements by boiling water.[4]

Aurous Cyanide, AuCN.—This compound is obtained by

[1] Weitz, *Annalen*, 1915, **410**, 117. [2] Granger, *Compt. rend.*, 1897, **124**, 498.
[3] Cavazzi, *Gazz.*, 1885, **15**, 40.
[4] Berthelot, *Ann. Chim. Phys.*, 1866, [4], **9**, 425; Mathews and Watters, *J. Amer. Chem. Soc.*, 1900, **22**, 108.

the addition of hydrochloric acid to a solution of the potassium double salt, and evaporation on the water-bath, the residue being washed in the dark. It is a fine yellow powder, showing iridescent colours, and consists of microscopic hexagonal tablets insoluble in water, and, in the dry state, unalterable in the air. It is not attacked by the single acids, but dissolves readily in aqua regia, as well as in ammonia, ammonium sulphide, and sodium thiosulphate.

Potassium Aurocyanide, $KAu(CN)_2$.—This compound, largely used in electro-gilding, is best obtained as follows: 7 parts of gold are dissolved in aqua regia, precipitated by ammonia, the fulminating gold well washed and brought into a boiling solution of 6 parts of pure potassium cyanide. The solution is then filtered and allowed to cool, when, if it is not too dilute, the salt separates out in colourless rhombic pyramids having a pearly lustre. These have a saline and at the same time metallic taste, and are soluble in 7 parts of cold, and in rather less than half their weight of boiling water. The mother-liquor of these salts contains as impurity potassium chloride and potassium carbonate, and yields on evaporation impure crystals. These are, therefore, decomposed with hydrochloric acid as above described, and the resulting aurocyanide dissolved in potassium cyanide.

Potassium aurocyanide is also formed when finely divided gold is treated in the presence of air with a solution of potassium cyanide [1] (p. 515):

$$4Au + 8KCN + O_2 + 2H_2O = 4AuK(CN)_2 + 4KOH.$$

Ammonium Aurocyanide, $NH_4Au(CN)_2$, is obtained by mixing a solution of the foregoing salt with one of ammonium sulphate, and removing the potassium sulphate by precipitation with alcohol. The crystals have a disagreeable metallic taste, and are easily soluble in water, alcohol, and ether.

Auric Cyanide, $Au(CN)_3$, is not certainly known in the free state, but exists in combination with hydrocyanic acid and other cyanides.[2]

Auricyanic Acid, $2HAu(CN)_4,3H_2O$, is obtained from the potassium salt by precipitation with silver nitrate. The precipitated silver salt is washed with cold water and decomposed by somewhat less than the requisite quantity of hydrochloric

[1] Elsner, *J. pr. Chem*, 1846, **37**, 333; Johnston, *Phil. Mag.*, 1836, [3], **9**, 266.

[2] Himly, *Annalen*, 1842, **42**, 340; and Gmelin, *Handbook*, **8**, 41.

acid. The filtrate yields on evaporation tabular crystals which are easily soluble in water, alcohol, and ether.

Potassium Auricyanide, $2KAu(CN)_4,3H_2O$, is obtained by mixing hot concentrated solutions of gold trichloride and potassium cyanide. On cooling it crystallises in large colourless efflorescent tablets. It is used for electro-gilding.

Ammonium Auricyanide, $NH_4Au(CN)_4,2H_2O$, is formed when auric hydroxide is dissolved in ammonium cyanide. It forms either four- or six-sided tablets which are easily soluble in water and alcohol, but not in ether.

Aurous Thiocyanate is only known in combination with other thiocyanates. *Potassium aurothiocyanate*, AuSCN,KSCN, is obtained with evolution of thiocyanic acid, when a neutral gold solution is poured into a hot solution of potassium thiocyanate. It crystallises in yellow obtuse prisms. When hydrochloric acid is added to the solution copper-red needles separate out, and silver nitrate precipitates the *double silver gold thiocyanate*, AuSCN,AgSCN. Ammonia also produces a white precipitate of *aurammonium thiocyanate*, $(AuNH_3)SCN$.

Auric Thiocyanate is not known in the free state, but if a solution of gold trichloride be precipitated with potassium thiocyanate in the cold, an orange-yellow precipitate of $KAu(SCN)_4$ is thrown down, which crystallises in slender needles and is partially decomposed by hot water.

Detection and Estimation of Gold.

248 When a gold compound is heated on charcoal in the reducing flame, a yellow malleable bead is obtained which dissolves in aqua regia. If this solution be dropped on to filter paper and one drop of stannous chloride added, a purple red colour is observed. Gold can be readily detected in its solutions inasmuch as it is obtained in the metallic state by reducing agents, the well-washed precipitate being dissolved and the solution tested with stannous chloride. This is best done by pouring the boiling solution which is supposed to contain gold into a small quantity of concentrated stannous chloride solution. If gold be present, the precipitated stannous hydrate has a purplish colour. One part of gold in 100,000,000 of water can thus be detected.[1]

In the ordinary method of analysis gold is precipitated along with tin, antimony, arsenic, and platinum. The method adopted for its separation is described under the last of these.

[1] Rose, *Chem. News*, 1892, **66**, 271.

The spark spectrum of gold has been mapped by Kirchhoff, Thalén, Huggins, and Krüss. The brightest lines are 6,277 5,960, 5,955, and 5,836 in the orange and yellow, and 5,230 and 4,792 in the green and blue; there are also several lines in the violet and ultra-violet. Gold compounds do not impart any tint to the non-luminous gas flame.

Assay of Gold Ores and Bullion.—The amount of gold contained in an ore is usually ascertained by fusing the ore with red-lead or litharge, charcoal, sodium carbonate, and borax. In this way a button of lead is obtained which contains all the gold and silver of the ore. This button is then cupelled, the residual bead of gold-silver alloy weighed, recupelled with more silver if necessary, treated with nitric acid, and the gold which remains weighed. In order to determine the value of gold bullion it is cupelled with lead with addition of so much silver that the quantity of the latter is about two and a half times that of the gold present. A gold-silver alloy is thus obtained which is rolled out and then boiled with nitric acid of specific gravity 1·26. The residual gold cornet having been well washed is placed in a small crucible and heated in a muffle to a point just below that at which gold melts, in order to render it coherent, after which it is cooled and weighed.

The assaying of gold is an operation of much importance and one in which great accuracy is needed. The errors attaching to the process are chiefly (1) errors in weighing, (2) loss of gold by absorption in the cupel and by volatilisation, (3) slight solution of the gold by the acid, (4) and most important, the presence of a portion of silver in the gold cornet, together with occluded gases. In order to compensate for these various errors, an allowance, called the *surcharge*, is made on each assay, the value of this allowance being determined by special experiments with known amounts of pure gold. In this way, and by carrying out all the processes with unvarying uniformity, as well as by making the assay on a number of samples placed in different parts of the muffle, very great accuracy can be attained. When every precaution is taken the limit of accuracy which can be obtained with high standard alloys appears to be one part in 50,000.[1]

Gold has also been estimated electrolytically by depositing it from solutions of its salts in the presence of potassium cyanide or thiocyanate.

[1] Rose, *Journ. Chem. Soc.*, 1893, **63**, 700.

The Atomic Weight of Gold was first determined with accuracy by Berzelius,[1] who ascertained the quantity of mercury necessary to precipitate gold from its chloride, and obtained as the mean of two experiments the number 196·4. At a later period [2] he determined the relation between gold and potassium chloride in potassium aurichloride, $KAuCl_4$, and obtained the number 196·69, whilst Levol [3] found the number 196·49 by reducing a solution of pure auric chloride with sulphur dioxide and determining the relation between the precipitated gold and the sulphuric acid which was formed.

The atomic weight has also been determined by Thorpe and Laurie, Krüss, and Mallet. The first-named chemists [4] started with potassium auribromide which was carefully heated to convert it into metallic gold and potassium bromide. The relation of gold to potassium bromide in this mixture was then determined, as well as the amount of silver necessary to precipitate the potassium bromide corresponding to a known amount of gold, and the amount of silver bromide thus formed. The mean result of these experiments was 197·28. Krüss [5] arrived at a somewhat lower number, 197·13, by the analysis of weighed amounts of the same salt. Mallet [6] finally obtained the number 197·22, intermediate between those of Thorpe and Laurie, and Krüss, by the analysis of auric chloride, auric bromide, and potassium auribromide. Other determinations by somewhat less reliable methods yielded him rather high numbers. The atomic weight is now (1922) taken as 197·2.

[1] *Schweiggers Journ.*, **7**, 44.
[2] *Berz. Jahresber.*, **25**, 41.
[3] *Ann. Chim. Phys.*, 1850, [3], **30**, 355.
[4] *Journ. Chem. Soc.*, 1887, **51**, 866.
[5] *Ber.*, 1887, **20**, 207; *Annalen*, 1887, **238**, 30, 242.
[6] *Proc. Roy. Soc.*, 1890, **46**, 71.

GROUP II.

Sub-group (a).	*Sub-group (b).*
The Alkaline Earth Metals :	The Magnesium Group :
Calcium.	Glucinum (Beryllium).
Strontium.	Magnesium.
Barium.	Zinc.
Radium.	Cadmium.
	Mercury.

249 The metals of this group are divalent in almost all their compounds. An apparent exception is the element mercury, which in addition to the normal derivatives forms a series of salts in which each atom of the metal replaces only one atom of hydrogen. It appears probable, however, that two atoms of the element are present in the molecules of these compounds, united to form a divalent group Hg_2''.

Some of the other metals form halogen compounds corresponding in composition with the mercurous compounds, but these are as yet but little known. All the metals form a basic oxide, which has the general formula $M^{II}O$, and also yield the corresponding hydroxide $M^{II}(OH)_2$, which in the case of the metals of sub-group (*a*) is soluble, and in that of the metals of sub-group (*b*) almost insoluble, in water. All of these elements combine directly with oxygen readily, forming the divalent oxide.

In the table given on pp. 52–3, it will be seen that glucinum occurs in the same sub-group as calcium, strontium, and barium; in its general properties, however, it is more closely allied with magnesium and zinc, and it is therefore described together with these metals.

The element radium belongs to this group, but it is described later on among the radioactive elements.

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THE ALKALINE EARTH METALS.

250 The name earth was used by the older chemists to designate all those non-metallic substances which were insoluble in water and did not undergo alteration when exposed to a high temperature. It was afterwards observed that some of these, such as lime and magnesia, were closely allied to the alkalis, inasmuch as they possessed an alkaline reaction and neutralised acids. These bodies were therefore termed *terræ alcalinæ*, and this name was subsequently also applied to baryta and strontia. As the other compounds of magnesium resemble the corresponding ones of zinc, cadmium, and glucinum more nearly than those of barium, strontium, and calcium, this metal is now no longer regarded as belonging to this group, the term " metals of the alkaline earths " being therefore confined to the metals contained in the oxides lime, strontia, and baryta.

The alkaline earths, like the alkalis, were supposed to be elementary bodies until Davy, in the year 1807, showed that each earth was a compound of a metal and oxygen.

The metals themselves very readily oxidise in moist air and decompose water at the ordinary temperature with evolution of hydrogen and formation of the hydroxide. The oxides fuse only at the temperature of the electric furnace, and combine with moisture with great avidity, forming the hydroxides, the solubility of which in water increases with the atomic weight of the metal. They also form peroxides having the formula $M^{II}O_2$, that of barium being obtained by the direct union of barium monoxide and oxygen. Like the alkali metals they unite with hydrogen to form hydrides, and they all combine directly with nitrogen to form nitrides. The salts for the most part crystallise well; the carbonates, phosphates, and sulphates are either very sparingly soluble or insoluble in water, as are also their salts with many organic acids.

CALCIUM. Ca=40·07. At. No. 20.

251 The very early application of mortar to building purposes shows that the ancients were well acquainted with the

properties of lime and its preparation by the burning of limestone. In the writings of Dioscorides and Pliny we find a description given of the process of lime-burning, as well as of that of slaking lime.

Calcium occurs very widely diffused in nature, especially as the carbonate, which occurs in various forms, such as calc-spar, aragonite, chalk, marble, limestone, coral, etc. United with magnesium carbonate, as magnesium limestone or dolomite, it forms whole mountain ranges, and this compound, when crystallised, is known as bitter-spar. Many other minerals contain calcium carbonate in isomorphous mixture; amongst these may be mentioned chalybite or brown-spar, $(Ca,Mg,Fe,Mn)CO_3$; mangano-calcite, $(Mn,Ca,Mg)CO_3$; plumbocalcite, $(Ca,Pb)CO_3$, etc. Calcium also occurs in large quantity as sulphate, either as the anhydrous compound, termed anhydrite, $CaSO_4$, or in the hydrated form, as selenite or gypsum, $CaSO_4,2H_2O$. Calcium phosphate, combined with calcium chloride or calcium fluoride, occurs in the well-known minerals apatite and osteolite. Calcium borate is also found in nature combined with many other metallic borates, whilst silicate of calcium occurs as an almost invariable constituent of all silicates. The solid constituents found in river and spring waters also consist mainly of calcium carbonate or calcium sulphate, and these, as well as phosphate and fluoride of calcium, are found in sea-water. The behaviour of these calcium salts during the evaporation of sea-water, and the forms in which they occur in mineral deposits which have been produced in this way, have been very fully dealt with by van't Hoff.[1]

Calcium salts form a never-failing component of the bodies of plants and animals, and cannot be replaced by any other salts. They accumulate in the leaves of plants; the roots and seeds, as a rule, yield only small quantities of them. The bones and teeth of animals contain large amounts of calcium phosphate, together with some carbonate and fluoride. Egg shells and the shells of mollusca, on the other hand, chiefly contain calcium carbonate. Calcium occurs also in the sun, in meteorites, and in certain of the fixed stars.

Preparation of Metallic Calcium.—Calcium was first prepared by Davy by the electrolysis of calcium chloride in the presence of mercury, the calcium remaining as a metallic powder upon heating the amalgam thus obtained. It was first obtained in a coherent metallic mass in 1856 by Matthiessen,[2] who electro-

[1] *Zeit. anorg. Chem.*, 1905, **47**, 244. [2] *Journ. Chem. Soc.*, 1856, **8**, 28.

lysed a mixture of the chlorides of calcium and strontium with a small amount of ammonium chloride in a porcelain crucible, the anode consisting of carbon, and the cathode of a thin iron wire, so that a high current density could be obtained. The metal prepared in this way had a yellowish colour and was not pure but probably contained calcium nitride and some strontium. The electrolysis of the chloride also yielded an impure product (Frei),[1] as did the action of sodium on the iodide,[2] and of a mixture of zinc and sodium on the chloride.[3]

Calcium was first prepared in the pure state by Moissan[4] in 1898 by the electrolysis of the fused iodide and by heating calcium iodide with a large excess of sodium. The calcium separates from the sodium on cooling in white crystals, and the excess of sodium is then removed by the action of alcohol, which acts upon the sodium before the calcium.

Both of these processes were costly, and the economical production of metallic calcium remained an unsolved problem until in 1902 it was found that the metal could be obtained comparatively easily by the electrolysis of calcium chloride provided that the temperature of the fused salt was kept as low as possible. This was effected by Ruff and Plato[5] by using a mixture of 83·5 parts of calcium chloride with 16·5 of calcium fluoride, which melts at 655°. Borchers and Stockem[6] carried out the electrolysis in a special form of cell and obtained the metal in the form of a spongy mass, which was then pressed together under the surface of the molten electrolyte, removed and melted under calcium chloride. The metal is now prepared as a coherent metallic mass on a moderately large scale from the chloride with or without admixture of fluoride by the contact electrode process. An iron rod is employed as the cathode, and this is gradually raised as the electrolysis proceeds, drawing with it the adhering calcium, the metal being protected from the action of the air by the layer of fused salt with which it is covered.[7] It is thus obtained in the form of irregular cylinders sometimes

[1] *Annalen*, 1876, **183**, 367.

[2] Liés Bodart and Jobin, *Ann. Chim. Phys.*, 1858, [3], **54**, 364.

[3] Caron, *Annalen*, 1860, **115**, 355.

[4] *Compt. rend.*, 1898, **126**, 1753.

[5] *Ber*, 1902, **35**, 3612.

[6] *Zeit. Elektrochem.*, 1902, **8**, 757; see also Arndt, *ibid*, 1902, **8**, 861.

[7] Goodwin, *Proc. Amer. Phil. Soc.*, 1905, **43**, 381, Wohler, *Zeit. Elektrochem*, 1905, **11**, 612; Rathenau, *Zeit. Elektrochem*, 1904, **10**, 508; Tucker and Whitney, *J. Amer. Chem. Soc*, 1906, **28**, 84.

weighing more than a quarter of a kilogram. Metallic calcium has not yet found any important technical application.

Metallic calcium is used as a purifying agent in the preparation of inert gases, as a dehydrating agent in the treatment of certain oils and as a means of fixing atmospheric nitrogen. It has also had a limited application as a reducing agent for metals and alloys, as a constituent of light aluminium alloys and as a hardening agent for lead base bearing metals, in the last case taking the place of tin in these alloys during a period when the price of tin was extremely high.

Heated metallic calcium has a remarkable absorbent power for gases and has been used for the production of high vacua.[1] It has been stated[2] that it exists in two forms, one of which is active and the other relatively inactive in this respect.

Properties of Calcium.—Calcium as prepared by the foregoing method contains about 0·4—1 per cent. of impurities. It is of a pure silver white colour, melts at 810°, and has the density 1·548. It sublimes even below its melting point when heated in a vacuum, and condenses as a crystalline layer on the cooler parts of the vessel. It is malleable and somewhat harder than lead. A fresh surface soon becomes yellowish in the air, but retains its lustre in dry air. The metal decomposes water slowly, and acts vigorously on acids. Calcium reacts with alcohols, particularly on heating, producing alkyloxides, $Ca(OAlk)_2$.[3] It burns brilliantly when heated in oxygen, the heat of oxidation being 3288 calories per gram. It is attacked by chlorine and sulphur at 400°, and combines readily, when heated, with nitrogen, phosphorus, silicon, and other non-metals.[4]

When the metal prepared by electrolysis is hammered, mild explosions accompanied by showers of sparks occur, the cause of which has not yet been ascertained.[5] Alloys of calcium with other metals decompose water when they contain more than 11% of calcium.[6]

[1] Soddy, *Proc. Roy. Soc*, 1907, [*A*], **78**, 429.

[2] Sieverts, *Zeit. Elektrochem*, 1916, **22**, 15.

[3] Perkin and Pratt, *Journ Chem. Soc*, 1909, **95**, 159

[4] Moissan, *Compt. rend*, 1898, **127**, 584; 1899, **128**, 384, Arndt, *Ber.*, 1904, **37**, 4733; Moissan and Chavanne, *Compt. rend.*, 1905, **140**, 122.

[5] Doermer, *Ber*, 1906, **39**, 211.

[6] Baar, *Zeit. Elektrochem.*, 1911, **70**, 352.

COMPOUNDS OF CALCIUM.

Calcium and Oxygen.

252 *Calcium Monoxide* or *Lime*, CaO, is formed in the pure state by the ignition of the pure carbonate, as Iceland- or calc-spar, or white marble, in a crucible in a current of indifferent gas; otherwise the decomposition is not complete (p. 139).

On the large scale lime is burnt in kilns, the interiors of which are usually egg-shaped. The limestone is mixed with coal or other combustible matter, one bushel of coal generally sufficing to make five or six bushels of lime. In some cases an arch is formed over the fire-grate with lumps of lime-stone, the kiln filled up with smaller pieces, a fire kindled below the arch, and this kept up for thirty-six to forty-eight hours. The kiln is then allowed to cool, the lime removed, and a fresh charge introduced. An improved and continuous process of lime-burning is now often employed in which the charge of limestone and coal is added from time to time at the upper part of the kiln, and the quicklime withdrawn at the lower part. A great saving of fuel is thus effected, and the smoke which is always given off from the common kiln is, in the improved kiln, drawn into a high chimney and completely burnt.

Pure lime is a white amorphous mass, having a specific gravity of 3·30; it shows signs of fusion in the oxy-hydrogen flame and can readily be melted and boiled in the electric furnace, a current of about 300 amperes at 50—70 volts being sufficient to maintain 500 grams of lime in ebullition; the melting point is about 1900°. The vapour condenses in the electric furnace in cubes and acicular prisms composed of aggregates of cubes, which have the sp. gr. 3·40 and gradually pass into a second crystalline modification which is doubly refracting.[1] It is also obtained crystallised in cubes by heating calcium nitrate in a porcelain flask.[2] On exposure to the air it combines with moisture, passing into the hydroxide, $Ca(OH)_2$, which then absorbs carbon dioxide. When water is poured on to quicklime the latter is converted into the hydroxide with great evolution of heat, the temperature rising in some cases as high as 150°. The evolution of heat may be well shown by strewing a few grains of gunpowder on to the lime whilst it is being slaked, when the powder will take fire.

[1] Moissan, *Compt. rend.*, 1892, **115**, 1034; 1902, **134**, 136. Compare Jouve, *ibid.*, 1901, **132**, 1117.

[2] Brugelmann, *Ann. Phys. Chem.*, 1877, **2**, 466.

Lime which has been fused slakes only after remaining in contact with water for two or three days.[1] Although lime unites so readily with water, it is in absence of this a very inert substance; thus it does not combine to an appreciable extent with dry chlorine, carbon dioxide, sulphur dioxide or oxides of nitrogen below 300—350°, whereas it is readily acted on by these substances in presence of moisture.[2] Dry hydrogen chloride begins to attack it at 40°.[3]

The most important use of lime is in the preparation of mortars and cements for building purposes, and its value for these purposes depends upon the nature of the limestone from which it has been prepared. The lime obtained from pure limestone slakes readily and is termed a "fat" lime, but if the limestone contains magnesia it only forms a thin mixture with water, and is termed a "poor" lime. When the quantity of magnesia rises to 25—30 per cent. the product is almost useless for building purposes. If the limestone used contains silica in considerable quantity, the resulting lime yields a mortar which hardens under water; it is known as hydraulic lime, and the mortar obtained from it as hydraulic mortar (p. 582). The presence of clay in the limestone frequently causes it to vitrify if too strongly heated, a hard crust of silicates being formed on the surface which causes it to slake very slowly. Such lime is said to be "dead burnt."

Ordinary mortar is a mixture of one part of lime made into a paste with water and mixed with three to four parts of sharp sand, the completeness of the subsequent hardening being dependent on the proper admixture of the ingredients. Mortar sets sufficiently to give stability to a structure in a few days, this being brought about almost entirely by the loss of water. It thus becomes porous, and the lime is then gradually attacked by the carbon dioxide of the air, which converts it slowly but completely into calcium carbonate, the mortar gradually hardening, and cementing the sand and building material together. Many years or even centuries elapse before the maximum of hardness is reached, and it appears that at the same time an extremely slow combination of the silica and lime takes place; thus Petzholdt[4] found 2·1 per cent. of combined silica in a

[1] Oddo, *Atti R. Accad. Lincei*, 1896, [5], **5**, i, 361; Gautier, *Compt. rend.*, 1899, **128**, 939.

[2] Veley, *Journ. Chem. Soc.*, 1893, **63**, 821; 1894, **65**, 1.

[3] Veley, *Ber.*, 1896, **29**, 577.

[4] *J. pr. Chem.*, 1839, **16**, 91; **17**, 464.

mortar 100 years old, and 6·2 per cent. in a sample 300 years old, the lime originally used only containing at most 0·11 per cent. In ordinary circumstances, however, this action plays no part in the hardening process.

In addition to its use for building purposes lime is used for the purposes of drying gases and liquids, and in numerous analytical processes, and also, when slaked, for the purification of coal-gas (Vol. I., p. 884), and the manufacture of caustic soda and bleaching powder.

Calcium Hydroxide, $Ca(OH)_2$.—This substance, also known as *slaked lime*, is obtained, as already stated, by the action of water on quicklime. It is a white impalpable powder, having a specific gravity of 2·078 (Filhol). Calcium hydroxide is likewise obtained as a white precipitate, when a solution of caustic potash or soda is added to a tolerably strong solution of calcium chloride. If a very strong or saturated solution of calcium chloride be employed in the above experiment, the whole mass becomes solid. This fact was observed in 1686 by Francisco Lana, and described by him as the " chemical miracle." Calcium hydroxide dissolves more readily in cold than in hot water; 100 parts of water at 10° dissolve 0·29 part, at 100°, 0·06 part (Maben),[1] at 150°, 0·017 part, and at 190°, 0·008 part (Herold).[2] The clear solution, evaporated in a vacuum over sulphuric acid, deposits the hydroxide either in the form of small tablets or of small prismatic crystals.

The solution of calcium hydroxide, usually known as lime water, possesses an alkaline reaction and taste. It quickly absorbs carbon dioxide from the air, and is used in medicine and in the laboratory. As the ordinary slaked lime often contains small quantities of baryta and strontia together with soluble salts of the alkalis, it is usual to treat the powder several times with water and only to employ the last solution.

Milk of Lime is calcium hydroxide suspended in water.

Calcium Dioxide, CaO_2, was discovered by Thénard, who obtained it by precipitating lime water with hydrogen dioxide. In order to procure the substance in the pure state the hydrogen dioxide must be added in excess to lime water. The precipitate at 13—14° possesses the composition $CaO_2,8H_2O$, and consists of microscopic tetragonal tablets or prisms, which are sparingly

[1] *Pharm. J.*, [3], 1883–4, **14**, 505. See also Guthrie, *J. Soc. Chem. Ind*, 1901, **20**, 223.

[2] *Zeit. Elektrochem.*, 1905, **11**, 417.

soluble in water and insoluble in alcohol;[1] at a slightly higher temperature $CaO_2,2H_2O$ is produced.[2] On exposure to the air the crystals effloresce, and when heated to 130° they lose their water, leaving behind a light powder of the anhydrous oxide. When further heated the substance loses half its oxygen without fusing. In contact with water, both the dihydrate and the anhydrous peroxide are reconverted to the octahydrate. A diperoxyhydrate, $CaO_2,2H_2O_2$, is also known.[3]

Technically it is manufactured by mixing and then compressing $Ca(OH)_2$ with Na_2O_2.[4] The pressed product is then treated with ice water. The dehydrated powder is used as an oxidising agent and antiseptic. It contains 13·5 per cent. of available oxygen, and a considerable amount of calcium hydroxide.[5]

Calcium and Hydrogen.

253 *Calcium Hydride*, CaH_2, is produced when metallic calcium is heated in a nickel boat to dull redness in a current of hydrogen. It forms a fused mass of slender transparent plates, has the sp. gr. 1·7, and does not decompose appreciably at 600° *in vacuo*. It is readily decomposed by water, yielding the hydroxide and hydrogen.

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2.$$

It burns brilliantly when heated in the air or oxygen, acts as a vigorous reducing agent, and is attacked by the halogens, sulphur, and phosphorus, when heated.[6] It is made technically by heating calcium in hydrogen in horizontal retorts, and is known as "hydrolith." One kilogram, when treated with water, yields about one cubic metre of hydrogen.[7]

Calcium and the Halogens.

254 *Calcium Fluoride*, CaF_2, occurs as the mineral fluor-spar, which has from early times been used in the fluxing of ores, whence its name is derived. Agricola says "Fluores lapides

[1] *Ann. Chim. Phys.*, 1818, **8**, 313.
[2] de Forcrand, *Compt. rend.*, 1900, **130**, 1250, 1308, 1388.
[3] Riesenfeld and Nottebohm, *Zeit. anorg. Chem.*, 1914, **89**, 405; **90**, 150.
[4] German Patents, 128617, 132706. *Cf.* also French Patent, 364249.
[5] Foregger and Philipp, *J. Soc. Chem. Ind*, 1906, **25**, 298.
[6] Moissan, *Compt. rend*, 1898, **127**, 29.
[7] Jaubert, *ibid.*, 1906, **142**, 788.

gemmarum similes sed minus duri, qui ignis calore liquescunt"; and then further: "Dum metalla excoquuntur, adhibere solent, reddunt enim materiam in igne non paulo fluidiorem."

Fluor-spar occurs largely in Derbyshire in veins, especially in the celebrated limestone caves in the Castleton valley. It is there found as a coloured variety which is commonly known as *Blue John*, and one of these large caverns is termed the Blue John cave. It is also found in Saxony and in many other countries. It crystallises in cubes and octahedra, and in combinations of these two forms, or in other forms belonging to the regular system. In the pure condition it is colourless; in general, however, it has a blue, violet, red, green, yellow, or brown colour, the cause of which, as in the case of coloured rock salt (p. 268), is not fully understood. Those samples which have a bright colour are worked up into vases, dishes, cups, etc. Calcium fluoride also occurs in small quantity in the ashes of certain plants, in bones, in the enamel of the teeth, in sea-water, and in the water of certain mineral springs. It is very nearly insoluble in water and dilute acids, melts at 1330°, and has the sp. gr. 3·18.

When precipitated calcium fluoride, obtained by mixing a solution of calcium chloride with one of a soluble metallic fluoride, is heated with water slightly acidified with hydrochloric acid, the precipitate is found to consist of microscopic octahedra.[1]

The property which fluor-spar possesses of becoming luminous when heated, giving rise to the term fluorescence, was first mentioned by Elsholz in 1677, and further described by Leibnitz in 1710.

Calcium Chloride, $CaCl_2$.—Isaac Hollandus in the fourteenth century describes, under the name of *sal-ammoniacum fixum*, a substance which he obtained by heating together sal-ammoniac and lime. Homberg in 1693 noticed that this salt, when fused, became phosphorescent, and hence it was long known as Homberg's phosphorus. Calcium chloride is found in solution in sea-water, and in many mineral springs. It also occurs as a constituent of a few minerals, such as tachhydrite, $CaCl_2,MgCl_2,12H_2O$, and apatite, $3Ca_3(PO_4)_2,(CaCl_2,CaF_2)$.

In order to prepare pure chloride of calcium, Iceland-spar, chalk, or white marble is dissolved in hydrochloric acid until the latter is nearly saturated. Chlorine water is then added, in order to oxidise any iron or manganese compounds which may be present. These impurities are next precipitated by the

[1] See also Defacqz, *Compt. rend.*, 1903, **137**, 1251.

addition of milk of lime, and the precipitate is filtered off. The slightly alkaline solution is then acidified with hydrochloric acid, and the solution evaporated either to the point of crystallisation or to dryness. Chloride of calcium is obtained on the large scale as a by-product in several manufacturing processes, such as in the ammonia-soda process, the Weldon chlorine process, and the manufacture of potassium chlorate.

The hydrated salt crystallises from a saturated solution in large hexagonal prisms, which have the composition $CaCl_2,6H_2O$. These melt at 30·2°, and deliquesce rapidly in the air, forming a thick liquid, to which the name of *oleum calcis* was formerly given. The crystals dissolve in water, producing a considerable diminution of temperature, the eutectic temperature being — 55°. Heated to 200° this hydrate loses four molecules of water, and a white porous hygroscopic mass of the *dihydrate* remains behind, which, heated more strongly, yields the anhydrous salt. Anhydrous calcium chloride is largely used as a means of drying gases and organic liquids. It melts at about 780°, and solidifies on cooling to a crystalline mass, which has a specific gravity of 2·26 and is also used as a desiccating agent.

When a solution of 103—127 parts of calcium chloride in 100 parts of water is cooled to 18–38°, a hydrate of the formula $CaCl_2,4H_2O$ separates out; it exists in two modifications, the more stable compound being less soluble in water than the other. The stable modification passes into the dihydrate, $CaCl_2,2H_2O$, at 45·3°, and the labile modification into the same hydrate at 38·4°; at 175·5° the monohydrate separates from the solution, and at 260° this is replaced by the anhydrous salt.[1]

100 parts of water dissolve

at 0°	10°	20°	40°	60°	80°	100°	170°	200°	260°
59·5	65·0	74·5	115·3	136·8	147	159	255	311	347

parts of $CaCl_2$ (Roozeboom). Calcium chloride is also very readily soluble in alcohol.

A solution of 50 parts of the anhydrous salt in 100 parts of water boils at 112°, one containing 200 parts boils at 158°, and one containing 325 parts boils at 180°. Such solutions are employed as baths for constant temperatures above 100°.

Calcium chloride absorbs dry ammonia, giving rise to a voluminous powder having the composition $CaCl_2,8NH_3$, which loses ammonia on exposure to the air, on solution in

[1] Roozeboom, *Zeit. physikal. Chem.*, 1889, **4**, 31.

water, or on heating, and takes fire when thrown into chlorine gas.

If calcium chloride solution be boiled with slaked lime and the solution filtered hot, a basic salt, which is known as *calcium oxychloride*, separates out on cooling in long white needle-shaped crystals, having the composition $ClCa{\cdot}O{\cdot}Ca(OH),7H_2O$. The halogen salts of calcium form compounds of the formulæ $CaCl_2$, $2ICl_3$, and CaI_4, analogous to the polyhalogen derivatives of rubidium and cæsium [1] (pp. 384, 388).

Calcium Bromide, $CaBr_2$, melting at 765°, and *Calcium Iodide*, CaI_2, melting at 740°, are salts very similar in their properties to calcium chloride. The basic iodide, $CaI_2,3CaO,16H_2O$, has been described.[2]

Calcium Subchloride.—When the spongy calcium obtained by the methods of Borchers and Stockem is melted in presence of calcium chloride, the molten metal is found to be surrounded by a mass of transparent, red pleochroic crystals.[3] These appear to consist of a subchloride of calcium; they have the composition CaCl, and react with water with formation of calcium chloride, calcium hydroxide, and hydrogen. An analogous *subiodide* was observed by Moissan.

The pure subchloride is prepared by heating calcium chloride with an equivalent of metallic calcium in a steel cylinder to 900—1000° for four hours.[4] The *subiodide* and *subfluoride* have also been prepared.

Chloride of Lime or *Bleaching Powder.*—This well-known bleaching agent and disinfectant is obtained as a dry powder by the action of chlorine on slaked lime.

The action of chlorine on milk of lime is analogous to its action on potash, a solution of calcium hypochlorite and chloride being obtained :

$$2Ca(OH)_2 + 2Cl_2 = CaCl_2 + Ca(OCl)_2 + 2H_2O,$$

and it was supposed by Balard in 1834 that the solid powder was also a mixture of chloride and hypochlorite, his views being for some time generally accepted. It was, however, pointed out by Fresenius [5] that a substance containing so much calcium

[1] Weinland and Schlegelmilch, *Zeit. anorg. Chem.*, 1902, **30**, 134; Meyer, *ibid.*, 1903, **30**, 113.
Millikan, *Zeit. physikal. Chem.*, 1917, **92**, 59.
Zeit. Elektrochem., 1902, **8**, 757.

[4] Wohler and Rodewald, *Zeit. anorg. Chem.*, 1909, **61**, 54.

[5] *Annalen*, 1861, **118**, 317.

chloride must be far more hygroscopic than bleaching powder is found to be, and a number of other constitutional formulæ were proposed, the most important being those of Stahlschmidt [1] and Odling.[2]

According to Stahlschmidt's supposition the action of chlorine on slaked lime takes place in the following manner:

$$3Ca(OH)_2 + 2Cl_2 = 2ClO{\cdot}Ca{\cdot}OH + CaCl_2 + 2H_2O.$$

On addition of water the calcium chloride dissolves and the basic hypochlorite decomposes into hypochlorite and free lime.

According to Odling's formula the calcium is combined with the negative radicals of both hydrochloric and hypochlorous acid, as shown by the formula $Cl{\cdot}Ca{\cdot}OCl,H_2O$, and this compound by the action of water is resolved into calcium chloride and hypochlorite:

$$2Cl{\cdot}Ca{\cdot}OCl = CaCl_2 + Ca(OCl)_2.$$

The subject has been carefully investigated by Lunge in conjunction with Schaeppi and Naef,[3] and the results of their investigations have shown that the latter view is probably the more correct one. By careful preparation it is possible to obtain a powder containing 44 per cent. of available chlorine (*i.e.*, chlorine which is evolved when an acid is added), whilst according to Stahlschmidt's formula the maximum quantity of available chlorine is only 39 per cent. Further, no calcium chloride can be extracted from bleaching powder by means of alcohol, and a large part of the chlorine may be expelled by the action of carbon dioxide, which could scarcely be the case if it contained calcium chloride. O'Shea [4] has also shown that for every molecule of CaO two atoms of chlorine can be added, and that of this chlorine half is available for the formation of hypochlorous acid, which further confirms Odling's formula. Dreyfus [5] has raised objections to this formula, but his conclusions have been shown by Lunge and Schoch to be untenable.[6]

All bleaching powder, however, yields a certain amount of calcium hydroxide when it is treated with water, and the formation of this is not accounted for by Odling's formula. By

[1] *Dingl. Polyt. Journ.*, 1876, **220**, 243.

[2] *Manual of Chemistry*, **1**, 56.

[3] *Dingl. Polyt. Journ.*, 1880, **237**, 63; *Annalen*, 1883, **219**, 129; 1884, **223**, 106.

[4] *Journ. Chem. Soc.*, 1883, **43**, 410.

[5] *Bull. Soc. chim.*, 1885, [2], **41**, 600.

[6] *Ber.*, 1887, **20**, 1474.

some investigators this lime is regarded as existing free in the bleaching powder, having been protected from the action of the chlorine by a layer of the chlorinated compound. According to Ditz,[1] this is not the case, the lime forming an essential part of the bleaching compound. He considers that bleaching powder is formed by a series of reactions, the first of which is represented by the following equation:

$$(1)\quad 2Ca(OH)_2 + Cl_2 = CaO,Cl{\cdot}Ca{\cdot}OCl,H_2O + H_2O.$$

This can be experimentally realised at $-10°$ to $-15°$, and the resulting powder loses one molecule of water below 100°, whilst the compound $CaO,Cl{\cdot}Ca{\cdot}OCl,H_2O$, which is left behind at this temperature, decomposes at 130—180°, losing one atom of oxygen and only losing the second molecule of water at a red heat. It is also completely decomposed by moist carbon dioxide, all the chlorine being liberated. At a somewhat higher temperature the action of chlorine on slaked lime containing not more than ½ per cent. of uncombined water produces a greater degree of chlorination, and this represents the second stage in the formation of bleaching powder:

$$(2)\quad a.\ 2[CaO,Cl{\cdot}Ca{\cdot}OCl,H_2O] + 2H_2O = 2Ca(OH)_2 + 2[Cl{\cdot}Ca{\cdot}OCl,H_2O].$$

$$b.\ 2Ca(OH)_2 + Cl_2 = CaO,Cl{\cdot}Ca{\cdot}OCl,H_2O + H_2O.$$

The final product at the close of this stage, therefore, has the composition $CaO,Cl{\cdot}Ca{\cdot}OCl,H_2O + 2[Cl{\cdot}Ca{\cdot}OCl,H_2O] + H_2O$.

This process may theoretically be indefinitely repeated, but in practice it is limited by the amount of uncombined water present in the slaked lime, and does not proceed beyond the stage at which the product has the composition $CaO,Cl{\cdot}Ca{\cdot}OCl,H_2O + 6[Cl{\cdot}Ca{\cdot}OCl,H_2O] + H_2O$ These higher products undergo a complicated decomposition when they are heated, oxygen and chlorine being evolved, and chlorate and chloride formed. They are also decomposed even by dry carbon dioxide, but the whole of the chlorine is not evolved.

The complex $Cl{\cdot}Ca{\cdot}OCl,H_2O$ has probably a greater molecular weight than corresponds with the simple formula, but its constitution has not yet been settled.

Tiesenholt,[2] on the other hand, maintains the older view of

[1] *Chem. Zeit.*, 1898, **22**, i., 7; *Zeit. angew. Chem.*, 1901, **14**, 3, 25, 49, 105; 1902, **15**, 749.

[2] *J. pr. Chem.*, 1901, [2], **63**, 30; **65**, 512.

Balard, and regards the reaction between lime and chlorine as reversible. Other views are held by some investigators, and the whole question cannot yet be regarded as definitely determined.[1]

Bromine, like chlorine, can react with quicklime and water to form a red compound, $CaOBr_2,H_2O$, which is probably a *calcium bromohypobromite* analogous to bleaching powder.

The Manufacture of Bleaching Powder.

255 *History of the Manufacture of Hypochlorites.*—Chlorine gas was first employed for bleaching in 1785 on the suggestion of Berthollet, and the first hypochlorite was manufactured for bleaching purposes in 1789, at Javel, near Paris, where chlorine was absorbed in potash liquor, whence the name "eau de Javel" which is still used for potassium hypochlorite (see p. 347). These processes were introduced into England in 1796; in 1798 "bleach liquor" was being made by absorbing chlorine in milk of lime, and in 1799 Tennant, of Glasgow, originated the absorption in *dry* hydrate of lime, thus making for the first time "bleaching powder," which sold at £140 per ton, but the price soon fell to £60. The chlorine was made directly from a mixture of salt, sulphuric acid, and manganese dioxide. In 1825—*i.e.*, immediately after the introduction of the Leblanc soda-process into the district—hydrochloric acid became available as a raw material, and the price was reduced to £27. Many methods were proposed to use or recover the manganese contained in the waste still liquors, but they proved unsuccessful, until Weldon by his process of 1866, and subsequent improvements, achieved such success, that in 1870 the price of bleaching powder fell to £8 10*s*. The combined Leblanc-Weldon process grew rapidly, attaining in 1877 an annual output of nearly 100,000 tons in the United Kingdom alone. Another method of generating chlorine utilised in making bleaching powder was the Deacon process, introduced and perfected from 1868 to 1876; the special method of utilising the weak chlorine thus obtained is described in the following pages; only a small portion of the total bleaching powder is, however, now made by Deacon's process. The latest source of chlorine for the

[1] Winteler, *Zeit. anorg. Chem.*, 1902, **33**, 161; *Zeit. angew. Chem.*, 1903, **16**, 32; Tarugi, *Gazz.*, 1904, 34, II., 254; Schwartz, *Zeit. angew. Chem.*, 1906, **20**, 138.

manufacture of bleaching powder is the electrolysis of chloride solutions. Hargreaves and Bird's process, started in 1892 at Farnworth, and now carried on in works erected in 1900, at Middlewich, and Castner's process, originating in Oldbury in 1891, and installed in 1897 on a large scale in Runcorn, both electrolyse sodium chloride (see p. 325). In a third process, proposed by Mond about 1898, zinc chloride solution is electrolysed. Abroad other processes besides the above are being utilised, and potassium chloride is electrolysed in a number of works. In 1900 there were in Europe twenty-five electrolytic alkali works producing chlorine, with a total of 40,000 horse-power, and in the United States, three works with 5,200 horse-power; since then the output has been considerably increased.

Electrolytic methods have also recently been introduced for manufacturing hypochlorite solutions, and though such processes as yield only one product, namely, the hypochlorite solution, cannot compete with any of the previously mentioned processes which make simultaneously two products, yet they are serviceable to paper-pulp and bleach works which are far removed from bleaching powder works. The first suggestion for such a process was due to Watt, a paper-maker, in 1851, but it was impracticable, as dynamo-electric machines were not then obtainable. Lidoff and Tichomiroff in 1882 introduced a process, and exhibited yarn and cloth bleached by it. Hermite in 1883 claimed for his process,[1] electrolysis of calcium chloride or magnesium chloride solutions, special advantages over bleaching with bleaching powder, and from this time forward a vast number of processes have been patented, by Kellner, Haas and Oettel, Schoop, and Atkins, all of whom use sodium chloride solutions, and many papers have been published on the theory of the process (see p. 269).[2]

In 1910, about 6,660 horse-power was employed in the manufacture of liquid bleach, producing about 13,120 kilos. of active chlorine per day.

Manufacture of Bleaching Powder.—The details of the methods for preparing the chlorine required in the manufacture of bleaching powder are described under the head of chlorine

[1] *J. Soc. Chem. Ind.*, 1885, **4**, 673; 1887, **6**, 170.

[2] Full details of these processes are given in *Monographien uber angewandte Elektrochemie*, Band 8; Engelhardt, *Hypochlorite und elektrische Bleiche*, 1903, Band 17; Abel, *Hypochlorite und elektrische Bleiche* (Theoretischer Teil), 1905, Band 38; Ebert and Nussbaum (*Praktish-angewandter Teil*), 1910.

(Vol. I., p. 178). For this purpose the chlorine should be as free as possible from carbonic acid, originating either from calcium carbonate in the native manganese, or in Weldon mud, or from the furnaces in the Deacon process, or from the corrosion of the carbon anodes, where such are used in electrolytic methods. Further, the chlorine must be freed from hydrochloric acid and much water vapour; this is effected by passing the gas through a long range of earthenware pipes cooled by exposure to the air. The lime employed requires to be specially free from clay, magnesia, iron, and manganese compounds, the last two of which discolour and gradually decompose the bleach, both when dry and when dissolved.

The absorption of the chlorine is effected in three different kinds of apparatus, (1) large roomy chambers, (2) small chambers filled with trays, (3) revolving cylinders, and of these the first is the most usual.

Ordinary Chambers.—Two only out of a set of four or more are shown in Fig. 127, one being in end elevation and the other in section, while Fig. 129 shows the same in plan, but with the middle portions cut out, as the total length is 80 to 100 feet. These chambers are made of timber framing, supporting sheet lead, so that the supports are all outside the lead; the floor is covered with asphalt or with earthenware tiles.

The chlorine is brought from the still (Figs. 126, 128) to the chambers by the central main, and can be directed into any chamber by removing the two hydraulic caps closing the main and the chamber, and substituting a bent pipe dipping into the two water lutes. The displaced air escapes from the lute (F) until the smell of chlorine is observed, when the bend is used to connect the chamber, as shown in Fig. 129, to the second pipe main adjacent, by which the gas is carried to any other chamber desired, entering at the lute corresponding to F and leaving by the open lute (G) until the chlorine begins to escape here also, when by placing a bend in (G) the gas may be directed by the main adjacent to any third chamber in the series, where the last trace of chlorine is absorbed. The main (G) also serves as an exhaust pipe for drawing off the last remaining quantities of the unabsorbed chlorine when the operation is complete. The exterior view, Fig. 127, shows the doors and bolts and the gallows for the swinging of the doors, which are closed gas-tight by a paste of tar and china clay, or of lime and water.

The chambers described rest upon the ground. Much labour

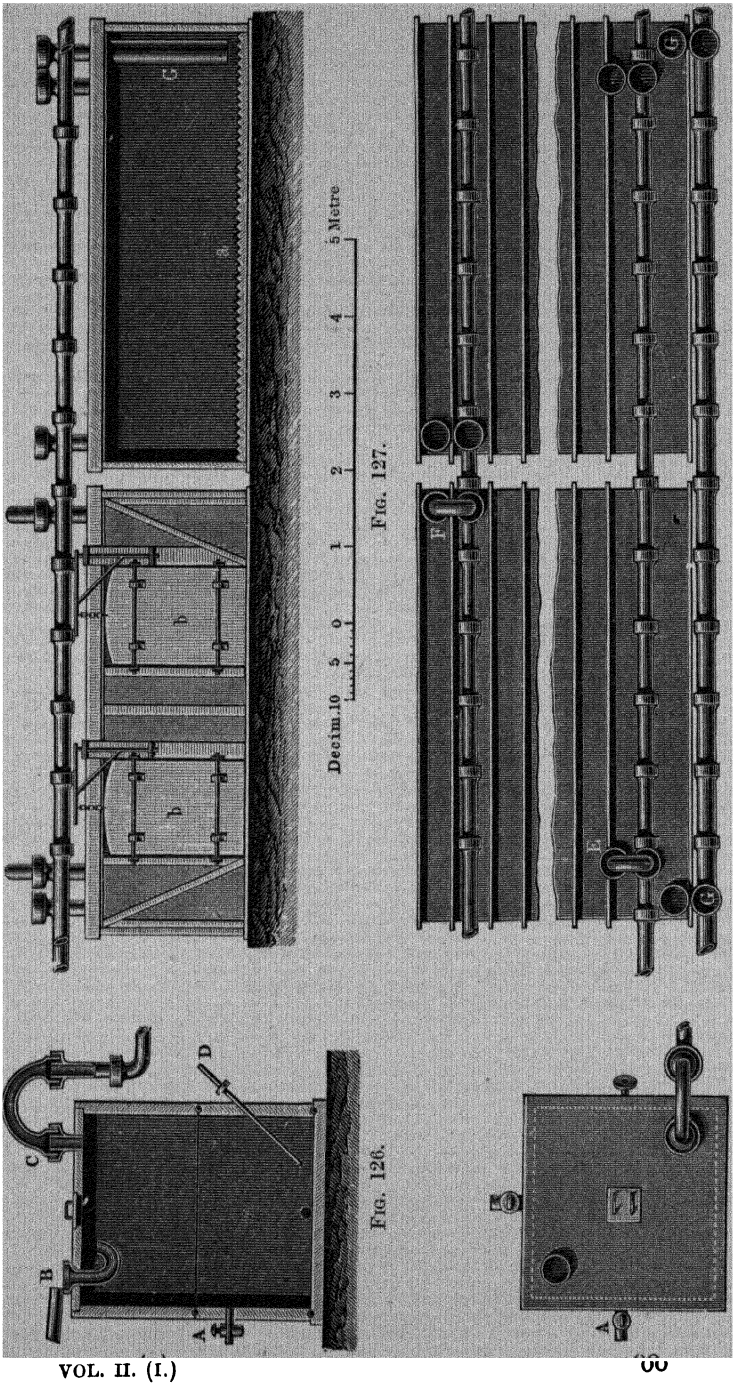


FIG. 126. FIG. 127. FIG. 128. FIG. 129.

and inconvenience are avoided by building the chamber on pillars and having a number of hopper holes in the floor, closed while the bleaching powder is being made, with lids which are covered with lime, to prevent leakage of chlorine. When the powder is ready to pack, the lids are lifted, and the powder is shovelled down the hoppers and through a sacking or rubber sleeve which connects the hopper to the head of the cask. In these chambers the absorption of chlorine occupies about six days. After the lime has been placed upon the floor of the chamber to the thickness of about four inches, it is deeply furrowed like a ploughed field by a special rake, and the chlorine is turned on until the chamber is full, as seen by means of windows placed at each end, the air and any surplus chlorine escaping from the chamber and passing by the circulating pipes into the next or some other chamber where there is more fresh lime. When the first chamber has been filled with chlorine it is allowed to stand for about two days, during which time the gas is completely or nearly completely absorbed, and the lime is then found to contain on an average from 25 to 30 per cent. of available chlorine. Any unabsorbed gas is then drawn off by means of the exit pipe (G), the doors are opened, and workmen enter and turn the material, as the bottom layers are still very weak in chlorine; the doors are then closed and more chlorine is admitted, the quantity being sufficient to raise the amount of chlorine, after absorption for a second period of two days, to from 35 to 37 per cent. The unabsorbed chlorine is drawn off as before, and the powder packed and sent to market.

Much trouble has been experienced in removing the residual chlorine from the finished chambers, and fatal results have followed the premature opening of the doors, so that in 1886 a penalty was imposed for opening the doors before the chlorine contents of the chamber had been reduced to less than two and a half grains per cubic foot. In the same year Brock and Minton introduced their lime sprinkler, a portable machine in which a stream of lime dust is allowed to fall on to a rapidly revolving paddle with a vertical shaft, so that the dust is scattered in a cloud and the gases are also put in motion and help to carry the lime dust to a considerable distance. Every 30 feet in the length of the chamber a large luted cap is provided, and these are lifted in turn, the sprinkler inserted, and one or more hundredweight of lime sprinkled in, when the absorption of the chlorine is almost instantaneous and so complete that the residual chlorine need not exceed one grain per cubic foot.

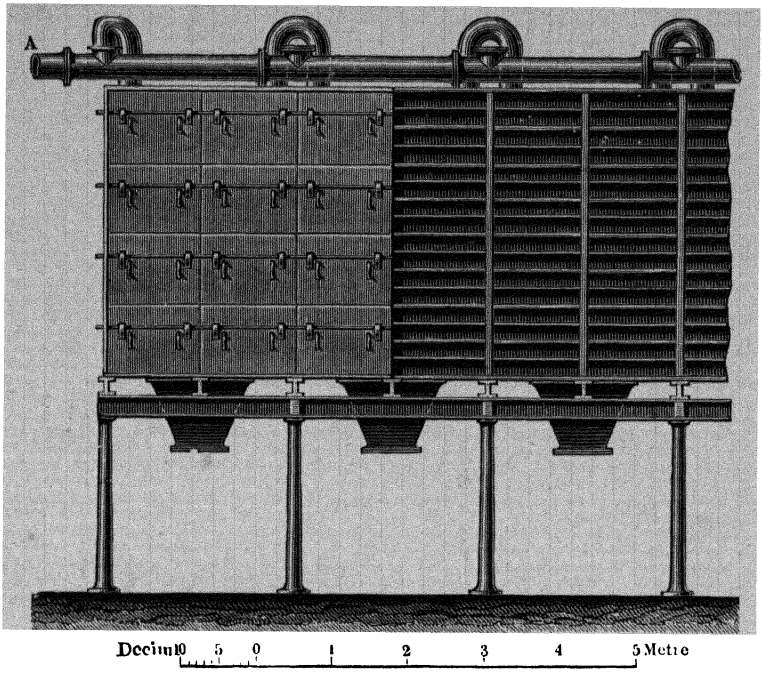


FIG. 130

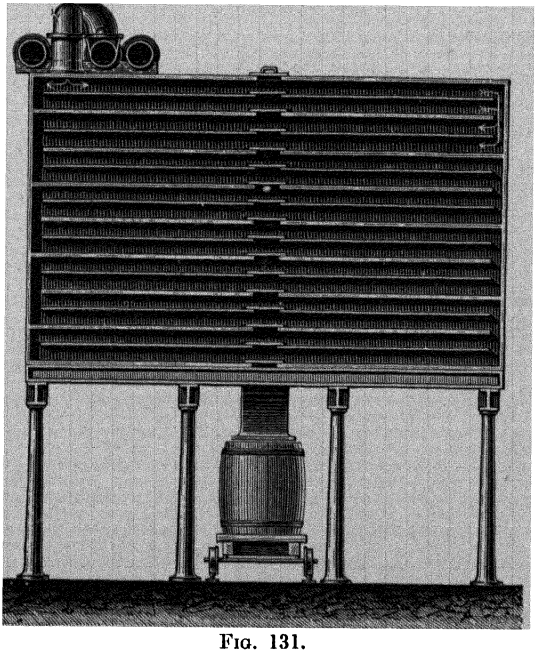


FIG. 131.

A different form of bleaching powder chamber was devised by Deacon for use with the specially weak chlorine made by his process. The principles of this process have already been referred to (Vol. I., p. 178). These chambers are shown in elevation and section in Figs. 130 and 131. The gas, containing only 5 to 7 per cent. chlorine, passes in through the tube (A), being drawn over the lime by means of exhausters. Each block, of which less than one half is shown in Fig. 130, is divided by vertical walls into fourteen sections; each section contains sixteen slate shelves 20 feet long by 4 feet wide, with a gap in the middle covered by a small loose piece, and the lime is spread on these shelves to the depth of about five-eighths of an inch. Part of the elevation shows the doors, which form the sides of the chamber, in position; the other part shows the arrangement of the shelves seen when the doors are down. The end section (Fig. 131) shows the mode in which the shelves are arranged and the way in which the chlorine is divided into streams during its passage downwards over the lime. The gas then passes upwards over a similar set of shelves, and thence by the gas mains into the next chamber. When the lime in one chamber has come up to strength, the small plates on each shelf are removed, and the bleaching powder is pushed into a barrel placed on a tramcar beneath, and in this way the product is easily packed.

During recent years several forms of continuous mechanical apparatus have been successfully adopted, in which the slaked lime is transported in a continuous stream by single or double conveyors in an opposite direction to the stream of chlorine, the finished bleaching powder being delivered direct into casks, thus avoiding the disagreeable task of hand packing.[1]

A complete analysis by Pattinson of good commercial chloride of lime giving 36·00 per cent. available chlorine shows the constituents to be:

Odling's calcium chloro-hypochlorite, $Ca\begin{cases}Cl\\OCl\end{cases}+H_2O$.	73·65
Ditto, but decomposed into the chlorate mixture $5CaCl_2 + Ca(ClO_3)_2$	0·67
Calcium hydroxide, $Ca(OH)_2$ . . . . 20·17 . .	22·55
Impurities from all the slaked lime employed, 2·38 . .	
Moisture originally present as such in the slaked lime or in the chlorine employed.	3·13
	100·00

[1] Mond, *Nature*, 1896, **54**, 477.

By the Griesheim-Elektron process a product containing 80–90 per cent. of active chlorine is produced. Milk of lime is saturated with chlorine, filtered and the solution rapidly evaporated in a vacuum. The calcium hypochlorite crystallises out and on drying in a vacuum a stable salt is obtained.[1]

Properties of Bleaching Powder.—Commercial bleaching powder contains on an average 35 to 37 per cent. of available chlorine, and forms a white powder, which absorbs moisture and carbon dioxide on exposure to the air. When kept, it undergoes a very slow and steady decomposition, for reasons which are at present undetermined; in closed bottles this decomposition is sometimes such as to burst the bottle by the gases evolved. When added to water it is apt to clot together into lumps, but by agitation it forms a creamy liquid which deposits a large amount of insoluble slaked lime, etc., whilst the clear solution contains calcium chloride, hypochlorite, chlorate, and some hydroxide.

When a slight excess of acid is added to a solution of bleaching powder, the whole of the chlorine is evolved in the free state, the hydrochloric acid and hypochlorous acid first formed acting on one another in the manner already described (Vol. I., p. 350):

$$CaCl_2 + Ca(OCl)_2 + 2H_2SO_4 = 2CaSO_4 + 2HCl + 2HClO,$$
$$2HCl + 2HClO = 2Cl_2 + 2H_2O.$$

Bleaching Processes.—Bleaching powder is largely employed in the bleaching of cotton, linen, and paper pulp. The methods employed are often exceedingly complex, varying not only with the nature of the material to be bleached, but also with the use to which the bleached goods are afterwards to be put, but in all cases the main impurities in the fibre are removed not by hypochlorite, but by treatment with an alkali. Thus by hot alkali solutions—*i.e.*, sodium carbonate or calcium hydroxide, but best of all caustic soda—various waxy, fatty, resinous, gummy, mucilaginous and colouring matters are extracted, and the fibre is thereby greatly lightened in colour, the loss in weight being about 8 per cent. in the case of cotton, 25 per cent. in that of flax, and 50 per cent. in that of esparto grass. The fibre is then treated with hypochlorite solution, which is rapidly converted into the chloride by acting upon certain of the residual organic impurities: this action is so energetic that if not properly controlled it may oxidise the cellulose itself, rendering the fibre brittle and

[1] German Patent, 188524, 1906.

useless. Strong solutions of bleaching powder are therefore never employed, and often very weak ones are used, containing as little as 0·1 per cent. of available chlorine. Such a solution may be allowed to act for a few hours, when the final whitening is frequently obtained by transferring the goods to a very dilute acid bath to remove basic colouring matters, and as chlorine is liberated from the residual hypochlorite in the fibre, the process is known by the workmen as a "stinking sour." To obtain brilliant whites it is often necessary to repeat the operations several times, and this is particularly necessary in the case of linen.

The amount of available chlorine in bleaching powder is usually ascertained by adding to a solution of a known quantity a standard solution of sodium arsenite until the liquid no longer turns iodised starch paper blue, the arsenite being thus oxidised to arsenate. Precautions must be taken to obtain a fair average sample for analysis; for this purpose many samples must be taken from various places and packages, taking care to obtain due proportions of fine powder and of lump, and these must be mixed without undue exposure to the air.

Calcium Chlorate, $Ca(ClO_3)_2$, is formed by leading chlorine into hot milk of lime, but cannot be obtained pure in this manner. The pure salt is obtained by neutralising calcium carbonate with chloric acid, and crystallises with $2H_2O$ in rhombic prisms which deliquesce in moist air; 100 parts of water at 18° dissolve 177·8 parts of $Ca(ClO_3)_2$.

Calcium and Sulphur.

256 *Calcium Monosulphide*, CaS, is obtained by heating the sulphate with powdered coal, or by leading sulphuretted hydrogen or a mixture of carbon dioxide and the vapour of carbon disulphide over incandescent lime (Schöne). It forms a yellowish-white mass insoluble in water, which in moist air smells of sulphuretted hydrogen. When prepared in the electric furnace it is formed in cubes which have the sp. gr. 2·4—2·5.[1]

Calcium monosulphide is luminous in the dark after it has been exposed to light. This fact was noticed in the year 1750 by Marggraf, who obtained the sulphide by calcining gypsum with combustible matter. In 1768 Canton described a method of producing the same effect by igniting calcined oyster-shells

[1] Müller, *Centr. Min.*, 1900, 178.

with sulphur; hence this substance was long known under the name of Canton's phosphorus. It is probable that the pure sulphide is not itself phosphorescent but is rendered so by the presence of traces of other substances. Thus the addition of traces of bismuth and sodium compounds renders the pure sulphide strongly phosphorescent, but not the addition of bismuth compounds alone.[1]

Calcium sulphide is the chief constituent of alkali-makers' waste (p. 314).

Calcium Hydrosulphide, $Ca(SH)_2$, is best obtained by passing sulphuretted hydrogen into a cream of precipitated calcium hydroxide and rather less than four parts of water: it crystallises with $6H_2O$ in colourless prisms, which readily melt in their water of crystallisation.[2] It decomposes when warmed in a stream of sulphuretted hydrogen, yielding calcium sulphide, and is also decomposed by carbon dioxide with evolution of sulphuretted hydrogen and formation of calcium carbonate. It is sometimes used as a depilatory in tan works.

Calcium Hydroxyhydrosulphide, Ca(SH)OH, is obtained by the action of a small quantity of water or of calcium hydroxide on the hydrosulphide,[3] and by the union of water and calcium sulphide, and forms crusts of small, colourless, four-sided needles; it readily dissolves in water, but the solution decomposes rapidly into calcium hydroxide and calcium hydrosulphide, the former separating out as a white precipitate. It combines with carbon disulphide, forming the *basic thiocarbonates*, $Ca(OH)_2,2CaCS_3,7H_2O$ and $2Ca(OH)_2,CaCS_3,10H_2O$, and it appears not unlikely that this substance takes part in the removal of carbon disulphide from coal gas in the lime purifiers (Vol. I., p. 884).

Several other hydroxyhydrosulphides have been prepared, some of which crystallise well, but their constitution is at present doubtful. All these hydrosulphides are oxidised by moist air with formation of calcium sulphite, thiosulphate, or sulphate and usually with separation of free sulphur.

Calcium Disulphide, CaS_2, is obtained in the form of yellow crystals, containing $3H_2O$, when milk of lime is boiled with excess of sulphur and the filtered solution allowed to cool.

Calcium Pentasulphide, CaS_5, is obtained by boiling calcium

[1] de Visser, *Rec. trav. chim.*, 1901, **20**, 435; 1903, **22**, 133. But see Breteau, *Compt. rend.*, 1915, **161**, 732; where a method of preparing phosphorescent calcium sulphide containing only bismuth is described.

[2] Divers and Shimidzu, *Journ. Chem. Soc.*, 1884, **45**, 270.

[3] Divers and Shimidzu, *loc. cit.*

sulphide or hydroxide with excess of sulphur for a long time, and forms a reddish-yellow mass, which, if treated with sulphuretted hydrogen in solution, undergoes the reverse reaction, and is converted into calcium hydrosulphide and sulphur. A lime-sulphur wash, used extensively as a fungicide, is prepared by boiling together 1 part of quicklime, 2 parts or more of sulphur and 10 parts of water. It contains mainly the thiosulphate and polysulphides of calcium together with some sulphate and sulphite.[1]

Calcium Sulphite, $CaSO_3$, is obtained by mixing a solution of a calcium salt with that of a normal sulphite. It forms a white powder which is only soluble to the extent of 0·043 gram in a litre of water at 18°.[2] It is easily soluble in sulphurous acid, and if this solution be allowed to stand exposed to the air, six-sided needles separate out which have the composition $CaSO_3,2H_2O$. A solution of this salt in aqueous sulphurous acid, which probably contains *calcium bisulphite*, $Ca(HSO_3)_2$, is met with in commerce, under the name of bisulphite of lime. It is obtained by passing sulphur dioxide into milk of lime, and is used by brewers as a mild antiseptic, and for cleansing and sterilising casks, etc. It is also used in the manufacture of wood pulp in and the purification of sugar.

When a nearly neutral solution of calcium bisulphite is electrolysed, *calcium hyposulphite*, CaS_2O_4, crystallises out at the cathode in silky needles, a yield of 30—40 per cent. of the theoretical amount being obtained.[3] This salt is easily oxidised in the air, and has been proposed as a decoloriser and antiseptic for solutions of cane-sugar.

Calcium Sulphate, $CaSO_4$, occurs in nature in the anhydrous state in the mineral anhydrite which is often found in limestone rocks, or together with deposits of common salt. More generally, however, the substance occurs as gypsum, $CaSO_4,2H_2O$, found frequently in large monoclinic crystals and known as selenite. The crystalline form of selenite is shown in Figs, 132, 133. The crystals are frequently twinned, and then exhibit the peculiar form shown in Fig. 134. It also occurs as fibrous gypsum or satin-spar, and as crystalline gypsum or alabaster, and has the specific sp. gr. 2·32.

[1] Auld, *Journ. Chem. Soc.*, 1915, **107**, 480.

[2] Weisberg, *Bull. Soc. chim.*, 1896, [3], **15**, 1247.

[3] Elbs and Becker, *Zeit. Elektrochem.*, 1904, **10**, 361; Frank, *Zeit. Elektrochem.*, 1904, **10**, 450.

This substance was known from early times as a mineral closely resembling calc-spar, because, like the latter, it became brittle on burning. In 1746 Pott described these two substances as being different earths, and stated that some chemists assumed that the substance artificially produced by the union of sulphuric acid with lime was gypsum, and termed it *gypsum artefactum;* in 1750 Marggraf showed that these two substances were identical.

Calcium sulphate also forms a hemihydrate, $2CaSO_4,H_2O$, first observed by Johnston[1] as a crystalline deposit in a boiler working at two atmospheres pressure. It is formed when gypsum is heated to 120—130°, and can be prepared pure by heating 20 grams of precipitated gypsum on the water-bath for one hour with 50 c.c. of nitric acid of sp. gr. 1·4, draining and drying. It has the sp. gr. 2·75.

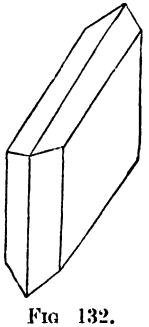


FIG 132.

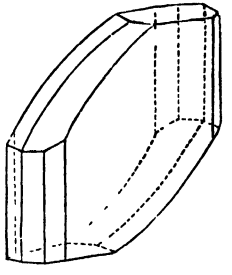


FIG. 133.

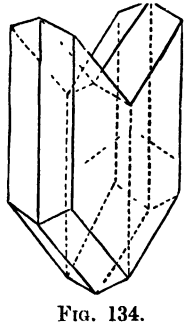


FIG. 134.

The anhydrous sulphate itself occurs in at least two modifications. Natural anhydrite is almost insoluble in water and the same form can be obtained by heating gypsum strongly. The second modification, which is known as soluble anhydrite, is obtained by completely dehydrating gypsum at 60—90° in a vacuum over phosphoric oxide, and sets with water even more rapidly than the hemihydrate. The relations between these forms, and the temperatures of transition of one into the other are extremely difficult to determine, on account of the slow rate at which the various changes occur, and our knowledge of them is mainly due to the elaborate investigations of van't Hoff.[2]

The transition temperatures between gypsum and the other

[1] *Phil. Mag.*, 1838, **13**, 325.

[2] van't Hoff, Armstrong, Hinrichsen, Weigert, and Just, *Zeit. physikal. Chem.*, 1903, **45**, 257. See also Cameron, *J. Physical Chem*, 1901, **5**, 556; Moye, *Chem. Zeit.*, 1906, **30**, 544; Cameron and Bell, *J. Amer. Chem. Soc.*, 1906, **28**, 1220.

varieties are as follows, the vapour pressure of the system at the temperature of transition being also given:

	Temp.	Vapour pressure.
(1) Gypsum—Natural anhydrite . .	63·5°	175 mm.
(2) Gypsum—Soluble anhydrite . . .	93°	588 ,,
(3) Gypsum—Hemihydrate	107°	971 ,,

These temperatures are considerably lowered by the presence of salts such as sodium chloride, magnesium chloride, etc.

The conversion of the hemihydrate to soluble anhydrite is readily reversible at 110° according to whether the surrounding atmosphere is dry or humid, and ordinary plaster of Paris consists chiefly of the hemihydrate.[1]

The solubilities of all these modifications and hydrates are also different, soluble anhydrite and the hemihydrate being the most soluble and the natural anhydrite the least soluble. The solubility of natural gypsum according to Hulett and Allen [2] is as follows, in grams of $CaSO_4$ per 100 c.c. of solution, a maximum of solubility occurring at 40°; the solubility, however, is greatly affected by the size of the particles which are in contact with the solution:

Temp.	0°	10°	25°	35°	40°
	0·1759	0·1929	0·208	0·2096	0·2097
	45°	65·3°	75°	100°	
	0·2084	0·1932	0·1848	0·162	

According to Marignac the solubility of the hemihydrate at 25° is about one part in 100 of water.

In presence of many other salts calcium sulphate dissolves more freely, probably in some cases owing to the formation of double salts. Thus according to Anton 1 part of gypsum dissolves in 122 parts of a saturated solution of sodium chloride.[3] Gypsum is tolerably soluble in boiling hydrochloric acid and in nitric acid, and separates out from the acid solution on cooling in glittering silky needles. When heated with sulphuric acid to 100° it is changed into a porous mass, of which a part dissolves and separates out again on cooling. This consists of

[1] Gallo, *Gazz.*, 1914, **44**, 1, 497; Gaudefroy, *Compt. rend.*, 1914, **158**, 2006; **159**, 263.

[2] *J. Amer. Chem. Soc.*, 1902, **24**, 667.

[3] See also Cameron and Brown, *J. Physical Chem.*, 1905, **9**, 210; Sullivan, *J. Amer. Chem. Soc.*, 1905, **27**, 529; Bell and Taber, *J. Physical Chem.*, 1906, **10**, 119.

microscopic prisms, which have the composition $CaSO_4,H_2SO_4$; it is decomposed by water into its two constituents. Gypsum dissolves very readily in a solution of sodium thiosulphate.

When gypsum is heated at about 120—130°, it loses water and is converted into burnt gypsum or plaster of Paris. This well-known substance when mixed with water combines with it, evolving heat, and subsequently solidifies, taking the form of the vessel in which it is contained. It is therefore largely used for ornamental plaster work, for making plaster casts, and as a cement. It was formerly supposed that the plaster consisted of anhydrous calcium sulphate, and that the setting was brought about by the direct combination of this with two molecules of water, re-forming gypsum, but the researches of Le Chatelier [1] have shown that the properly burnt plaster still contains about 7 to 8 per cent. of water, and consists of the hemihydrate $2CaSO_4,H_2O$. When this is mixed with water, part of the hydrate, which is much more soluble than either the anhydrous salt or the hydrate with two molecules of water, dissolves in the water to form a saturated solution. This solution, however, is supersaturated with respect to the hydrate $CaSO_4,2H_2O$, and some of the dissolved salt crystallises out in this form, thus allowing the water to dissolve more of the hemihydrate; the same process is then repeated until the whole of the hemihydrate is converted into gypsum. The latter separates in long thin prisms which interlace to form the solid cake which remains. According to Rohland, however, the hardened mass, after setting, must be regarded as a solid solution of the calcium sulphate in water.[2]

If the gypsum be heated too strongly in the burning it only takes up water very slowly and is said to be dead-burnt; this is due to the whole of the water having been driven off, leaving the anhydrous calcium sulphate. Such plaster when exposed to moist air gradually takes up 6—7 per cent. of water, and if then mixed with water it sets slowly, but with a normal hardness.

Another form of the anhydrous sulphate is made by heating gypsum above the temperature of decomposition of the hemihydrate, but below that of the " dead-burnt " sulphate. This is known as hydraulic or Estrich gypsum, and when mixed with water only hardens after an interval of days or weeks. It occurs in pseudomorphs after the hemihydrate, and appears to be

[1] *Ann. des Mines*, 1887, 345.
[2] *Zeit. anorg. Chem.*, 1904, **40**, 182.

intermediate in properties between the soluble and insoluble or " dead-burnt " anhydrite (van't Hoff).[1]

An artificial calcium sulphate is now prepared by precipitating a solution of calcium chloride with dilute sulphuric acid, and is sold under the name of pearl hardening or annaline. It is used by paper-makers as a filling for writing paper. In addition to its employment for plaster work and casts, gypsum is also used as a manure.

Calcium Potassium Sulphate, $CaSO_4,K_2SO_4,H_2O$.—This compound is formed when the solutions of the two salts are mixed together (H. Rose), and occurs as the mineral syngenite. When an intimate mixture of equal weights of the anhydrous salts is stirred up with less than its weight of water, the mass becomes suddenly so solid that it cannot be poured out of the vessel. If four to five parts of water are employed, the solidification takes place somewhat more slowly but still more rapidly than in the case of gypsum alone. Casts made of this mixture possess a polished surface, and are in this respect superior to those made of gypsum.

Double salts, $K_2SO_4,2CaSO_4,3H_2O$ and $K_2SO_4,5CaSO_4,H_2O$, are also known.[2]

Calcium Sodium Sulphate, $CaSO_4,Na_2,SO_4$, occurs in nature as the mineral glauberite. Sodium sulphate does not act upon plaster of Paris as potassium sulphate does. If, however, a mixture of one part of precipitated calcium sulphate and fifty parts of Glauber's salt be heated to 80° with twenty-five parts of water, a mass of needle-shaped crystals is obtained, which have the formula $CaSO_4,2Na_2SO_4,2H_2O$, and these when further heated are transformed into small crystals of glauberite (Fritzsche).

Calcium Thiosulphate, $CaS_2O_3,6H_2O$, is prepared by heating calcium sulphite with sulphur in water. It forms six-sided triclinic prisms, soluble in their own weight of cold water. When the solution is heated to 60° the salt is decomposed with separation of sulphur. This salt is used in the production of antimony cinnabar, Sb_2OS_2.

[1] Compare Rohland, *Zeit. anorg. Chem*, 1903, **35**, 194; **36**, 332.

[2] van't Hoff, *Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 935; 1905, 305.

Calcium and the Elements of the Nitrogen Group and Boron.

257 *Calcium Nitride*, Ca_3N_2.—Calcium at a dull red heat combines vigorously with nitrogen, forming this compound, the metal becoming incandescent. The preparation is best effected in a nickel tube, the calcium being placed in a nickel boat or dish. The nitride forms brownish-yellow microscopic crystals, and has the sp. gr. 2·63 at 17°. It is decomposed by steam, forming ammonia and calcium hydroxide, and hence this compound supplies a means of converting atmospheric nitrogen into ammonia. It burns when heated in oxygen, and is readily reduced by hydrogen and attacked by the halogens, sulphur, and phosphorus.[1] The formation of this compound is utilised for the isolation of argon from the air (Vol. I., p. 950).

Calcium Nitrite, $Ca(NO_2)_2,4H_2O$, can only be obtained by metathesis between calcium chloride and silver nitrite.[2]

Calcium Nitrate, $Ca(NO_3)_2$.—The alchemist Baldewein, or Balduinus, first prepared this compound whilst searching for a method of absorbing the "Spiritus mundi." He dissolved chalk in nitric acid, and observing that the solid product became rapidly moist on exposure to air, concluded that this substance would prove to be of great power. In the year 1674 he noticed that the solid residue after being heated and then exposed to sunshine appeared luminous in the dark, and from this time the compound prepared as above was termed Baldwin's phosphorus. Calcium nitrate forms monoclinic crystals containing $4H_2O$, is very deliquescent, and dissolves readily in alcohol as well as in water. The anhydrous salt is a white porous mass, and is often found as an efflorescence on the walls of stables and other places through which urine and other organic liquids percolate. The name lime-saltpetre, or wall-saltpetre, has been given to this salt, which was formerly universally employed for the artificial preparation of nitre.

Large quantities of this salt are now made in Norway from atmospheric nitrogen by an electrical process.[3] In the form of a basic salt with lime it acts as an excellent fertiliser.

Only one definite basic nitrate exists, $Ca(NO_3)_2,CaO$, but this

[1] Moissan, *Compt. rend.*, 1898, **127**, 497.

[2] Oswald, *Ann. Chim.*, 1914, [9], **1**, 32.

[3] Norton, *Utilisation of Atmospheric Nitrogen* (U.S. Dept. Commerce and Labor: Washington, 1912).

forms a series of hydrates with $\frac{1}{2}$, 1, 2, 3 and 4 molecules of water.[1]

Calcium Phosphide.—An impure phosphide is prepared by heating lime to a moderate red heat in a Hessian crucible, through the lid of which passes a piece of gas pipe reaching to the bottom, and sufficiently wide to allow of the passage of sticks of phosphorus, which are added in pieces weighing about 15 grams.[2] It forms a very hard, dark mass which is decomposed by water with formation of liquid hydrogen phosphide, P_2H_4, and is employed for the preparation of this substance (Vol. I., p. 641). A crystalline phosphide, Ca_3P_2, corresponding in composition with the nitride, is formed when calcium phosphate is reduced by lampblack in the electric furnace, and the amorphous compound is formed when phosphorus vapour is passed over heated calcium. It yields pure phosphine with water, and burns in oxygen at 300°.[3]

Phosphates of Calcium.—The phosphates of calcium are all decomposed by water, the solid residue in contact with the solution being an equilibrium mixture, the composition of which depends on the concentration of phosphoric acid and calcium in the solution. Thus at 25°, the monocalcium and dicalcium salts can exist together in equilibrium with a solution containing 77 grams of CaO and 317 grams of P_2O_5 per litre. With a greater proportion of acid the monocalcium salt alone is stable, with a lower proportion, the dicalcium salt. When the concentration of acid is still further diminished the solid in equilibrium is either *tricalcium phosphate*, $Ca_3(PO_4)_2$, or *hydroxyapatite*, $3Ca_3(PO_4)_2,Ca(OH)_2$. The latter salt is the only stable phase in faintly acid, neutral, or alkaline solutions and therefore of practical importance as probably the only phosphate of calcium which exists under normal soil conditions.[4]

When the pure salts are treated with water, the dicalcium salt is decomposed to a smaller extent than either the mono- or tri-calcium salt.[5]

[1] Bassett and Taylor, *Journ. Chem. Soc.*, 1914, **105**, 1926. Compare Cameron and Robinson, *J. Physical Chem.*, 1907, **11**, 273.

[2] Gattermann and Haussknecht, *Ber.*, 1890, **23**, 1176.

[3] Moissan, *Compt. rend.*, 1899, **128**, 787; Renault, *ibid.*, 883.

[4] Bassett, *Zeit. anorg. Chem.*, 1907, **53**, 34, 49; 1908, **59**, 1; *Journ. Chem. Soc.*, 1917, **111**, 620. Compare Cameron and Seidell, *J. Amer. Chem. Soc.*, 1905, **27**, 1503; Cameron and Bell, *ibid.*, 1905, **27**, 512; 1906, **28**, 1222.

[5] Cameron and Seidell, *J. Amer. Chem. Soc.*, 1904, **26**, 1454. See also Rindell, *Compt. rend.*, 1905, **134**, 112; Buch, *Zeit. anorg. Chem.*, 1907, **52**, 325.

Normal Calcium Orthophosphate or *Bone-phosphate*, $Ca_3(PO_4)_2$. This compound occurs together with calcium fluoride in apatite, $3Ca_3(PO_4)_2,CaF_2$ or $Ca_3(PO_4)_2,Ca_2(PO_4)F$, in which a portion of the fluorine is sometimes replaced by chlorine. Phosphorite and estramadurite are massive varieties of apatite which occur in Estramadura, in Spain. Coprolites, which are found in many sedimentary deposits, and doubtless have an animal origin, consist mainly of calcium orthophosphate. Another pure form of the same compound is the mineral osteolite, and it also occurs as sombrerite, a mineral found on some of the small islands of the Antilles, especially Sombrero, and containing crystals of the mineral ornithite, $Ca_3(PO_4)_2,2H_2O$. Calcium phosphate is also the chief inorganic constituent of bones, forming about 80 per cent. of burnt bones; the other constituents being magnesium phosphate, calcium carbonate, and calcium fluoride.

Pure calcium phosphate is obtained as a white precipitate by adding an excess of common sodium phosphate to an ammoniacal solution of chloride of calcium. It is nearly insoluble in water, but is decomposed by long contact with boiling water into an insoluble basic residue and a soluble acid salt. This decomposition takes place slowly in the cold, and for this reason an exact determination of the solubility of the orthophosphate is impossible.[1] Calcium orthophosphate dissolves readily in water containing ammoniacal salts, sodium nitrate, common salt, and other salts. It is also readily soluble in all acids, even in aqueous carbonic acid. This explains the absorption of the calcium phosphate by the roots of plants; it is then accumulated in the seeds and fruits.

Dihydrogen Dicalcium Orthophosphate, $H_2Ca_2(PO_4)_2$, or $HCaPO_4$.—When a solution of calcium chloride is mixed with one of ordinary sodium phosphate, a white crystalline precipitate of the above compound containing $4H_2O$ is thrown down. This compound occurs in urinary concretions, and is sometimes deposited from urine in microscopic crystals grouped in rosettes or stellæ, and known as stellar phosphate. It is scarcely affected by cold water.

Tetra-hydrogen Calcium Phosphate, $H_4Ca(PO_4)_2$.—This salt is obtained in rhombic tablets by dissolving either of the foregoing salts in the requisite quantity of phosphoric acid and allowing the solution to evaporate spontaneously, or by crystallisation

[1] R. Warington, *Journ. Chem. Soc.*, 1873, **26**, 983.

at 160° of a solution of calcium carbonate in orthophosphoric acid in which the ratio $P_2O_5 : CaO$ is 4 : 6.[1] If this is treated with cold water it is partially decomposed into the hydrated dicalcium salt, whilst with boiling water the same salt is produced in the anhydrous form (Erlenmeyer).[2]

Superphosphate of Lime.—A mixture of the last mentioned compound and calcium sulphate is manufactured on the large scale, and known in commerce as *superphosphate of lime.* It is usually prepared by acting on bone-ash, coprolites, phosphorites, or other form of mineral phosphate with two-thirds of its weight of sulphuric acid. It seems probable [3] that the principal reaction is best represented by the equation—

$$5Ca_3(PO_4)_2 + 11H_2SO_4 \longrightarrow 4CaH_4(PO_4)_2 + 2H_3PO_4 + 11CaSO_4.$$

This mixture is largely employed as a manure, especially for wheat crops. About 900,000 tons of superphosphates were manufactured in Great Britain in 1913, but production was restricted in the period 1914—1918, and neither production nor price is yet stabilised. The present price (1922) is approximately 3*s.* per unit (*i.e.*, per 1 per cent. per ton.)

Calcium Ammonium Phosphate, $Ca(NH_4)PO_4,7H_2O$, is precipitated when an ammoniacal solution of ammonium phosphate is added to a solution of calcium chloride in citric acid. It is readily decomposed by water.[4]

Calcium Hypophosphite, $Ca(PO_2H_2)_2$, is used in medicine and is prepared by boiling phosphorus with milk of lime. On evaporating the clear solution, the salt crystallises in bright, six-sided monoclinic prisms.

Calcium Arsenide, Ca_3As_2, corresponds in composition with the phosphide and is obtained in a similar manner. It is a transparent, reddish-brown, crystalline mass of sp. gr. 2·5, and is decomposed by water with production of arsine and calcium hydroxide. When heated in excess of oxygen it burns brilliantly, forming calcium arsenate,[5] which can be obtained as the dihydrate, $Ca_3(AsO_4)_2,2H_2O$, by the interaction of alkaline solution of calcium chloride and disodium hydrogen arsenate.

Calcium Orthoarsenate, $CaHAsO_4,H_2O$, identical with the mineral *haidingerite*, results from interaction between arsenic

[1] Bassett, *Proc. Chem. Soc.*, 1906, 315.
[2] See also Viard, *Compt. rend.*, 1898, **127**, 178.
[3] Aita, *Annali. Chim. Appl.*, 1918, **10**, 45.
[4] Lasne, *Bull. Soc. chim.*, 1902, [3], **27**, 131.
[5] Lebeau, *Compt. rend.*, 1899, **128**, 95.

oxide, lime and water at 35° C., when the concentration of arsenic oxide in the solution is over 27·5 per cent. With less arsenic oxide, monocalcium orthoarsenate, $CaH_4(AsO_4)_2$ results.[1] It can also be prepared by pouring an acidified solution of calcium chloride into a slightly acid solution of disodium hydrogen arsenate. It retains water of crystallisation when dried at 100°, but can be dehydrated at 175°.[2]

Calcium Boride, CaB_6, is obtained by the reduction of calcium borate with aluminium and carbon in the electric furnace. It forms a black powder consisting of transparent microscopic crystals of sp. gr. 2·33, which are sufficiently hard to scratch rubies. It is not affected by water, but is readily attacked by chlorine at a red heat and by many oxidising agents, and burns when strongly heated in the air.[3]

Calcium and Carbon.

258 *Calcium Carbide*, CaC_2.—This compound was obtained by Moissan by heating pure lime and sugar charcoal to a very high temperature in an electric furnace:

$$CaO + 3C = CaC_2 + CO.$$

It is best prepared pure by passing acetylene into liquid ammonia containing metallic calcium [4] and heating the resulting compound, $CaC_2,C_2H_2,4NH_3$, or by the action of acetylene on calcium hydride, the compound CaC_2,C_2H_2, being first formed.[5]

It forms colourless transparent crystals,[6] melts at a higher temperature than platinum, and is decomposed by water with formation of the hydrocarbon acetylene:[7]

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2.$$

Chlorine has no action on calcium carbide, but the latter slowly reacts with liquid bromine to give hexabromoethane and calcium bromide.[8]

Calcium carbide is formed in small amount during the electrolysis of calcium chloride or fluoride with a carbon cathode. It acts as a strong reducing agent.

[1] C. N. Smith, *J. Amer. Chem. Soc.*, 1920, **42**, 259.
[2] Robinson, *J. Agric. Res.*, 1918, **13**, 281.
[3] Moissan and Williams, *Compt. rend.*, 1897, **125**, 629.
[4] Moissan, *ibid.*, 1898, **127**, 911.
[5] *Ibid*, 1903, **136**, 1522.
[6] *Ibid.*, 1898, **217**, 917.
[7] *Ibid.*, 1894, **118**, 50.
[8] Barnes, *Chem. News*, 1919, **119**, 260.

Calcium carbide containing about 80 per cent. of the pure substance is manufactured on a very large scale by heating a mixture of limestone with coke or small coal in an electric furnace, the product having a greyish-black appearance. The chief impurities of this material are sulphide, phosphide, and silicide of calcium, the silicides of carbon and iron, and graphite.[1] It is employed for the preparation of acetylene for lighting purposes, the illuminating power of this gas being 12 to 15 times greater than that of ordinary coal-gas. Theoretically 1 kilo.

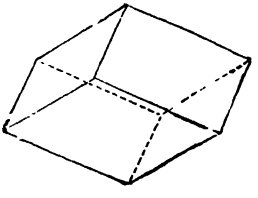


FIG. 135.

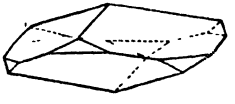


FIG. 136

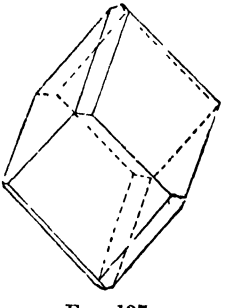


FIG. 137.

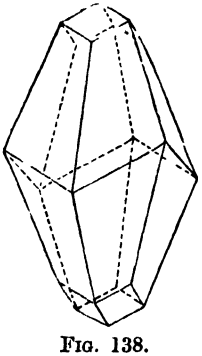


FIG. 138.

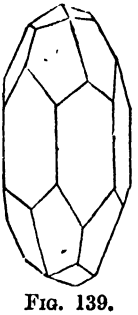


FIG. 139.

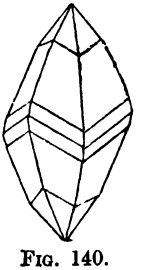


FIG. 140.

should yield 349 litres of acetylene. The commercial product rarely yields more than 300 litres. Calcium carbide is also used for manufacturing calcium cyanamide (p. 581).

Calcium Carbonate, $CaCO_3$.—This compound occurs widely distributed and in enormous masses in nature, forming whole mountain ranges, being found as limestone of various kinds, marble, calc-spar, and chalk. It also forms the greater part of egg shells, shells of mollusca and coral, and is contained together with calcium phosphate in burnt bones. Calcium carbonate is

[1] Le Chatelier, *Bull. Soc. chim.*, 1897, [3], **17**, 793; Moissan, *ibid.*, **21**, 865.

dimorphous: it exists in the first place as *calc-spar*, which has a specific gravity varying from 2·70 to 2·75, and crystallises in forms of the hexagonal system (p. 201). Some of the more important of these are seen in Figs. 135—143, a common twin

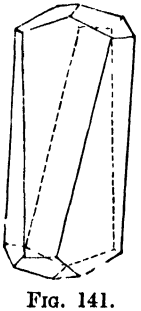


FIG. 141.

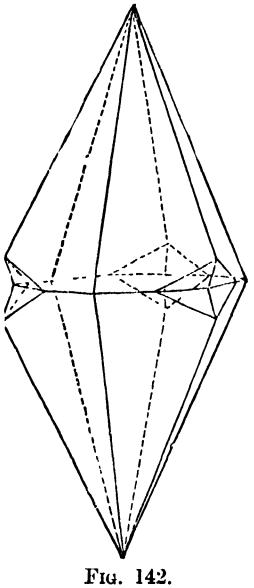


FIG. 142.

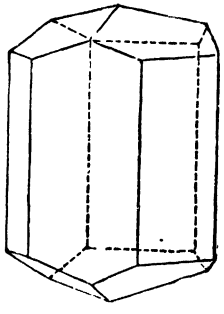


FIG. 143.

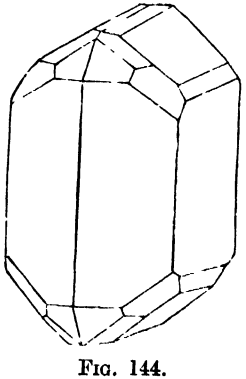


FIG. 144.

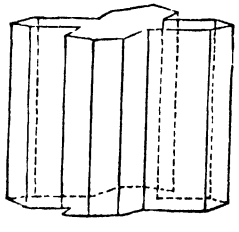


FIG. 145.

crystal being shown in Fig. 142. The primary form, Fig. 135, is a rhombohedron having angles of 104°5′ and 74°5′. The second form of calcium carbonate is known as *aragonite*, having a specific gravity of from 2·92 to 3·28, and crystallising in the form of rhombic prisms, Fig. 142 (Class 8, p. 209). Another crystalline form often exhibited by aragonite is that of the

penetration twins shown in Fig. 145. A distinction between the two minerals was first drawn by Werner in 1788, and Haüy showed somewhat later that they crystallised in two distinctly different forms. For many years this difference was believed to be due to the presence of strontia in aragonite, and it was not until 1819, when Mitscherlich discovered the law of dimorphism, that it was satisfactorily understood.

When a calcium salt is precipitated by the carbonate of an alkali metal, or when carbon dioxide is passed through lime water, the precipitate which falls down is at first flocculent and amorphous, but gradually becomes crystalline, forming either calcite or aragonite, according to the temperature of precipitation and the nature and concentration of the calcium salt and of the alkali carbonate used.[1] That formed by passing a small quantity of carbon dioxide through cold lime water soon becomes crystalline, the crystals being those of calc-spar, whilst aragonitic crystals are deposited when the lime water is hot (G. Rose). Calc-spar crystals are deposited when a solution of calcium carbonate in carbonic acid is allowed to evaporate spontaneously at the common temperature; but if the solution be heated to 90° aragonite crystals separate out. Another form of calcium carbonate,[2] *μ-calcite*, and a hexahydrate have been described.

At ordinary pressures, calcite is the stable form at all temperatures, and the change from aragonite to calcite which occurs at about 470° when aragonite is slowly heated [3] is accompanied by the evolution of a small amount of heat.[4]

One litre of water dissolves 14 milligrams of calcium carbonate at 18°. In presence of free ammonia or ammonium carbonate it is still less soluble. On the other hand, it readily dissolves in water containing carbonic acid in solution, this phenomenon having been first investigated by Cavendish in 1767. The increased solubility in presence of carbon dioxide probably depends on the formation of calcium bicarbonate, $Ca(HCO_3)_2$, which has been shown to exist [5] as a definite compound in aqueous solution.

The amount of calcium carbonate dissolved increases with the partial pressure of the carbon dioxide up to a certain maxi-

[1] Adler, *Zeit. angew. Chem.*, 1897, **14**, 431; Meigen, *Chem. Zentr.*, 1903, II, 1411; 1905, I., 1363; Linck, *Zeit. Kryst. Min.*, 1906, **41**, 633.

[2] Johnston, Merwin and Williamson, *Amer. J. Sci.*, 1916, [4], **41**, 473.

[3] Bocke, *Zeit. anorg. Chem.*, 1906, **51**, 244.

[4] Foote, *Zeit. physikal. Chem.*, 1900, **33**, 740.

[5] Cavazzini, *Gazz.*, 1916, **46**, [2], 122.

mum, which, according to Treadwell and Reuter,[1] is 1·15 grams of calcium carbonate per litre at 15°. When the partial pressure of the carbon dioxide is zero, the solution at 15° contains 0·385 gram of calcium bicarbonate (0·238 gram of calcium carbonate) per litre, there being no free carbon dioxide in the solution.

When calcium carbonate is heated to about 550° it commences to decompose into quicklime and carbon dioxide, but if the latter is not removed the decomposition is not complete, even if the temperature be raised considerably (p. 138). The pressure of carbon dioxide amounts to one atmosphere at 825°. Boiling water slowly dissociates the carbonate with loss of carbon dioxide.[2]

When heated to 1400° under a pressure of 30 atmospheres of carbon dioxide the carbonate sinters and partially decomposes but does not melt.[3]

Double Carbonates, $Na_2CO_3,CaCO_3,2H_2O$ and $K_2CO_3,CaCO_3$, have been prepared.[4]

Calcium Cyanamide, CN·NCa.—A crude calcium cyanamide is made by heating calcium carbide in atmospheric nitrogen, or by passing nitrogen over a mixture of lime and carbon at about 2000°.[5] The absorption of nitrogen by the carbide is greatly accelerated by the presence of calcium chloride[6] and similar substances. It forms a black powder and contains about 20 per cent. of nitrogen. This material is used as a fertiliser, the nitrogen becoming available for the plant in the form of ammonia; it is also used for the manufacture of ammonia, cyanides, urea, etc.

Calcium and Silicon.

259 *Calcium Silicide*, $CaSi_2$, was first prepared in an impure state by Wöhler[7] by the action of sodium on fused calcium chloride and silicon, but was obtained pure by Moissan and

[1] *Zeit. anorg. Chem*, 1898, **17**, 170, where the literature of the subject is quoted.

[2] Cavazzini, *Gazz.*, 1917, **47**, [2], 49.

[3] Bocke, *Zeit. anorg. Chem*, 1906, **50**, 247.

[4] Barre, *Compt. rend.*, 1912, **154**, 279.

[5] German Patent, 150878; *Journ. Chem. Soc.*, 1904, **86**, i., 562.

[6] German Patent, 163320 (Nov. 1, 1901). See also Bredig, *Zeit. Elektrochem.*, 1907, **13**, 69: and especially Kameyama, *J. Coll. Eng. Tokyo Imp. Univ*, 1920, **10**, 173, 209, 249.

[7] *Annalen*, 1863, **125**, 255; **127**, 258.

Dilthey,[1] who heated lime with an excess of silicon in a graphite tube placed in an electric furnace. It forms a crystalline mass of silver-grey colour and metallic lustre, is as hard as quartz, and has the sp. gr. 2·5. It is very slowly attacked by water, with evolution of pure hydrogen, but is rapidly acted on by concentrated hydrochloric acid, hydrogen and silicon hydride being evolved and silicon produced. It will burn in the oxy-hydrogen flame, is decomposed at a red heat by hydrogen chloride and by chlorine, and ignites spontaneously in fluorine.

Silicates of Calcium.—These compounds exist in most mineral silicates, many consisting mainly if not altogether of silicates of calcium and isomorphous metals. Among the more important of these are wollastonite, $CaSiO_3$; okenite, $CaH_2Si_2O_6,H_2O$; xonalite, $4CaSiO_3,H_2O$; apophyllite, $4H_2CaSi_2O_6,KF,4H_2O$. Le Chatelier[2] has also prepared the following anhydrous silicates artificially: $CaSiO_3$, Ca_2SiO_4, $Ca_3Si_2O_7$, and Ca_3SiO_5.

Calcium Sodium Silicate occurs in many localities in Scotland in the mineral pectolite, $4CaO,Na_2O,H_2O,6SiO_2$, which fuses easily to a transparent glass, and corresponds most nearly to ordinary lime-soda glass artificially produced.

Calcium Borosilicates occur native as danburite, $CaO,B_2O_3,2SiO_2$, and datolite, $CaO,B_2O_3,2SiO_2$, both of which melt readily to a clear glass, and are interesting in their relation to the boro-silicate glass hereafter described.

HYDRAULIC MORTARS AND CEMENTS.

260 *Hydraulic Mortars.*—When limestone contains about 8 per cent. and upwards of clay, the lime obtained from it yields a mortar which has the property of setting under water and is therefore known as *hydraulic mortar.* Such mortars may also be obtained from "fat" lime by mixing it with certain silicates; thus many Roman buildings are still standing which were constructed with a hydraulic mortar prepared from lime and a volcanic tufa termed *puzzuolana,* found at Puzzuoli, near Naples, and consisting of a mixture of various silicates. This mortar is described both by Pliny and Vitruvius. In place of puzzuolana baked clay and numerous other silicates may be employed.

Cements.—These substances, which differ from hydraulic mortars inasmuch as they do not contain any admixture of free

[1] *Compt. rend.*, 1902, **134**, 503. [2] *Ann. des Mines*, 1887, 345.

lime, are obtained either by the careful heating of argillaceous limestone, or by calcining a mixture of a suitable clay with the requisite quantity of limestone. *Roman cement*, originally manufactured by James Parker in 1796, was prepared in the former manner, the crude material employed being originally the clay nodules found on the coast of Essex and Kent, termed *septaria*. *Portland cement* is manufactured from limestone and clay, most of the manufacture in this country being carried out in the valley of the Medway, the river mud of which is very suitable for the purpose. The limestone and clay are ground together, and the mixture, termed "slip" or "slurry," is usually fed to long rotary kilns fired with powdered coal in which the slurry is first dried by the hot gases and finally raised to the clinkering temperature, some 1,400° C. In some cases the slurry is dried on drying beds by means of waste heat from the kilns, in which it is afterwards calcined either discontinuously, being mixed with coal or coke as in old-fashioned lime-kilns, or continuously in gas-fired kilns. The carbon dioxide is thus completely eliminated, and the lime produced combines with the clay, forming chiefly calcium silicate and aluminate. The cement clinker drawn from the kiln is broken up and then ground in centrifugal mills, ball mills or tube mills. The following analyses of English (1 and 2) and German (3 and 4) Portland cements give the composition of the material:

	1.	2.	3.	4.
Lime	59·06	55·06	62·81	57·83
Silica	24·07	22·92	23·22	23·81
Alumina	6·92	8·00	5·27	9·38
Ferric oxide	3·41	5·46	2·00	5·22
Magnesia	0·82	0·77	1·14	1·35
Potash	0·73	1·13	1·27	0·59
Soda	0·87	1·70		0·71
Calcium sulphate	2·85	1·75	1·30	1·11
Clay, Sand	1·47	2·27	2·54	—

When the powder is mixed with water to a paste heat is evolved, and the mixture if left at rest stiffens in a few hours and continues to harden, becoming solid within a day, and gaining considerable strength within a week; it does not, however, attain its full hardness for many months. Water only is required for the setting, and the water is all absorbed;

the cement will consequently set in a closed space or under water, and therefore goes by the name of Hydraulic Cement. It is much stronger than ordinary mortar, and is chemically a different body. The cement is used very largely in engineering and building works, both by itself and especially in conjunction with steel reinforcement, forming the so-called "reinforced concrete" or "ferro-concrete" structures: it is also employed for constructing water-tight tanks and chemical plant, and for making thin porous diaphragms for the electrolytic preparation of the alkalis.

The Setting of Cements.—The cause of the setting of cements has been the subject of much discussion; the explanations formerly given were very incomplete, but the researches of Le Chatelier[1] have thrown considerable light on the subject. He examined the action of polarised light on the crystalline substances which can be observed under the microscope in Portland cement, and compared these optical properties with those of a number of calcium silicates and aluminates which he prepared artificially. From these experiments he concluded that the chief constituents of cement are tricalcium orthosilicate, $3CaO,SiO_2$; tricalcium aluminate, $3CaO,Al_2O_3$; and tricalcium aluminoferrite, $3CaO,2(Al,Fe)_2O_3$, properly made cement containing no free lime. On the other hand, S. B. and W. B. Newberry[2] consider that the essential constituents of the cement are the tricalcium silicate and dicalcium aluminate. On the addition of water, the calcium compounds are decomposed with formation at first of free calcium hydroxide, and there are then formed crystalline hydrated calcium silicate and aluminate, the crystals of which form an interlaced mass, thus bringing about the setting of the cement. The setting takes place long before the formation of the hydrated crystals is complete, and as the action goes on the cement becomes continuously harder. There is therefore no such difference between the setting and hardening actions as in the case of ordinary mortar.

GLASS.

261 Ordinary glass consists essentially of a solid solution of the silicates of calcium and of the alkalis, although for special purposes the calcium silicates may be wholly or partly replaced by numerous other silicates, and phosphoric and boric acids

[1] *Annales des Mines*, 1887, 345. [2] *J. Soc. Chem. Ind.*, 1897, **16**, 887.

may be in part substituted for silicic acid. The subject of the composition and manufacture of glass may therefore be conveniently considered here.

Glass differs from the simple silicates of which it is composed, inasmuch as it is almost insoluble in water and acids. It fuses at a high temperature, and on cooling passes through all stages of viscosity until the solid state is reached, and whilst in the plastic condition can not only be shaped and cut, but may also be readily welded, the gentlest contact serving to effect a permanent junction. As glass may be varied in composition by imperceptible degrees, it is clear that it is not composed of single substances in a vitreous condition like fused silica, SiO_2, or fused boric anhydride, B_2O_3, but of a mixture of various substances such as $CaO,Na_2O,6SiO_2$ with Na_2SiO_3, or $CaSiO_3$ and SiO_2, forming together a complex solution the components of which have so feeble a rate of crystallisation that when cooled no separation takes place from the melt, which gradually becomes vitreous and solid, so that no definite solidifying or melting point is observed. Certain kinds of glass, however, contain components which have a quicker rate of crystallisation, and when these components separate the glass is said to devitrify. Cold glass can flow: thus a straight glass rod supported horizontally at the ends only, will in time take a permanent sag by its own weight. Probably, then, glass is really a super-cooled liquid.

Historical.—The manufacture of glass appears to have been discovered by the Egyptians, although the ancients themselves attributed the discovery of glass-making to the Phœnicians. Glass vessels of various sizes, both colourless and coloured, have been found in Egyptian tombs which belong to an age prior to that in which the Phœnicians occupied themselves with glass-making. Indeed, the latter nation appear rather to have been engaged in exporting the glass made in Egypt, and especially at Thebes, to different parts of the ancient world, than to have established any original manufacture of their own. In the tombs of Beni Hassan near Thebes, which were built more than 2000 years B.C., we find paintings representing Egyptians carrying on the processes of glass-blowing. From these, as well as from the glass vessels which are found in the tombs, it appears that the Egyptians were not only acquainted with the art of glass-making and of working in glass, but likewise with that of cutting and

colouring glass, by which they imitated precious stones. Thus an urn has been found made of white glass and ornamented with patterns in white and in light- and dark-blue glass showing the ring of Thoutmosis, who reigned in the 17th century B.C. Specimens illustrating all the stages of the process of glass-making, and dating from about 1400 B.C., have been found at Tell el Amarna.[1]

Aristophanes is the first Greek author who mentions glass (ὕαλος), *i. e.* a drop of rain, and in his *Clouds* he refers to a glass lens which was used as a burning-glass. Amongst Latin authors, Cicero is the first to mention Egyptian glass, and we find that at the time of Augustus the Egyptian glass was highly valued in Rome, so much so that when this emperor subdued Egypt (29 B.C.), a portion of the tribute was ordered to be paid in glass; this material afterwards being so highly valued by the Romans that Aurelius levied an import duty upon it.

Glass works were established in Italy, France, and Spain at an early date. These glass-houses, however, only manufactured common objects for everyday use, and it was not until after the introduction of Egyptian workmen to Rome that artistic glass-ware was made in Europe. This took place during the reign of Tiberius, and the art made such rapid progress that in the time of Nero, Roman glass rivalled in every respect the original Egyptian manufacture. According to Pliny, Egyptian soda and sand were employed in the manufacture of glass, and he remarks that in India rock-crystal was used for this purpose, and that in his time the material which was most highly valued for making glass was that which approached most nearly to this mineral. Manganese was used as a decolorising agent and the materials employed to produce coloured glasses were identical with those at present in use.

After the fall of the Western Empire the glass manufacture followed Constantine to Byzantium, and for five centuries the Eastern capital became a renowned seat of the glass manufacture. On the decay of the Empire of the East, the glass-makers wandered to various parts of Europe, many being attracted to the Venetian Republic. Here glass-making greatly flourished. As a protection against fire, it is said, the manufacture of

[1] For further information see Sir Gardner Wilkinson, *The Manners and Customs of the Ancient Egyptians*, vol. iii., p. 88, edit., 1837; and *Tell el Amarna*, by W. M. F. Petrie (London, 1894).

glass was removed in the year 1289 from the city of Venice to the adjacent island of Murano, and here during the 16th and 17th centuries the Venetian glass manufacture attained its highest development, the elaborate productions of Venetian art becoming famous throughout the civilised world. No fewer than 8,000 men were, it is stated, employed at that time in the manufacture, and so important did this branch of Venetian trade become, that strict laws were promulgated to prevent the secrets of glass-making from becoming known to foreign workmen, the supervision of the glass-houses being confided to the chief of the Council of Ten. The Venetian glass industry received, however, a check in the 17th century, from which it has recovered only in recent years.

In the early Middle Ages an independent manufacture of glass arose in Germany, and glass-painting is entirely of German origin; the manufacture of glass mirrors appears also to be a German invention. At first the glass was coated with a plate of metal, and it was not until the 15th century that the amalgam process was introduced. In addition to table-glass and window-glass, artificial gems, glass rings, and other objects of art were manufactured in Germany. Agricola, in his treatise *De re Metallica*, published in the year 1530, gives the first drawing of the interior construction of a glass-furnace, and in this work, as well as in Mathesius' *Sarepta or Bergpostill* (1564), we find explicit and interesting directions concerning the manufacture of glass as carried on in Venice, Germany, and Bohemia. In the last-named country the glass industry began to flourish in the 16th century, the purity of the quartz found there enabling manufacturers to produce the colourless glass for which the Bohemian glass-houses have long been famous and in which they still excel. When the Venetian glass manufacture fell into decay, Bohemian glass replaced Venetian, but in time the Bohemian manufacture again suffered a relapse, owing to the heavy import duties which were levied upon glass-wares as well as to the fact that other Governments held out inducements to the Bohemian workmen to settle in foreign countries; like the Venetian manufacture, it is only in recent years that the Bohemian glass industry has recovered its original position.

In the meantime many of the German princes patronised the glass-makers, and each became celebrated for some peculiar manufacture. Thus a glass-house at Potsdam was well known for its manufacture of ruby glass. This glass-house was established

under the direction of Joh. Kunkel, and in 1685 he published the first edition of his *Ars Vitraria Experimentalis*, in which he gave a translation of the collection of receipts published at Florence by Antonius Neri in 1612, and added to them remarks of his own and those of E. Merret.

Glass-works were also set up in France at an early date, but it was not until the 18th century, when workmen were introduced from Germany, that a pure kind of French glass-ware was made. De Nehou in 1688 erected a glass-works at Paris; this was afterwards removed to St. Gobain, where it soon became and still remains the most important plate-glass works in the world.

The first manufacture of glass of which we hear in England is that of window-glass established in the 15th century. The product cannot, however, have been very good, for in an old deed made in 1439 by the Countess of Warwick and a glazier of Westminster named Prudde, it is distinctly stipulated that no English window-glass is to be used. In the reign of Elizabeth, French artists were brought to London, and these carried on their trade of making window-glass at Crutched Friars in 1557, whilst flint-glass was first manufactured at a glass-house at Savoy House in the Strand. Mirror-glass, used for looking-glasses, coach-windows and similar purposes, was first manufactured in England at Lambeth by Venetian workmen brought over in 1670 by the Duke of Buckingham. The first large plate-glass works were established in 1771 at St. Helens under the name of the Ravenshead or the British Plate-glass Company.

The glass industry was introduced into Russia in the 17th and 18th centuries by German and Bohemian workmen. In the United States the same manufacture appears to have been established by Robert Hewes, a citizen of Boston, who erected a glass-house in the forest which existed in New Hampshire. The manufacture of Hewes does not seem to have been successful, and in 1800 another attempt was made to establish a glass-house at Boston, which also failed, until a German of the name of Lint took charge of the works in 1803, and the State of Massachusetts agreed to pay a bounty on all glass manufactured by him.

262 *The Materials used in Glass Manufacture.*—Silica is used in the forms of quartz, ignited flints, white sand, and ordinary sand. Potash is used in the form of purified potashes.

Soda was used, in the form of the native carbonate, trona, by the Egyptians, and in the form of artificial carbonate made from kelp by the early European glass-makers until 1831, when the cheaper soda ash made by the Leblanc process was used. More recently the soda has been added in the form of sulphate. Laxmann in 1764 tried to use the native sodium sulphate from Siberian salt-lakes, and in 1803 Baader succeeded in employing salt-cake made as in the Leblanc soda process; and when in 1656 Pélouze found a method of obtaining salt-cake practically free from iron, the use of salt-cake became almost general. Only the soda of the sodium sulphate mixes and combines with the other glass materials, carbon is specially added to reduce the sulphuric anhydride, and the gaseous products thus formed escape with the furnace gases; no practicable process has been suggested by which the sulphur compounds can be condensed and utilised. Lime is used in the form of calc-spar, marble, chalk, or limestone. Lead is used as red lead, white lead, and litharge.

It is almost impossible to obtain materials perfectly free from iron, and as ferrous oxide, even in small quantities, imparts to glass a deep green tint, whereas ferric oxide gives to the glass a light yellow colour, scarcely visible when present in small quantities, and carbon imparts to the glass a deep yellow or brown tint, a decolorising agent is generally added with the object of oxidising the carbon and neutralising the green colour due to ferrous iron; for this purpose manganese dioxide (pyrolusite), arsenious oxide, or saltpetre is used in the manufacture of lime glass, whilst red lead is employed in the manufacture of flint glass.

263 *Composition of Glass.*—The several kinds of glass commonly met with may be roughly divided according to their composition into four chief varieties:

I. Soda-lime glass; II. Potash-lime glass; III. Potash-soda-lime-iron glass, whose composition is regulated mainly by the cheapness of the raw materials available; and IV. Potash-lead glass. The following table shows the composition of these kinds of glass:

	SiO_2.	K_2O.	Na_2O.	CaO.	PbO.	$(Al,Fe)_2O_3$.
I.	71–78	0–2	12–17	5–15	—	1–4
II.	72–76	12–15	0–3	8–10	—	1
III.	60–65	3–5		18–20	—	6–11
IV.	40–50	8–11	—	—	38–53	1

I. *Soda-lime glass* is remarkable for the comparatively low temperature at which it fuses and the consequent ease with which it can be worked, and also for its cheapness, while it can be obtained as clear and colourless as the more expensive kinds of glass. Owing to the ease with which it may be blown, welded and otherwise worked with simple sources of heat, it is used for making glass tubes and laboratory apparatus. On the large scale it is employed as window-glass and plate-glass, and is then known as crown glass. Its specific gravity varies from 2·4 to 2·6, and its refractive index is about 1·530 for the D line.

II. *Potash-lime glass*, or *Bohemian glass*, possesses a high fusing point and requires a high temperature to work it; it is less acted upon by solvents than the other kinds of glass. The above properties fit it especially for the manufacture of chemical apparatus, and in particular for combustion tubes.

III. *Common* or *bottle glass* is distinguished by its yellow, brown, or green colour, due to the iron and other impurities present in the cheap raw materials used, such as common coloured sand, basalt, wood ashes, the residual alkaline and lime-salts from alkali works, gas works, and soap works, common salt, salt-cake, clay and rocks containing felspar. The iron silicate being comparatively easily fusible allows of the diminution of the more costly alkali silicates. This glass is more difficultly fusible than soda-lime glass, and is also more readily attacked by acids. A soda-lime-alumina glass is much used for beer, wine and spirit bottles, as it is mechanically strong and relatively insoluble.

IV. *Potash-lead glass*, *Flint glass*, *Crystal* or *Strass* is distinguished by being very fusible and easily worked, although the heating must be done in an atmosphere free from reducing gases, as these reduce the lead silicate to metallic lead, thus making the glass opaque and black. The glass has a higher specific gravity, viz., 3·0–3·8, brighter lustre, and greater refractive power, viz., 1·70–1·78 for the D line, than any of the preceding kinds of glass. *Crystal* contains an extra proportion of lead and is used for optical purposes, whilst *strass* contains a still larger proportion; these are distinguished by high refractive indices and great lustre. Lead glass is more easily attacked by aqueous solutions than the preceding kinds, and is therefore not suitable for chemical apparatus, although it is sufficiently resistant for the manufacture of many articles in common use, especially table glass.

Special glass of unusual composition.—Besides potash-soda-lime-lead glass, many kinds of glass are made in which magnesium, zinc, barium, antimony, arsenic, aluminium, lithium, didymium, thallium, iron, and manganese oxides replace partially or even completely the first-named oxides, and in which the silica is partially replaced by boric and phosphoric oxides. Boro-silicate glass containing zinc and barium oxides is remarkably resistant to the action of water and is known as Jena glass. Another boro-silicate glass is used for high temperature thermometers. Many different glasses are used for optical purposes, their mean refractive index varying from 1·49 for a boro-silicate lime glass to 1·65 for a lead-barium silicate glass, their dispersion C–F varying from 0·007 to 0·020. Phosphate-silicate glass containing alkali, alumina, and baryta is used for microscope objectives, and a remarkable glass consisting of a boro-silicate of barium, zinc, and aluminium, and entirely free from alkalis, is used for photographic objectives. Other kinds of glass particularly transparent to the ultra-violet rays are used for astronomical objectives, and special electric glow lamps. On the other hand a dark green glass containing ferrous oxide is quite opaque to radiant heat. Glasses of particular shades of red, green, and blue-violet are used in colour photography, and glass of other shades is employed for isochromatic monotone photographs and for photographing microscopic objects after the use of particular stains. Lastly, glass of pure fused silica must be mentioned, articles of which are now manufactured on a considerable scale and are found very valuable in the laboratory and in technology, *e.g.*, in the concentration of sulphuric acid. (See Vol. I., p. 927).

264 *Thermal Expansion of Glass.*—The necessity for annealing glass and the mode of preparation of toughened glass alike depend on the thermal expansion of the glass. A very interesting case of a glass nearly free from thermal expansion is found in quartz glass obtained by fusing pure quartz in the oxy-hydrogen flame or electric furnace, and drawing, welding, and blowing the vitreous melt into the required forms. Such quartz glass vessels may be dropped white hot into cold water without cracking, *i.e.*, will withstand a sudden temperature change of over 1000°. The coefficient of expansion of quartz glass per 1° C. is 0·00000052, whilst that of ordinary soft soda-glass is 0·000023 to 0·000027. Jena or resistance glass, extensively used for making glass laboratory vessels, will withstand temperature

shocks of 190° C., while Bohemian glass, having a higher thermal expansion, will barely stand shocks of 95° C. The thermal expansion of a glass depends upon its chemical composition and may be calculated from the percentage composition by multiplying each percentage by the following factors and summing the products;[1] the factors are:

B_2O_3	0·000,000,003
SiO_2	027
ZnO	060
P_2O_5	066
BaO	100
PbO	100
CaO	166
K_2O	283
Na_2O	333

An example of a special glass with a very low expansion coefficient, viz., 0·0000045, is the particular glass used for incandescent gas lamps.

For the manufacture of thermometers it is of great importance that the glass shall regain its original volume as rapidly as possible after it has undergone a change of temperature. Special glass for this purpose is now made under the name of Jena normal-glass which has the following composition:

B_2O_3	SiO_2	Na_2O	ZnO	CaO	Al_2O_3	Mn_2O_3	Total
2 0	67 3	14 0	7·0	7·0	2·5	0·2	100 0

After being heated to 100° thermometers of this glass only show a depression of the zero of 0·06°, whilst ordinary thermometers show depressions of from 0·4 to 1·0°.[2]

A further improvement is effected by enclosing within the thermometer bulb a small rod of another kind of glass having the same coefficient of expansion, but a much larger thermal after-effect, when the depression of the zero is corrected.[3] The importance of mercurial thermometers reading reliably at high temperatures has led to the introduction of instruments filled above the mercury with nitrogen, and the pressure exerted by this on the bulb has necessitated the use of glass of very high melting point. By careful attention to the composition of such glasses, the range of thermometers has been gradually extended from 360° up to 450°, 550°, and even 575°.

[1] See Hovestadt, *Jenaer Glas* (Gustav Fischer, Jena, 1900).

[2] *Zeit. Instrumentenkunde*, 1883, **3**, 377; 1891, **11**, 330; 1892, **12**, 402.

[3] Schott, *Zeit. anal Chem*, 1898, **37**, 585.

The Manufacture of Glass.

265 The materials employed for the manufacture of the glass are first fritted together in melting pots. These pots require great care in their preparation and are made of the most refractory kind of fire-clay, such as that found at Stourbridge. When

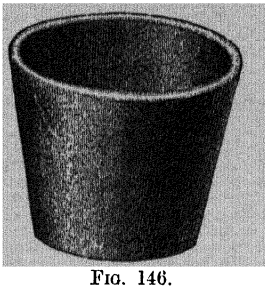


Fig. 146.

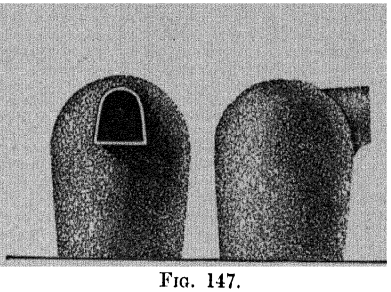


Fig. 147.

charcoal or gas is used as fuel the pots are open (Fig. 146); when, however, coal is employed, and especially in flint-glass making, the pots are hooded or covered at the top, having a mouth in

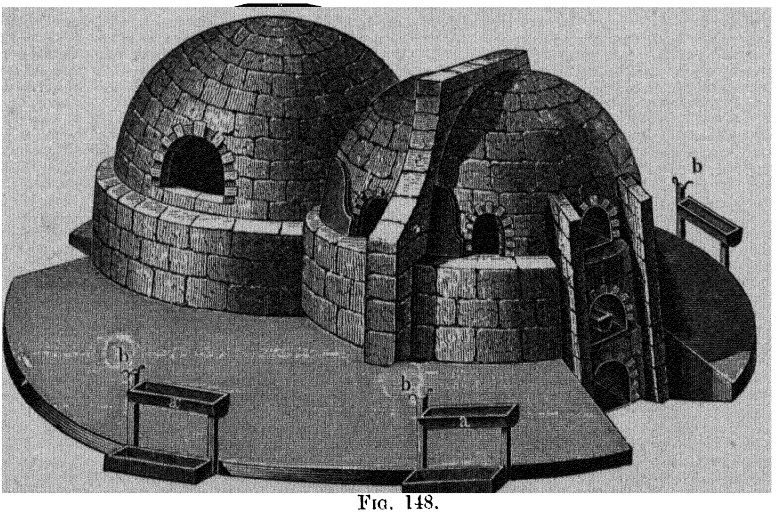


Fig. 148.

front like a muffle as seen in Fig. 147. The melting-furnace is built of sandstone, or of moulded blocks of special fire-clay. The construction of the oldest form of glass-furnace, as used in the time of Agricola, is shown in Fig. 148. It is hemispherical and is heated by a wood fire placed in the lowest opening;

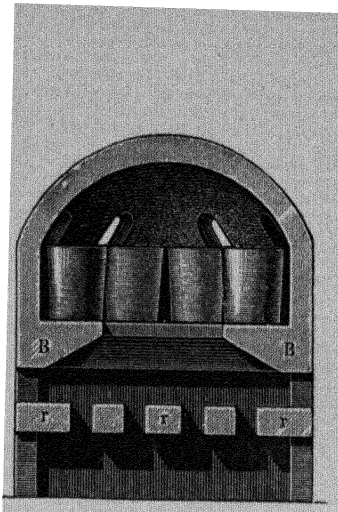


FIG. 149.

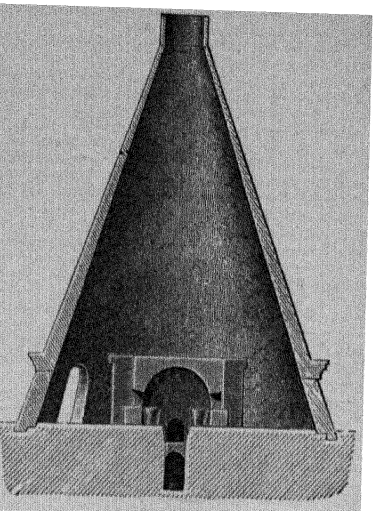


FIG. 150.

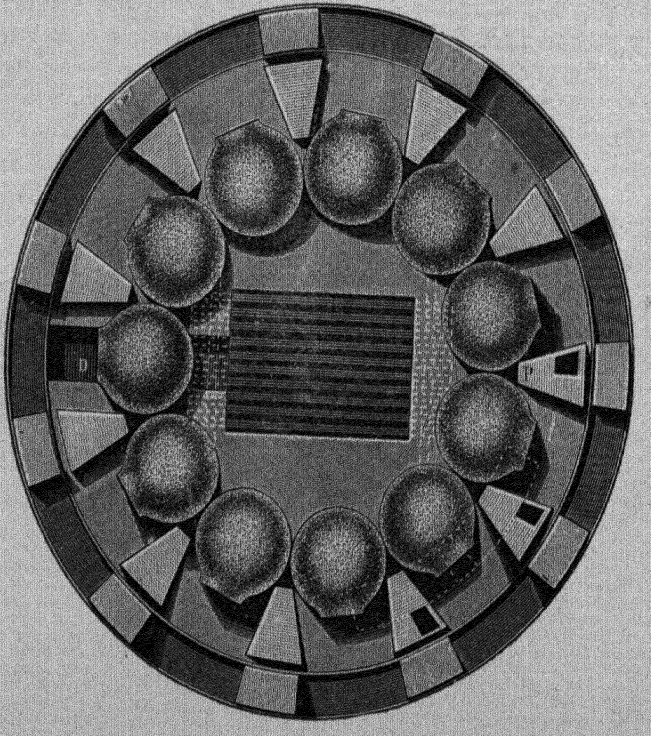


FIG. 151.

the second opening gives access to the melting-pot, whilst the upper space serves as the annealing oven. The small Bohemian furnace, in which wood is employed as a fuel, shown in Fig. 149, was formerly common in Germany. The older glass-houses were usually built in the form of a truncated cone, open at the top, from 60 to 80 feet in height, and from 40 to 50 feet in diameter

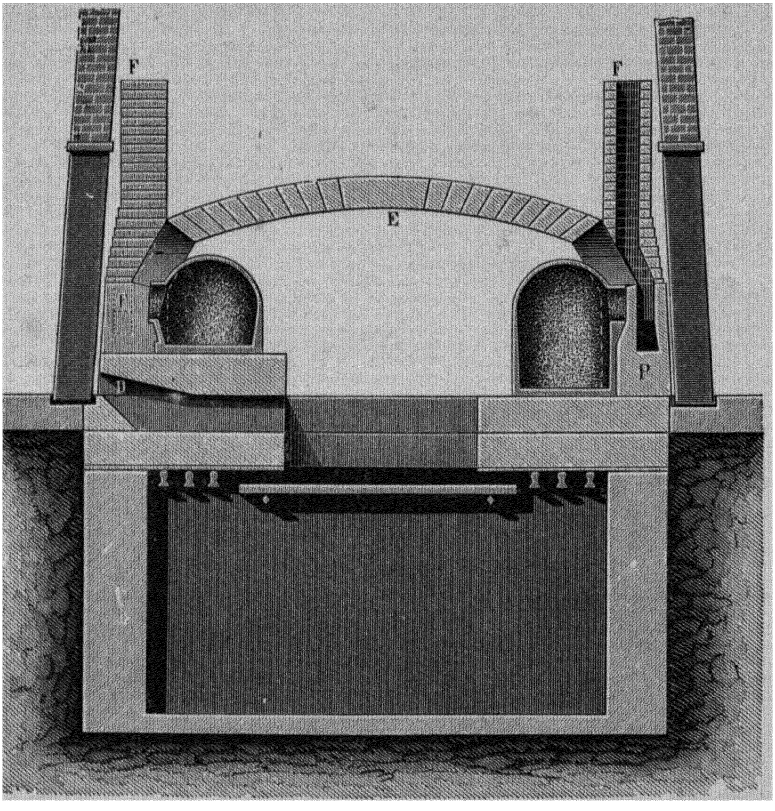


Fig. 152.

at the base, the centre of the area being used for the melting-furnace, capable of holding from 5 to 10 glass-pots or crucibles for melting the materials. The wood used in early times as fuel was gradually replaced by coal, and this change necessitated an alteration in the form of the furnace. In order to insure complete combustion, and to bring about a sufficiently high temperature when the fuel used is coal, the arrangement shown in Fig. 150 is made use of, the whole of the furnace being enclosed in a conical chimney.

Figs. 151 and 152 show the construction of a modern English flint-glass furnace in plan and in vertical section. Ten large glass-pots are placed round the walls of the furnace, with their mouths towards the outside, opposite corresponding holes in the external wall of the furnace, so that the molten glass can be readily withdrawn. A small pot is placed above the firing-hole (D). The grate for the coal fire is situated in the centre of the furnace and the flames striking on the arch or crown (E) (Fig. 152) play round each pot and find their way through the flues (F) in the pillars into the common chimney.

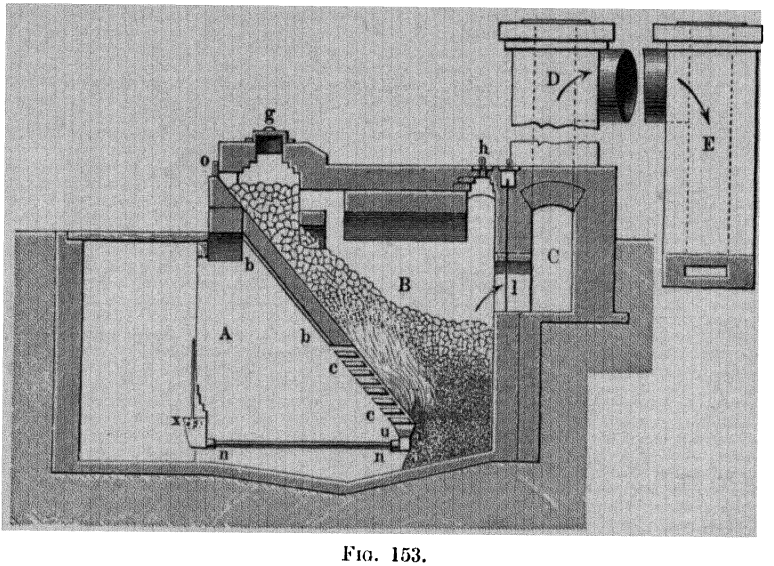


FIG. 153.

Amongst modern glass-furnaces that invented by Siemens is the most successful. Fig. 153 shows the original Siemens gas generator, which is situated at some distance from the melting-furnace. In this the coal falls down through the opening (g) on to the inclined plane (bb), whence it passes on to the bars (cc) of the furnace. Here an incomplete combustion takes place and the coal lying above the grate undergoes dry distillation; the gases pass through the flues (C) (D) and (E), and are led into the melting-furnace, the construction of which is seen in Fig. 154. Here the gas passes at first through the flue (C′) to the regenerator (D′), where it is heated, and thence passes by the flues (E′ F′) into the furnace, whilst the air necessary for the combustion of the gas is allowed to enter through the air passages; the products

of combustion pass from the furnace by a flue not shown, but placed behind (F′) and thence by the flue (e′) to the second regenerator (d′) and so to the flue (c′) and to the chimney. After

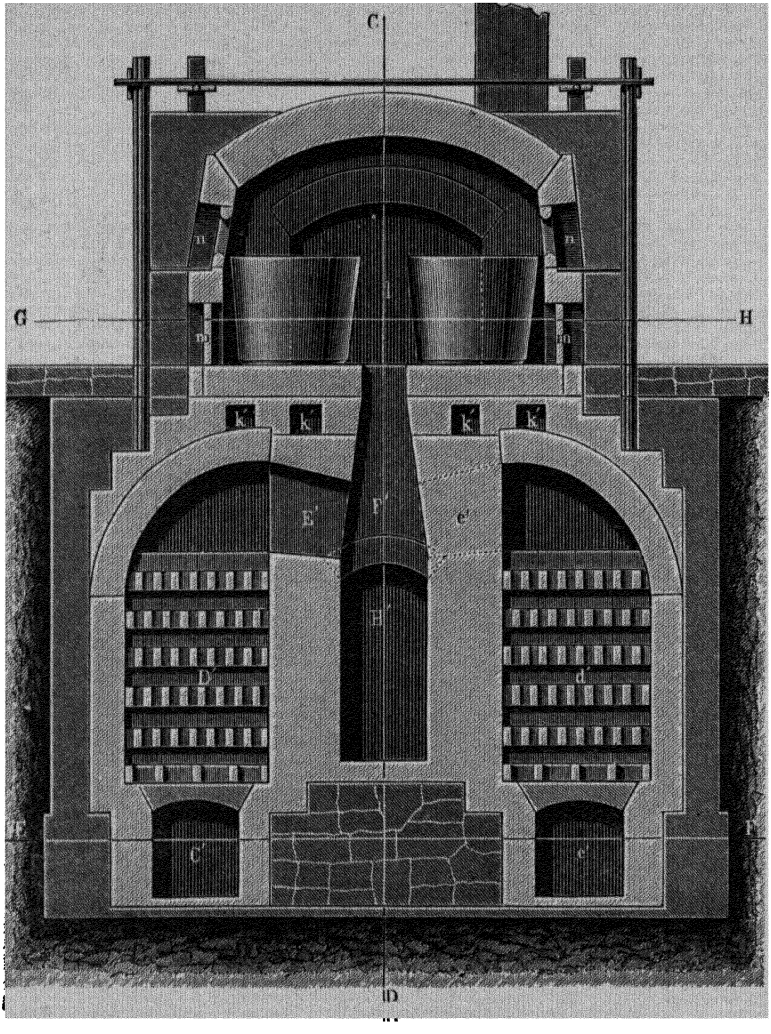
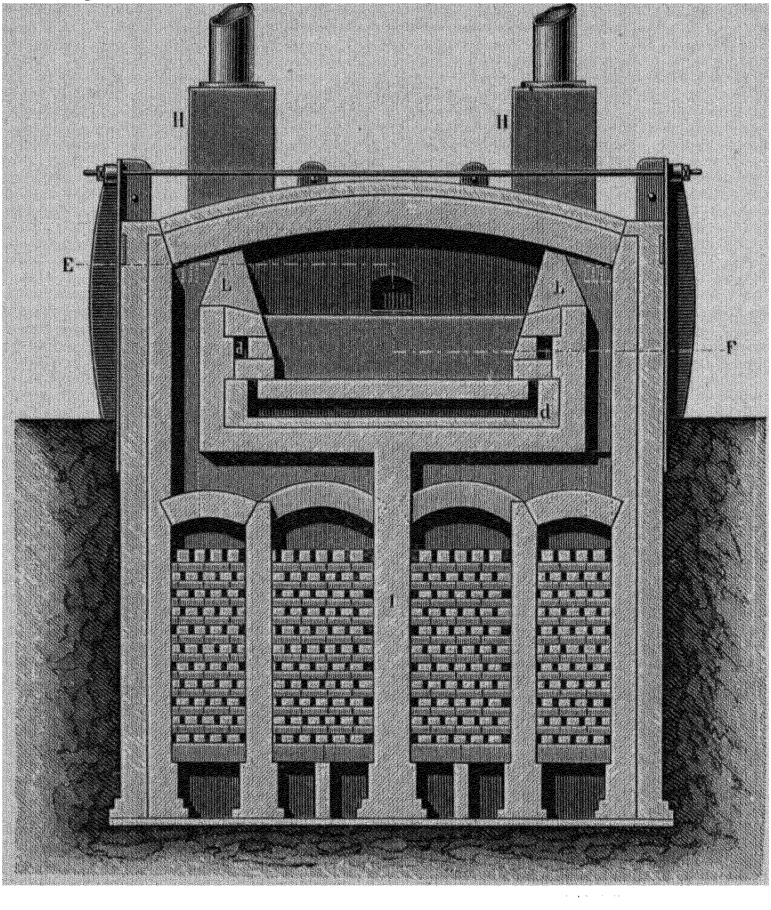


FIG. 154.

about twenty minutes the regenerator (D′) has cooled, while the regenerator (d′) has been heated to a fairly high temperature, and by now altering the position of large valves in the several flues, the direction of the gas is reversed, so that it is heated on its way to the furnace by the regenerator (d′), while the waste

gases from the furnace impart a portion of their heat to the regenerator (D'). Whilst the construction of glass furnaces is generally on the above lines, all common types of gas-producers are now employed in conjunction with them.

Fig. 155 shows a vertical cross section, Fig. 156 a horizontal



Decim. 10 5 0 1 2 3 Metre

FIG. 155.

section, and Fig. 157 a vertical longitudinal section of an improved form of a Siemens glass-melting furnace. This furnace resembles the one last described, in having the regenerative arrangement for recovering the waste heat as shown at (D'd') Fig. 154, but is remarkable for an improved method of construction and mode of working, the glass being placed in *tanks* instead

of in *pots*. In the older forms of glass-furnace the materials are first charged into the glass-pots, then fritted and melted down

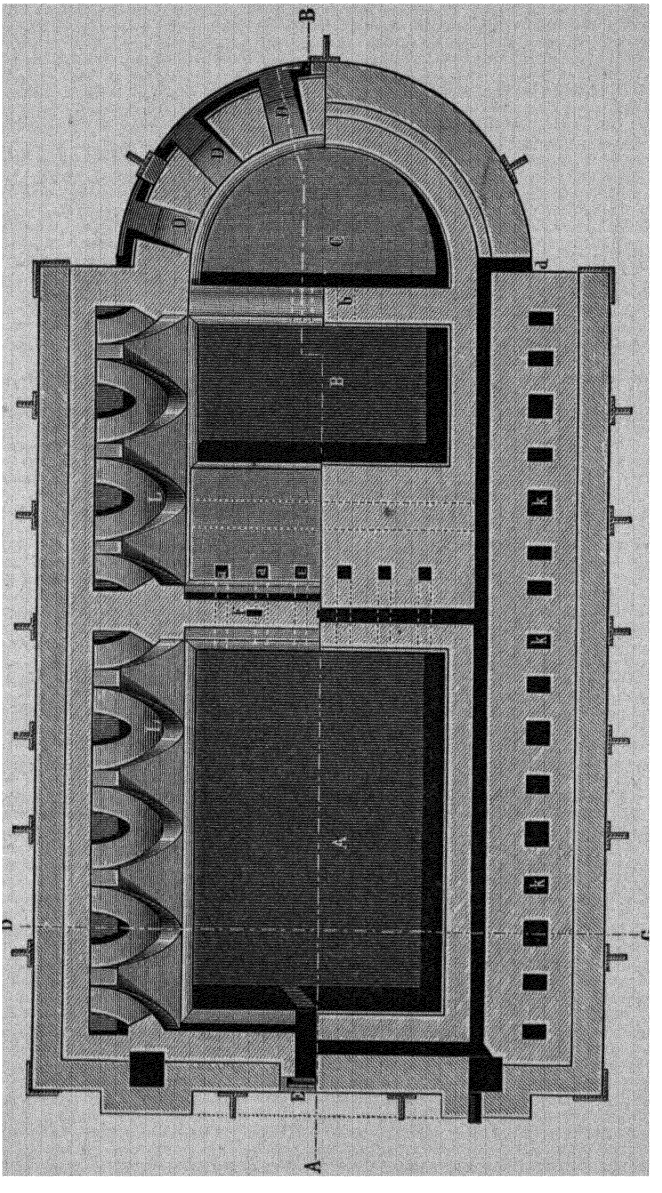


Fig. 156.

and worked out completely, after which the pots are re-charged and the process repeated. Hence a considerable loss of time and

waste of fuel take place through the intermittent nature of the work. Siemens' improvement has for its object the rendering of the process of glass-making a continuous and more uniform one. It consists of an arrangement of tanks (A), (B), (C), Fig. 157, of which (A) serves to receive the raw materials; in this tank they are fritted together and afterwards fused. From (A) the liquid "metal" flows into (B), the clarifying compartment, whence it passes into (C), the working compartment, from which it can be withdrawn by the workmen in the usual manner through the doors (D, D). The compartment (A) is fed with raw materials through the charge-aperture (E) at the back of the furnace. This compartment (A) is separated from the tank (B) by a division wall (F), Fig. 156, in which a series of passages is formed, one of which is seen at (a a), Fig. 157. Through these passages the melted glass flows, and from (B) it passes to the tank (C) through the passages (b) in the division wall (G). The sides and bottom of the tank are honeycombed with air-passages (d d d), through which cold air is caused to circulate by the draught produced in the chimney (H), and thus the tank walls are maintained in a cool condition so as to enable them better to withstand any injurious action of the melted glass. The gas-ports are shown at (k k), and the heated air issues from corresponding openings passing in diverse directions over the upper edges of the wall. By this means an effectual intermixture of the combustible gas and the heated air is produced, and the air is prevented from coming into immediate contact with the surface of the melted glass in the tanks. By arranging the gas- and air-ports along the sides of the tanks, the temperature in the different parts of the furnace can be regulated according to the various stages of the preparation of the glass in the several compartments.

The materials required for the formation of the glass are, if possible, always mixed with broken glass of the same kind, technically termed "cullett," for the purpose of increasing the fusibility of the mass. The materials, however, are not placed in the pots until these are heated up to a high temperature. The furnace is kept very hot until the first portion of the material added has been fused, and then a second portion is introduced. When all the solid matter is dissolved, the glass is still full of small bubbles of gas, and is of a spongy nature and not yet in a fit state for working. Moreover, the surface of the melted mass is covered by a layer of salts chiefly consisting of chlorides and sulphates of potassium and sodium which have escaped perfect

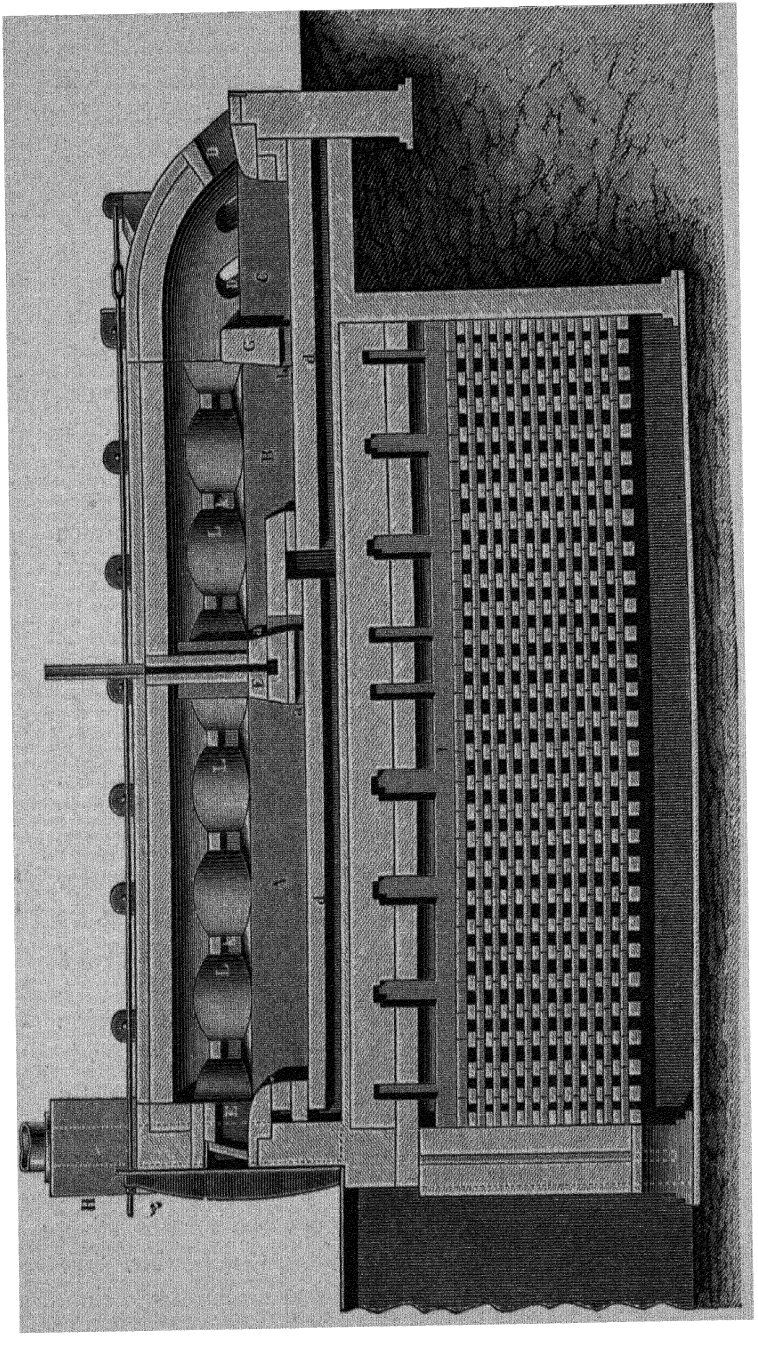


FIG. 157.

vitrification; this is termed *glass-gall* or *sandiver*. Formerly, when impure materials were more generally employed than is now the case, large quantities of this scum were formed. Now, however, its formation is avoided by the use of purer materials and by the addition of charcoal if salt-cake is employed, care being taken not to add an excess, as otherwise the glass assumes a yellow colour. The last process in glass-making is termed the "fining," and consists in the removal by subsidence of the heavier non-vitrified particles, and the escape of the bubbles of gas to the surface. For this purpose the glass must be brought into as liquid a state as possible, and consequently at this stage of the operation the temperature is raised to the highest point. When all the gas-bubbles and the glass-gall have disappeared, the temperature of the furnace is allowed to fall slowly, the object being to reduce the fluidity of the glass to the point at which it becomes viscid and in a workable condition. Glass is worked either by the skill of the glass-blower, for the production of the ordinary hollow- or blown-glass articles, or by casting in presses, or, lastly, by pouring the "metal" out on to iron tables and rolling it into plates. The tools described by Blancourt in his work *On the Art of Glass*, printed in London in 1699, are almost the same as those now in use.

It should be mentioned that oil firing is now being used to some extent, a mixture of air and oil being sprayed into the furnace.

Annealing.—All articles made of glass require to be very slowly and homogeneously cooled, for those portions of the glass which are on the outside solidify first, and leave the interior portions still warm, and these, unable to contract on cooling, are left in a state of tension; hence glass which has been quickly cooled cracks and falls to pieces with the slightest disturbance, such as is caused by a very slight scratch. All glass therefore requires to go through the *annealing* process. This consists in submitting the glass articles to a very slow cooling. The construction of an old type annealing oven is shown in Fig. 158; in most modern glass-houses continuous annealing furnaces, or "lehrs," are employed, consisting of long brick chambers heated to about 550° C. at one end and about 200–300° C. at the other, with an even temperature gradient along the chamber. The glass to be annealed is fed in at the hotter end, usually on iron trays or carriages, and travels slowly during a period of several hours to the cooler end, whence it is removed sufficiently annealed to stand natural cooling to the ordinary temperature.

The fact of the brittleness of glass when suddenly cooled is well seen in the so-called *Rupert's Drops* (Fig. 159), obtained by allowing a little melted glass to fall drop by drop into cold water. By merely breaking off the thin point the whole mass is converted with a slight detonation into a fine powder. Similarly an ordinary thick tumbler made of unannealed glass flies to pieces when the slightest scratch is made on the interior surface, as when a small piece of flint is allowed to fall into the glass.

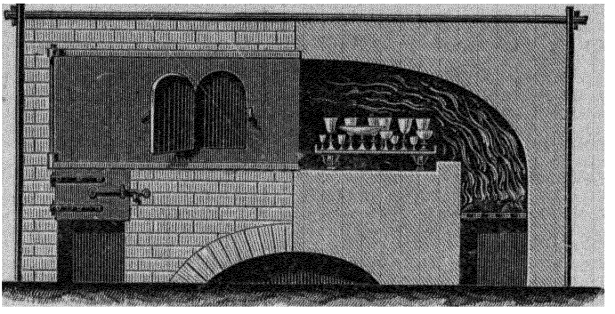


FIG. 158.

Toughened Glass is a particular kind of strained and partly annealed glass, discovered by De la Bastie. The glass articles, heated almost to redness, are suddenly immersed in oil heated to 300°, and are then allowed to cool gradually, or sheets of glass are allowed to cool between plates of suitably heated metal. The glass thus prepared is able to withstand sudden



FIG. 159.

changes of temperature better than the untoughened glass; it is also not readily broken when dropped, but when by increasing the severity of the blow it is broken it falls into fine splinters. Although a crack may occur in the vessel of toughened glass without the whole mass breaking up, yet it cannot be cut with a diamond, and the plates have accordingly to be made of the size ultimately required.

Laboratory Glass Working.—The methods of constructing special pieces of apparatus, though they cannot be here described,

are of considerable importance to the research chemist, and to those engaged in the examination of any gaseous products; assistance in acquiring this art may be obtained from special manuals on the subject.[1]

266 *Decomposition of Glass.*—It is of especial importance for the chemist that his glass vessels should satisfactorily withstand the action of chemical reagents. Bernard Palissy, Lavoisier, and Scheele were well aware of the solvent action of water upon glass, and they explained this by the solution of the alkaline silicates, whilst the insoluble silica or lime silicate floated about in the liquid. In his celebrated researches on the atomic weights of the elements, Stas [2] describes a series of preliminary experiments made for the purpose of ascertaining the kind of glass which is least subject to such deterioration. He found that glass containing lead or alumina was readily acted upon by acids, whilst potash-lime glass withstood this action best, and he prepared a glass of the following composition, which was sufficiently capable of resisting solvents and at the same time fusible enough to enable it to be worked into the various forms of chemical apparatus:

SiO_2	K_2O	Na_2O	CaO
77·0	7·7	5·0	10·3 = 100.

Emmerling [3] found the solvent action of boiling solutions on glass vessels to be within certain limits proportional to the time during which the action takes place, and naturally it is also proportional to the surface exposed to the action of the liquid. Dilute alkalis attack glass very much more rapidly than neutral or acid solutions, and hence it follows that in order to diminish the errors which occur in quantitative analysis from the solvent action of reagents upon glass, the long continued contact of alkaline liquids must especially be avoided, any such liquid being acidified before evaporation; it is also advisable to avoid the use of new glass vessels, which are attacked much more rapidly than old ones. It appears that the most resistant glasses have approximately the molecular composition 8·6 SiO_2 : 1 CaO : 1·2 $(Na_2,K_2)O$, the relative proportion of soda to potash making little difference.[4]

[1] *The Methods of Glass Blowing*, Shenstone, 1886; *Glass-Blowing and Working*, Bolas, 1898.

[2] *Nouvelles Recherches, etc., Mem. Acad. Belg*, **35**, 216.

[3] *Annalen*, 1869, **150**, 257.

[4] Weber and Sauer, *Ber.*, 1892, **25**, 70; Mylius and Foerster, *ibid.*, 1889, **22**, 1092; 1892, **25**, 97.

The number of milligrams of glass destroyed per hour on an exposed surface of one square decimetre by various solutions is given approximately by the following figures, the glass being such as is used for making flasks, beakers, etc., and known as (1) Bohemian glass, (2) Jena glass. Water at 20°, (1) 0·0040, (2) 0·0002; water at 80°, (1) 0·50, (2) 0·02; sulphuric acid 5 per cent. at 100°, 1·7, (2) 0·0; sodium carbonate 10 per cent. at 100°, (1) 20·0, (2) 8·0; sodium hydroxide 8 per cent. at 100°, (1) 15°0, (2) 17°0.

Glass is slowly attacked by the moisture and the carbon dioxide contained in the air, so that the surface gradually becomes spotted with minute crystals of sodium carbonate or with minute drops of potassium carbonate solution, and this action is accelerated in hot saturated air. Badly prepared window glass, especially that rich in alkalis, becomes opaque in the course of time. This is due to a similar decomposition of the surface, so that the carbonates of the alkalis being washed away, an iridescent coating consisting of a thin film of calcium silicate remains. This iridescence is especially well seen in antique glass which has been buried in the earth for a considerable length of time. A similar iridescent surface is now produced artificially by heating ordinary glass under pressure in contact with hydrochloric acid. Boro-silicate glasses, and especially those containing zinc and barium, are particularly permanent on exposure to the air. The decomposition of the surface of glass is often not to be seen until the glass is heated, when the surface dehydrates and cracks.

Devitrification of Glass. Réaumur's Porcelain.—In 1739, Réaumur observed that if a piece of glass were surrounded by sand or gypsum, and heated strongly for a considerable length of time, it was converted into a porcelain-like mass, to which he gave the name of *porcélaine par dévitrification.* According to the experiments of Pélouze, Benrath,[1] and Stolba,[2] the porcelain-like glass possesses the same composition as ordinary transparent glass. Devitrification results from the gradual precipitation or crystallisation of certain ingredients of the vitreous solution, and the liability to devitrify depends on the composition of the glass.

[1] *Die Glasfabrikation*, 1875, 18.

[2] *J. pr. Chem.*, 1863, **90**, 465; 1864, **93**, 118.

Opaque, Coloured and Matt Glass.

267 *Milk-glass.*—The ordinary opalescent or milk-glass is either soda-glass or flint-glass which has been rendered opaque by the addition of an insoluble powder, such as bone-phosphate or mineral-phosphate.

Enamel.—Another opaque variety of glass is known under the name of *enamel.* This name originally signified lead-glass rendered white by oxide of tin, but oxide of antimony and sulphate of barium are now also employed. Enamel is used for covering the surface, or for "enamelling" iron vessels used for cooking and for chemical manufacturing purposes. Enamels may be coloured by any of the materials next described for colouring glass, such coloured enamels being used for making ornaments by fluxing them on to plates or articles of gold or copper, to which they readily adhere.

Ruby Glass.—The older chemists were acquainted with the fact that glass could be coloured a ruby-red tint by means of various gold compounds. Thus Neri describes a method of preparing ruby glass by adding to the glass-maker's materials the residue from the evaporation of a solution of gold in aqua regia. General attention, however, was drawn to this subject in the 17th century, after the discovery of the *purple of Cassius*, obtained as a dark-red powder by mixing the chlorides of gold and tin (p. 524). Amongst other chemists, Kunkel occupied himself with the preparation of this gold pigment, and obtained from the Elector Frederic William the sum of 1,600 ducats for his experiments.

In his *Ars Vitriaria Experimentalis* he says: "There was a certain *Doctor medicinae*, by name Cassius, who discovered the *præcipitatio Solis cum Jove:* to this perhaps Glauber may have given occasion, but I leave this undecided. The aforesaid Doctor Cassius endeavoured to bring it into glass, but when he tried to form a glass with it, or when he took it out of the fire it was as colourless as crystal, and he could not bring any permanent red out of it. He may, however, have observed, being a man curious about these things, amongst the glass-blowers that when they softened glass in the flame of the lamp the colour underwent a change. Thus he came to try the same plan with gold glass, and obtained a splendid ruby colour. When I learnt this, I set to work at once, and I know best what trouble I had

to hit the proper composition, and to find out how to get it always red."

The secret which is involved in the above words is explained in the *Laboratorium Chymicum*, which appeared after his death: "This ruby glass possesses the property that when the glass is melted with the ☉ (gold) it comes out of the fire as clear as crystal, and in order to become red must be heated again in a mild fire."

On the addition of purple of Cassius, or of gold chloride, to a melt of glass, the latter remains perfectly colourless when quickly cooled; but when reheated to the point at which it becomes soft, the whole mass attains a ruby-red colour. By the addition of tin or silver compounds, a variety of tints between a rose-red colour and a red-purple colour can be obtained. It is probable that the colour is due to metallic gold in so finely divided a state that the substance only allows red light to pass through it: indeed, the presence of fine particles of gold in ruby glass has been detected by the ultramicroscope.[1] The amount of gold contained in ruby glass is very small, amounting to from 0·05 to 0·06 per cent.

Cuprous oxide also colours glass a fine and intense red, but inasmuch as this compound readily undergoes oxidation and as cupric oxide imparts to glass a light green colour, a reducing agent such as iron scale is added to the materials. Oxidation is also prevented by poling the molten mass with pieces of fresh wood. The glass on cooling appears of a light green colour, but becomes red on re-heating. The preparation of this glass was also understood in early times. Klaproth found both copper and iron in a sample of old Roman glass, and in the beginning of the 17th century, Neri described a method of calcining copper in order to colour glass, and stated that iron filings, iron scale, or other reducing agents must be added in order that the colour might come out a bright red. Kunkel also employed himself with the preparation of this glass, but in later times the art was lost, and it was not until the year 1828 that Engelhardt examined the question and obtained a prize which the Berlin Polytechnic Society had offered for the discovery, since which time the method has been generally practised. Cuprous oxide possesses a very strong colouring power, and for this reason copper-ruby is generally flashed on to colourless glass, as otherwise the

[1] Zsigmondy, *Zeit. physikal. Chem.*, 1906, **56**, 65; see also Garnett, *Proc. Roy. Soc.*, 1905, **76**, [*A*], 370.

colour would be altogether too intense. The glass-blower brings the requisite quantity of colourless glass on to his blowpipe, and dips this into the molten coloured glass so as to cover the former with a thin film, and the compound glass is then blown and shaped in the usual way. By examining the cut edge of a piece of flashed copper ruby glass the thin layer of coloured glass resting on a very much thicker layer of colourless glass is distinctly visible. By grinding or etching through the flashed colour highly decorative effects may be obtained; this art of flashing and grinding was known to the ancients, as is shown by the celebrated Portland Vase made of black glass flashed over with a milk white glass.

Ferric oxide (colcothar) also imparts a red colour to glass, but the tint is less brilliant than either of the two just described.

Yellow Glass is prepared by the addition of potassium antimonate or of antimony-glass (a fused and imperfectly oxidised sulphide of antimony); other yellow colours are obtained by the use of silver chloride and silver borate. Organic bodies also impart a yellow tint to glass. This must have been observed by Thomas Aquinas, who describes a mode of preparation of artificial topaz by placing a piece of aloe-wood over the vessel in which the glass is melted. It was formerly believed that this brown colour was due to carbon. Splitgerbe has, however, shown that it is caused by the presence of the sulphides of the alkali metals obtained by reduction from the sulphates contained in the material used for glass-making.

Green Glass is obtained by the addition of cupric oxide, as was known to the ancients, the above substance being found in antique glass. According to Seneca, Democritus of Abdera was acquainted with a method for producing the emerald artificially, and Theophrastus, about 300 B.C., described a mode of colouring glass green by means of copper. Other green tints are obtained by the addition of oxide of chromium and ferrous oxide, the latter giving a dull bottle-green colour.

Blue Glass.—Cobalt oxide colours glass a fine *blue*, and this oxide has been used from early times for this purpose.

Violet Glass.—The *violet* colour of glass is obtained by the addition of black oxide of manganese and nitre.

Black Glass.—A fine *black* opaque glass is obtained by the addition of sesquioxide of iridium to colourless glass, and a common black glass is prepared by adding large quantities of ferric oxide, with which copper oxide or cobalt oxide is frequently mixed.

Paste.—The property of glass to attain a variety of tints by the addition of various metallic oxides is made use of for the production of imitation gems or paste, and this art has now attained such perfection that it is difficult even for an adept to ascertain upon mere inspection of a stone whether it is genuine or only an imitation. Strass is employed for the basis of paste, because of its high refractive power and bright lustre. According to Donault-Wieland *topaz* is formed by adding to 1,000 parts of strass, 40 parts of antimony-glass and 1 part of purple of Cassius. *Ruby* is obtained from the ingredients of the topaz mixture by fusing 1 part of this with 8 parts of strass and allowing the fused mass to remain at the temperature of the furnace for thirty hours. *Emerald* is prepared by fusing 1,000 parts of strass, 8 parts of cupric oxide, and 0·25 part of chromium oxide. *Sapphire* can be made by the addition of 15 parts of cobalt oxide to 1,000 of strass; *amethyst* requires the addition of 8 parts of manganese dioxide, 5 of cobalt oxide, and 2 of purple of Cassius; whereas *beryl* or *aqua-marine* is prepared by adding 7 of antimony-glass and 0·4 of cobalt oxide to the 1,000 of strass, and *Syrian garnet* or *carbuncle* requires 500 of antimony-glass and 4 parts each of manganese dioxide and purple of Cassius to the same quantity of strass. These special tints can, however, be readily varied at pleasure.

Avanturine Glass has received its name from a rare form of quartz which occurs in Spain and the Altai, containing spangles of mica or other mineral. Avanturine glass is more beautiful than the natural mineral, and the method of its manufacture is said to have been discovered by chance in the 13th century by Briani in Venice. The artificial avanturine was largely employed for the preparation of ornaments and especially for Venetian mosaic work. The details of its preparation were long kept secret, and the process was only carried out by a few of the highest Venetian families. In the year 1847 Pettenkofer[1] investigated the preparation of the antique hæmatine, an opaque red glass, and in the preparation of this material he obtained by accident avanturine glass. Many not wholly successful attempts have been made to determine the exact conditions under which the avanturine is thus formed. Avanturine glass is a white soda-lime glass, containing an excess of alkali, coloured red by cuprous oxide and containing an enormous number of minute spangles of metallic copper, probably produced by the partial

[1] *Dingl. Polyt. Journ*, 1847, **145**, 122.

decomposition of cuprous silicate.[1] According to Hautefeuille, a green cupric glass is first prepared; to this iron filings are gradually added until it becomes red and opaque; hæmatine glass is thus formed, which is then well covered with ashes, and allowed gradually to cool, when the artificial avanturine glass is formed.

Matt Glass.—The etching of glass with hydrofluoric acid was known in the 17th century, but it is only recently that this process has been employed for the decoration of glass, and now etched glass is much used in place of the more expensive cut-glass. Gaseous hydrofluoric acid as well as many soluble fluorides produce a dull or matt surface on glass possessing also a considerable degree of opacity, but liquid hydrofluoric acid produces, according to the concentration of the acid, a more or less transparent matt-surface. According to Tessié de Mothay and Maréchal, the best mode of obtaining opaque-etching by means of hydrofluoric acid is to employ a bath made of 1,000 parts of water, 250 parts of crystallised double fluoride of hydrogen and potassium, 250 parts of commercial hydrochloric acid, and 140 parts of potassium sulphate. This last salt renders the fluorides of calcium and lead which may be formed less soluble, whereby they are separated out in the crystalline form on the portions of the glass which have been etched and thus tend to render the surface more opaque.

The matt-surface is now usually produced on glass by exposing it to a sand blast, the parts which are to remain smooth being protected by paper. Reagent bottles may readily be indelibly labelled in this manner. The matt-surface on whole sheets of glass is obtained by grinding with sand.

Quartz Glass and Fused Silica Ware.—The fact that quartz can be easily fused in the electric furnace and worked up into articles for chemical use is referred to in Vol. I., p. 926. Such articles are now manufactured both in this country and abroad, white sand or selected quartz being fused, and made into tubes, rods, muffles, flasks, etc., the value of which for chemical research can hardly be overestimated.

Detection and Estimation of Calcium.

268 The fact that certain compounds of calcium impart a red colour to the flame of the spirit-lamp was first observed by

[1] Auger, *Compt. rend.*, 1907, **144**, 422.

Ribbentrop in 1796. The spectrum of a non-luminous gas flame tinted by calcium chloride exhibits a number of lines, of which the green line Caβ is the most characteristic, the orange line Caα being also very prominent (see Fig. 21, p. 164). This spectrum is mainly due to the chloride and oxide and not to the vapour of the metal itself, and is also yielded by calcium compounds which do not volatilise in the flame, when they are moistened with hydrochloric acid and placed on a platinum wire in the hottest portion of the flame. Certain silicates containing calcium which are not decomposed by hydrochloric acid must be first heated with ammonium fluoride, the residue then decomposed by sulphuric acid, and treated as above. By means of the spectroscope as small a quantity as 0·00006 of a mgrm. of calcium chloride or similar salt may be detected. At the temperature of the electric arc the calcium compounds show the spectrum of metallic calcium, consisting of a number of fine bright lines.

Calcium may be detected in presence of relatively large amounts of strontium and barium by the addition of a solution of barium fluoride which precipitates the calcium as fluoride.[1]

Calcium may be separated from the alkali metals by the addition of a solution of ammonium carbonate, calcium carbonate being precipitated. As has been stated, this latter salt is not altogether insoluble in water, and it is, therefore, preferable to precipitate the lime as calcium oxalate by the addition of ammonium oxalate in neutral or ammoniacal solution; this salt is slightly soluble in water (0·0068 gram per litre at 25°), but much less soluble in dilute ammonium oxalate solution, which is therefore used instead of water for washing the precipitate. This reaction is usually employed for the estimation of calcium; the washed and dried precipitate, which has the composition $CaC_2O_4,2H_2O$, is either gently ignited, by which means it is converted into the carbonate; or it is strongly ignited, when the carbonate is converted into caustic lime. The amount of oxalate may also be ascertained volumetrically by treating the precipitate with dilute sulphuric acid and titrating with potassium permanganate. Calcium is also occasionally estimated as the sulphate. The precipitation by sulphuric acid must, however, be made in presence of alcohol, and the precipitate must also be washed with the same liquid.

The Atomic Weight of calcium was first accurately determined

[1] Karaoglanow. *Zeit. anal. Chem.*, 1917, **56**, 138.

by Erdmann and Marchand,[1] by the ignition of calc-spar and of precipitated calcium carbonate. From their experiments it appears that the atomic weight of calcium is 39·68, 39·70, 39·73, or as a mean of the three numbers 39·7 (pp. 10, 11). Baup[2] obtained the number 39·67 as the result of the analysis of organic lime salts. Hinrichsen,[3] by the careful ignition of calc-spar, has obtained the number 40·14 (O = 16), and Richards,[4] by the analysis of the chloride, found 40·13. The most probable value is now (1922) taken as 40·07.

STRONTIUM. Sr = 87·63. At. No. 38.

269 The name of this element is derived from that of Strontian, a village in Argyllshire, in which a peculiar mineral, strontium carbonate or strontianite, was originally found. At first this mineral was mistaken for barium carbonate, but in the year 1790 Crawford suggested that it contained a peculiar earth, founding his opinion upon experiments which had been made on the mineral by Cruikshank. This was confirmed in 1792 by Hope,[5] and independently by Klaproth,[6] a year afterwards. Sir Humphry Davy in 1807 first obtained the metal strontium.

Strontium occurs chiefly as the sulphate or *celestine*, $SrSO_4$, and as the carbonate or *strontianite*, $SrCO_3$. Many specimens of aragonite and of calc-spar contain small quantities of strontium carbonate; and the same may be said of many kinds of limestone, marble, chalk, and other rocks,[7] and also many iron ores and other minerals,[8] although the strontium is generally present only in very small traces. *Baryto-celestine* is a mineral which contains the sulphates of barium and strontium, and the latter compound occurs also in small quantities in different varieties of heavy-spar. Strontium occurs as a silicate in *brewsterite*, $H_4(Ba,Sr,Ca)Al_2Si_6O_{18},3H_2O$. Small quantities of the chloride and sulphate of strontium occur in solution in many brine-springs as well as in different minerals waters. It is also present in chalk waters, such as that of the London basin, and has been found in plants, being in some cases derived

[1] *Annalen*, 1844, **52**, 210; 1848, **66**, 219 [2] *Ibid*, 1844, **52**, 212.
[3] *Zeit. physikal. Chem.*, 1901, **39**, 311; 1902, **40**, 746.
[4] *J. Amer. Chem. Soc.*, 1902, **24**, 374.
[5] Account of a mineral from Strontian, *Trans. Roy. Soc. Edinb.*, 1792, **4**, 3.
[6] *Crell. Ann.*, 1793, **2**, 189, and 1794, **1**, 99.
[7] Hillebrand, *J. Amer. Chem. Soc.*, 1894, **16**, 81.
[8] Hartley and Ramage, *Journ. Chem. Soc.*, 1897, **71**, 533, 547.

from the calcareous fertilisers which have been applied to the soil. Strontium has also been found in sea-water in the ashes of *Fucus vesiculosus* and in the spicules of certain radiolaria (Bütschli).

Preparation of Metallic Strontium.—Davy obtained the metal strontium by the electrolysis of either the moistened hydroxide or the chloride. It was afterwards prepared by Bunsen and Matthiessen,[1] who electrolysed a fused mixture of strontium chloride and ammonium chloride, using a thin iron wire as cathode, and obtained the metal in pieces weighing half a gram or less. The metal prepared by them was yellow and probably contained nitride. It has been obtained in a pure condition by Borchers and Stockem by the application of the method which they had employed successfully for the preparation of calcium (p. 547).

It has also been prepared indirectly from strontium amalgam, but the metal obtained by simply heating the amalgam does not appear to be pure. Strontium amalgam can be obtained by heating a saturated solution of strontium chloride to 90° with 20 per cent. sodium amalgam,[2] but is more conveniently prepared by electrolysing a solution of strontium chloride with a mercury cathode, washing the product with water, pressing between folds of filter paper and then heating to 150°.[3]

In order to prepare pure strontium, the amalgam containing 8 per cent. of strontium is heated *in vacuo* to 700°, and then to about 1000° in hydrogen. The mercury is thus completely removed and a compact mass of the hydride obtained. This is then heated in small quantities in vacuo in an iron tube contained in a porcelain tube. The hydride decomposes, and the strontium volatilises and is condensed on a polished hollow steel tube, cooled by a stream of water. The metal thus obtained contains 98·6—99 per cent. of strontium, and may be obtained still less impure (99·4 per cent. Sr) by redistillation *in vacuo*.[4] Glascock has prepared it from the fused chloride,[5] and it may be obtained in quantity by a method [6] analogous to that employed for the manufacture of calcium, using a bath of 15 per cent.

[1] *Journ. Chem. Soc.*, 1856, 107.

[2] Franz, *J. pr. Chem.*, 1869, **107**, 253.

[3] Guntz and Roederer, *Bull. Soc. chim.*, 1906, [3], **35**, 494.

[4] *Compt. rend.*, 1906, **142**, 400; *Bull. Soc. chim.*, 1906, [3], **35**, 503; also *Compt. rend.*, 1910, **151**, 813.

[5] *J. Amer. Chem. Soc.*, 1910, **32**, 1222.

[6] Neumann and Bergoe, *Zeit. Elektrochem.*, 1914, **20**, 187.

potassium chloride and 85 per cent. strontium chloride, fusing at 628°, and a current density of 20—50 amperes per sq. cm. of cathode. Pure strontium is a crystalline, silver-white metal of sp. gr. about 2·5; it has the same hardness as lead, melts at about 800°, and volatilises freely at 950°. It very rapidly loses its lustre in the air and takes fire when simply rubbed with a hard body, whilst the finely-divided metal inflames spontaneously in the air, forming a mixture of oxide and nitride. The metal burns with a dazzling red flame when heated in oxygen, and is also readily attacked by the halogens, hydrogen chloride, sulphur, hydrogen sulphide, phosphorus, etc. It decomposes water and alcohol, and is readily dissolved by acids (Guntz and Roederer). It is less electro-positive than calcium and the alkali metals. Strontium behaves towards liquid ammonia like the alkali metals (p. 329).[1]

STRONTIUM COMPOUNDS.

270 The preparation of strontium compounds free from calcium and barium is a matter of considerable difficulty. It is not easy to effect a separation of isomorphous salts, hence calcium and strontium cannot be separated by means of their chlorides, nor strontium and barium by means of their nitrates. The purification is best accomplished by dissolving the crude carbonate in hydrochloric acid, precipitating foreign metals by strontium oxide, followed by chlorine water, and then precipitating most of the barium by the addition of concentrated hydrochloric acid. Sulphuric acid is then added, and the greater portion of the mixed sulphates converted into carbonate by ammonium carbonate. The precipitate is next dissolved in dilute nitric acid and fractionally precipitated with sulphuric acid until no barium is contained in the precipitate. Calcium is removed from the nitrate by repeated precipitation of the strontium nitrate by alcohol.[2]

Strontium Monoxide or Caustic Strontia, SrO.—This substance is obtained by the ignition of the nitrate in the form of a greyish-white porous mass, which becomes crystalline at about 2,500° and melts at about 3,000° (Moissan). When brought into contact with a small quantity of water the monoxide unites with it to form a white powder of *strontium hydroxide*, $Sr(OH)_2$.

[1] See also Roederer, *Bull. Soc. chim*, 1906, [3], **35**, 715.

[2] Sörensen, *Zeit. anorg. Chem.*, 1896, **11**, 305. See also Richards, *ibid.*, 1905, **47**, 145.

This body possesses a specific gravity of 3·625, and when strongly heated is reconverted into strontia. The hydroxide is easily soluble in hot water, and the solution, on cooling, deposits transparent tetragonal crystals of the hydrate $Sr(OH)_2,8H_2O$; 100 parts of cold water dissolve 2·0, and of boiling water 41·66 parts of the crystals. Strontia water has a strongly alkaline reaction and possesses caustic properties less marked than the solutions of the alkalis.

Considerable quantities of strontium hydroxide are used in the refining of sugar.

Strontium Dioxide, SrO_2.—Pearly scales of the hydrated dioxide, $SrO_2,8H_2O$, separate out on mixing a solution of the hydroxide with hydrogen dioxide; these lose water on heating, leaving the anhydrous dioxide as a light white powder which does not melt at a red-heat, but gradually loses oxygen (Schöne).[1] The anhydrous peroxide may also be prepared [2] by heating strontia in oxygen at a pressure of 105 to 126 kilos. per sq. cm. and a temperature of 400—500°.

Strontium Hydride, SrH_2, is prepared by heating strontium, or its amalgam, or an alloy containing 55 per cent. of cadmium, in hydrogen, and is a white solid, which forms at a red heat and decomposes when more strongly heated, its dissociation pressure being 100 mm. at 1000°. In its general properties it closely resembles calcium hydride.[3]

Strontium Chloride, $SrCl_2$, is obtained by dissolving strontianite in hydrochloric acid. The hot concentrated solution deposits, on cooling, long hexagonal needles, $SrCl_2,6H_2O$, which are isomorphous with the corresponding hydrate of calcium chloride. They possess a sharp, bitter taste, have a specific gravity of 1·603, and effloresce on exposure to the air. On heating, these crystals yield the anhydrous salt as a white powder, which melts at 873° and when again cooled forms a white semi-transparent glassy mass having a specific gravity of 3·05. According to Mulder 100 parts of water dissolve :

At	0°	20°	40°	60°	80°	100°	118·8°
$SrCl_2$	44·2	53·9	66·7	83·1	92·4	101·9	116·4.

The hexahydrate passes into the dihydrate, $Sr_2Cl,2H_2O$, at

[1] See also Riesenfeld and Nottebohm, *Zeit. anorg. Chem.*, 1914, **89**, 405; **90**, 150.

[2] Pierce, Brit. Pat., 130840.

[3] Guntz, *Compt. rend.*, 1901, **133**, 1209; **134**, 838; Gautier, *ibid*, **134**, 100, 1108.

65·5° in contact with a saturated solution. Chloride of strontium also dissolves in alcohol. The commercial salt frequently contains calcium chloride.

A crystalline compound, $SrCl_2,ICl_3,8H_2O$, has been described.

Basic halides of strontium, $SrCl_2,SrO,9H_2O$; $SrBr_2,SrO,9H_2O$; $SrI_2,SrO,9H_2O$; are known.[1]

Strontium Sulphide, SrS, can be obtained crystallised in cubes by heating the sulphate with carbon in the electric furnace,[2] and is also formed by heating the carbonate with sulphur, and the carbonate or oxide in a stream of sulphuretted hydrogen.[3] Like the sulphides of calcium and barium, it is strongly phosphorescent in the presence of small amounts of certain foreign substances, whilst the pure sulphide does not possess this property. The most brilliant green phosphorescence is obtained in the presence of traces of sodium carbonate and chloride and bismuth nitrate, but manganese salts produce a similar phosphorescence.[4] Strontium sulphide is readily hydrolysed by water to give equimolecular proportions of hydrosulphide and hydroxide: these do not combine, as in the case of barium, and pure strontium hydroxide may be crystallised from the solution.[5]

Strontium Sulphate, $SrSO_4$, is found in large, well-developed rhombic crystals and as a fibrous amorphous mass. It frequently possesses a light blue colour, whence it takes its name celestine (*cœlestis*). When sulphuric acid or a soluble sulphate is added to a solution of a strontium salt, the sulphate is thrown down as a white precipitate possessing a specific gravity of 3·707, and fusing when strongly heated. It is but very slightly soluble in cold, and still less in boiling water. One litre of water at 18° dissolves 0·114 gram (Kohlrausch). Strontium sulphate is much more easily soluble in acids and in solution of common salt, as well as in other salt solutions, but is less soluble in sulphates or dilute sulphuric acid, and is completely decomposed by boiling with a solution of an alkali carbonate. When the salt is dissolved in hot concentrated sulphuric acid, crystals of celestine separate out on cooling, but when it is treated with concentrated sulphuric acid at 100°, and the solution digested

[1] Millikan, *Zeit. physikal. Chem*, 1917, **92**, 59.

[2] Mourlot, *Compt. rend.*, 1898, **127**, 408; Muller, *Centr. Min.*, 1900, 178.

[3] Mourelo, *Compt. rend.*, 1897, **124**, 1024, 1237; **125**, 775.

[4] *Ibid.*, 1897, **125**, 1098; 1898, **126**, 420, 904, 1508; **127**, 229, 372; 1899, **128**, 557, 1239. See also Lenard and Klatt, *Ann. Phys. Chem.*, 1889, **38**, 90; Waentig, *Zeit. physikal. Chem.*, 1905, **51**, 435.

[5] Bruckner, *Zeit. Elektrochem.*, 1920, **26**, 35.

with an excess of the salt at a somewhat higher temperature, the compound $H_2SO_4,SrSO_4$ separates out as a granular crystalline powder, which when exposed to moist air changes into small glittering tablets having the composition $H_2SO_4,SrSO_4,H_2O$.

Strontium Nitrate, $Sr(NO_3)_2$, is obtained by dissolving the carbonate in warm dilute nitric acid. When the solution is evaporated down, the anhydrous salt separates out in transparent octahedra or in combinations of the octahedron and the cube. When a dilute solution is cooled down, the hydrate, $Sr(NO_3)_2,4H_2O$, separates out in large, well-developed monoclinic crystals which quickly effloresce on exposure to the air. One hundred parts of water dissolve, according to Mulder:

At	10°	20°	40°	60°	80°	100°	107·9°
$Sr(NO_3)_2$	54·9	70·8	91·3	94·0	97·2	101·1	102·9.

The transition point for the tetrahydrate and the anhydrous salt is 31·3°. Strontium nitrate is insoluble in concentrated nitric acid, and only very slightly soluble in absolute alcohol; it possesses a cooling taste, and has a specific gravity of 2·962 (Schröder). When thrown on to red-hot charcoal it deflagrates, burning with a red flame, and is on this account largely used for pyrotechnic purposes.

The *nitride*,[1] *arsenide*,[2] *phosphide*,[3] and *boride*[4] of strontium closely resemble the corresponding calcium compounds.

Strontium Carbonate, $SrCO_3$, occurs as strontianite in crystals which are isomorphous with those of aragonite. This compound is obtained in the form of a white impalpable powder having a specific gravity of 3·62, when a strontium salt is precipitated by an alkali carbonate. When gently ignited it loses all its carbon dioxide and is converted into strontia. In a current of carbon dioxide, it is converted into oxide at 1155°.[5] One litre of water dissolves 11·0 mgrms. of this salt at 18°.[6] It is less soluble in water containing ammonia, but dissolves considerably in a solution of ammonium chloride and of ammonium nitrate. When boiled with ammonium chloride it is converted into strontium chloride.

[1] Gautier, *Compt. rend.*, 1902, **134**, 1108.
[2] Lebeau, *ibid.*, 1899, **129**, 47.
[3] Jaboin, *ibid.*, 1889, **129**, 762.
[4] Moissan, *ibid.*, 1897, **125**, 629.
[5] Brill, *Zeit. anorg. Chem.*, 1905, **45**, 275.
[6] Bineau, *Ann. Chim. Phys.*, 1887, [3], **51**, 290. Compare Kohlrausch and Rose, *Zeit. physikal. Chem.*, 1893, **12**, 241; Hollemann, *ibid.*, 1893, **12**, 125.

Detection and Estimation of Strontium.

271 Strontium salts colour the flame a magnificent crimson. When examined by the spectroscope the spectrum is found to consist of numerous bright lines or bands due to the salts and oxide of the metal, of which eight are specially characteristic, six in the red, one in the orange, and one in the blue. The orange line, termed Sr α (6045 Å.U.), the red, Sr β, and Sr γ, and the blue line, Sr δ (4608 Å.U.), are the most intense, and therefore the most valuable for the discrimination of this element.[1] By means of spectrum analysis $\frac{6}{1000}$ mgrm. of strontium chloride can be detected. H. Fox Talbot[2] was the first to describe the spectrum of strontium. He examined the spectrum of the red fire of theatres and distinguished many of the strontium lines, especially the blue line, Sr δ (p. 158). In order to detect strontium the bead, either alone or moistened with hydrochloric acid, is brought into the flame. If strontium be supposed to be present as sulphate the bead is held for a few moments in the reducing portion of the flame, and then moistened with hydrochloric acid in order to convert the strontium sulphide which is formed into strontium chloride. The strontium salts containing non-volatile acids are melted on a platinum wire with a small quantity of sodium carbonate. The fused bead is then reduced to a fine powder and dissolved in a little hot water, and the residue, which contains strontium carbonate, moistened with hydrochloric acid, and the chloride brought on a wire into the non-luminous flame.

Strontium is separated from the alkali metals by precipitation with ammonium carbonate, and is usually estimated quantitatively as the sulphate by precipitating the solution with sulphuric acid in the presence of alcohol and washing the precipitate with a weaker alcohol. In order to separate it from calcium the mixed carbonates are converted into nitrates, and these are treated with absolute alcohol or amyl alcohol,[3] which leave the nitrate of strontium undissolved.

Atomic Weight of Strontium.—The atomic weight of strontium was determined by Marignac[4] from the amount of silver required to precipitate a known weight of pure crystallised strontium chloride, and also from the amount of strontium

[1] See Riesenfeld and Wohlers, *Ber.*, 1906, **39**, 2628.

[2] *Brewster's Journ. of Science*, 1826, **5**.

[3] Browning, *Amer. J. Sci.*, 1892, **43**, 50.

[4] *Annalen*, 1858, **106**, 165.

sulphate formed from the chloride; he thus obtained the numbers 86·64 and 86·76 respectively. Richards,[1] from the determination of the amount of silver required to precipitate a known quantity of pure strontium bromide and the quantity of silver bromide formed, obtained as the average of a number of consistent experiments the figure 87·663 (O = 16). A later determination[2] of the ratio of silver to strontium chloride gave the value 87·661.

On the basis of Richards' work, and after revision of the fundamental values,[3] the figure 87·62 was taken as the atomic weight of strontium. In 1910, Thorpe and Francis[4] determined the ratios $2Ag : SrBr_2$, $2AgBr : SrBr_2$, $2Ag : SrCl_2$, $2AgCl : SrCl_2$, $SrBr_2 : SrSO_4$, $SrCl_2 : SrSO_4$, and arrived at a mean value of 87·65. The figure at present (1922) adopted as the atomic weight of strontium is 87·63.

BARIUM. Ba = 137·37. At. No. 56.

272 Our knowledge of the barium compounds commences with that of the natural sulphate or heavy-spar. This substance was first examined in the year 1602 by a Bolognese shoemaker, V. Casciorolus, who noticed that it possessed the remarkable property of becoming phosphorescent when ignited with carbonaceous matter. To this material the discoverer gave the name of *lapis solis*, but it became better known as Bolognian or Bononian phosphorus, from the place in which it was first prepared, whence specimens of the shoe-maker's handiwork found their way into the laboratories of the alchemists of the time. The mineral which yielded this phosphorus, termed Bolognian spar, was first believed to be a peculiar kind of gypsum, and hence it was termed *gypsum spathosum*. In consequence of its high specific gravity, Cronstedt termed it *marmor metallicum*, and Marggraf in 1750, finding that it contained sulphuric acid, ranked it amongst what were then termed the heavy fluor-spars. The nature of this mineral remained for some time obscure, and the learned mineralogist v. Justi wrote in 1760 concerning it as follows: "Our analysis has here reached its limits; we know of no smelting operation by which anything can be got out of this spar. Many profound

[1] *Zeit anorg. Chem.*, 1895, **8**, 253.
[2] Richards, *ibid.*, 1905, **47**, 145.
[3] *Proc. Chem. Soc.*, 1909, **25**, 7.
[4] *Proc. Roy. Soc.*, [A], 1909–10, **83**, 277.

chemists and skilful assayers have here tried their art in vain." The next step in our knowledge of this subject was made in the year 1774, when Scheele, who was engaged in his investigation on the black oxide of manganese, examined a specimen of this mineral, which he found to contain a new earth, and this when brought in contact with sulphuric acid yielded a salt insoluble in water, which could be brought into a soluble condition by ignition with carbon and an alkali. Gahn afterwards showed that this earth was contained in heavy-spar, and Bergman gave it the name *terra ponderosa*. Guyton de Morveau in 1779 proposed the name barote (from βαρύς, heavy), and this name, slightly altered to baryta by Lavoisier, was soon generally adopted. The suggestion that this earth was the oxide of a metal was frequently made, but the fact was not proved until after Davy's discovery of the decomposition of the alkalis.

Barium occurs in nature chiefly as the sulphate or heavy-spar, $BaSO_4$, which is often found together with galena and other metallic ores, though also found not associated with metallic veins. Another source of barium compounds, less widely distributed, is the carbonate or witherite, $BaCO_3$, whilst other minerals containing barium are barytocelestine, $(Ba,Sr,Ca)SO_4$, barytocalcite, $BaCO_3,CaCO_3$, alstonite, $(Ba,Ca)SO_4$, and psilomelane $(Mn,Ba)O,MnO_2$. Many other ores of manganese, especially manganese dioxide, contain small quantities of barium. Barium also occurs as an essential constituent of certain silicates; thus, for instance, brewsterite, $H_4(Sr,Ba)Al_2Si_6O_{18},3H_2O$, harmotome, $H_2(K_2,Ba)Al_2Si_5O_{15},4H_2O$, and hyalophane or baryta-felspar, $(K_2,Ba)_2Al_2Si_8O_{24}$. Many other felspathic rocks also contain traces of barium, and this element occurs likewise in several other minerals and in some soils. It is also found not infrequently in the ash of trees. Traces are found in mineral waters and in sea-water. Thus, for instance, the old sulphur well at Harrogate contains 6·6 grains of barium chloride per gallon (Hayton Davis),[1] whilst an artesian well at Ilkeston,[2] and the water of the Boston Spa,[3] each contain about 40 parts of barium chloride per 100,000. From sea-water, barium finds its way into sea-plants, and in smaller quantities into the shells and skeletons of sea animals.

Preparation of Metallic Barium.—Davy's first attempts to obtain metallic barium by the electrolysis of baryta were not

[1] Thorpe, *Phil. Mag.*, 1876, [5], **2**, 52. [2] White, *Analyst*, 1899, **24**, 67.
[3] Richards, *ibid.*, 1901, **26**, 68.

very successful. Afterwards finding that this did not succeed he prepared it from an amalgam, having heard from Berzelius that he and Pontin had succeeded in obtaining it in that way. Davy repeated these experiments and electrolysed baryta, barium chloride, and other barium salts in presence of mercury, heating the amalgam which was thus formed in a tube containing rock oil, when the barium was left behind as a silver-white powder. Bunsen [1] also prepared barium amalgam by the electrolysis of barium chloride in presence of mercury, and attempted to obtain the pure metal by heating this. It has, however, been found that the metal prepared in this way is invariably impure, and cannot be obtained quite pure even by distillation.[2] Small globules of impure barium were obtained by Matthiessen [3] by the electrolysis of fused barium chloride, but the metal was first prepared in a state of purity by Guntz,[4] who employed the same method as for strontium (p. 613). Crude barium, obtained from the amalgam, is converted into the hydride, and this is melted in hydrogen and then heated to 1200° *in vacuo*. The barium volatilises, and is condensed on a polished steel tube. It can also be prepared by heating baryta with 10 per cent. of its weight of aluminium *in vacuo* at 1200° and redistilling in vacuo,[5] by distilling a mixture of baryta and silicon in an exhausted steel tube,[6] or, better, by electrolysis of a fused mixture of potassium and barium chlorides using a high cathodic current density.[7]

Barium is a silver-white metal, of sp. gr. 3·78, melts at about 850°, and boils at about 1150°. It rapidly oxidises, sometimes inflaming spontaneously in the air, and decomposes both water and alcohol. It combines readily with hydrogen and nitrogen when heated in these gases.

[1] *Pogg. Ann.*, 1854, **91**, 619.

[2] Guntz, *Ann. Chim. Phys*, 1905, [8], **4**, 5; Stansfield, *Mem. Manch. Phil. Soc*, 1901, **46**, No. 4.

[3] *Annalen*, 1855, **93**, 277.

[4] *Compt. rend*, 1905, **141**, 1240.

[5] Guntz, *ibid.*, 1906, **143**, 339.

[6] Matignon, *ibid.*, 1913, **156**, 1378.

[7] Neumann and Bergoe, *Zeit. Elektrochem*, 1914, **20**, 187.

COMPOUNDS OF BARIUM.

Barium and Oxygen.

273 *Barium Suboxide*, Ba_2O.—When baryta is heated to 1100° with an atomic proportion of magnesium, half the magnesium distils off, leaving a dark-coloured residue, which is considered by Guntz [1] to be a mixture of barium suboxide and magnesia. It decomposes water, yielding an amount of hydrogen equivalent to half the barium in the original baryta, and absorbs both nitrogen and hydrogen. A similar dark-coloured mass is obtained by heating barium with baryta.

Barium Monoxide or *Baryta*, BaO, is formed when the metal burns in the air, but is usually obtained by heating the nitrate in an iron crucible, until no further evolution of red fumes is observed. The mass fuses and is apt to froth over unless care be taken. Mohr has proposed to mix the nitrate with its own weight of sulphate of barium; this prevents the frothing, and for many purposes the presence of insoluble barium sulphate does not matter. If only a small quantity of baryta is required it is best obtained by igniting the iodate, which gives off its iodine and five-sixths of its oxygen without fusing or frothing:

$$2Ba(IO_3)_2 = 2BaO + 2I_2 + 5O_2.$$

It is also prepared by heating barium carbonate to a white heat, the reaction proceeding more readily if this be mixed with one-tenth of its weight of lamp-black or wood-charcoal, carbon monoxide being then evolved:

$$BaCO_3 + C = BaO + 2CO.$$

The material thus obtained sometimes contains a small amount of barium cyanide. Baryta is thus obtained as a greyish-white porous mass, which has a specific gravity of 4·73 (Karsten), 5·46 (Filhol), and melts at about 2,000°, crystallising on cooling in cubes, which have a specific gravity of 5·72. It combines with water with great evolution of heat forming the hydroxide, becoming incandescent if only sprinkled with water. It also unites with oxygen at a red heat, the oxygen being evolved on further heating, and it has therefore been used for the manufacture of oxygen (Vol. I., p. 246).

[1] *Compt. rend.*, 1906, **143**, 339.

Barium Hydroxide, $Ba(OH)_2$, is formed as a white powder by the reaction just described. The hydroxide melts at a low red-heat, forming an oily liquid, which on cooling solidifies to a crystalline mass, and this does not give off water even when more strongly heated. It is prepared on the large scale from barium sulphide, which is heated in earthenware retorts, into which a current of moist carbon dioxide is passed. Superheated steam is then passed over the carbonate, when the following decomposition takes place :

$$BaCO_3 + H_2O = Ba(OH)_2 + CO_2.$$

It may also be prepared on the large scale by the electrolysis of a solution of barium hydrosulphide.[1] It has a specific gravity of 4·495 (Filhol), and when brought into contact with water forms a crystalline hydrate, $Ba(OH)_2,8H_2O$. This hydrate is soluble, and when a saturated solution is cooled it separates out in tetragonal prisms which are isomorphous with strontium hydroxide. On exposure to air these crystals fall to a white powder with loss of seven molecules of water, forming the monohydrate. They melt in their water of crystallisation at 77·9° (Richards and Churchill),[2] 78° under 732 mm. pressure (Bauer); [3] this solution boils at 103°, and at 109° deposits rhombic crystals of the hydrate with $3H_2O$, which lose $2H_2O$ over sulphuric acid (Bauer). A hydrate with $16H_2O$ is also known. One hundred parts of water dissolve :

At	0°	20°	40°	60°	80°
$Ba(OH)_2$	1·65	3·9	8·3	21·0	101·5 parts.

A solution of the hydroxide is termed *baryta water*, and is largely used in the processes of chemical analysis. It has a more strongly alkaline reaction than lime water, and rapidly absorbs carbon dioxide. It is employed, as has been stated in Vol. I., p. 607, for the estimation of the carbon dioxide contained in the atmosphere, for which purpose it must be free from hydroxides of the alkali metals.

Barium Dioxide, BaO_2.—When heated to redness in a current of dry oxygen, pure baryta absorbs the gas with rapidity, forming the dioxide (Gay-Lussac and Thénard); it is also formed by heating baryta and potassium chlorate to low redness (Liebig

[1] Brocket and Ransom, *Compt. rend.*, 1903, **136**, 1258.
[2] *Zeit. physikal. Chem.*, 1898, **28**, 313.
[3] *Zeit. anorg. Chem.*, 1905, **47**, 401.

and Wöhler). The hydroxide when heated to redness in a current of air also yields the dioxide (Boussingault). In Brin's process for the manufacture of oxygen it is obtained as an intermediate product by heating pieces of baryta of the size of walnuts to 700° in steel retorts, and passing air through these under an additional pressure of 15 lb. per square inch. The product obtained by any of these methods is a greyish porous mass, and usually contains silica, lime, and also ferric oxide derived from the vessels in which it is prepared. To obtain it in the pure state it is treated in the manner already described under hydrogen peroxide (Vol. I., p. 338); then when dried at 130° it forms an impalpable white powder, which can hardly be distinguished from magnesia. It can readily be prepared on the small scale by adding hydrogen peroxide to a solution of baryta water. It fuses at a bright red-heat with loss of one atom of oxygen, and combines with water to form the hydrate $BaO_2,8H_2O$, crystallising in microscopic hexagonal plates, which are only very slightly soluble in water. It also forms mono- and di-peroxyhydrates, BaO_2,H_2O_2 and $BaO_2,2H_2O_2$.[1] The dissociation pressure of barium peroxide is 760 mm. at 795°: its decomposition is greatly facilitated by admixture with silica, and many other metallic and non-metallic oxides.[2]

Barium and Hydrogen.

274 *Barium Hydride*, BaH_2, is formed when barium amalgam is heated in an iron boat to 1400° in a current of hydrogen. It forms a grey, crystalline mass of sp. gr. 4·21, melts at about 1200° and is decomposed by water.[3] When heated in nitrogen, hydrogen is evolved and the nitride produced.

Barium and the Halogens.

275 *Barium Chloride*, $BaCl_2$, is most readily obtained by dissolving witherite in dilute hydrochloric acid. As, however, this mineral contains calcium, lead, iron, and manganese compounds, an excess of barium carbonate is added to the solution and the liquid allowed to remain in contact with it for some

[1] Riesenfeld and Nottebohm, *Zeit. anorg. Chem*, 1914, **89**, 405.

[2] Hedvall, *ibid.*, 1918, **104**, 163; Hedvall and Zweigbergk, *ibid.*, 1919, **108**, 119.

[3] Guntz, *Compt. rend.*, 1901, **132**, 963; Gautier, *ibid*, 1902, **134**, 1108.

time. In this way the oxides of the above metals are precipitated, while the rapidity of the precipitation can be increased by the addition of a small quantity of baryta water. The clear solution is then neutralised with hydrochloric acid and evaporated to the point of crystallisation. On the large scale the salt is easily prepared from heavy-spar. For this purpose 100 parts of the finely powdered mineral are mixed with from 35 to 50 parts of carbon, from 15 to 25 parts of limestone, and from 40 to 60 parts of calcium chloride. This mixture is heated in a reverberatory furnace, and the mass lixiviated with water, when insoluble calcium sulphide remains behind and the barium dissolves as chloride.

Barium chloride crystallises with $2H_2O$ in colourless rhombic tablets (Fig. 160), which do not undergo any alteration in the air and have a specific gravity of 3·097. 100 parts of water dissolve :

At	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°	104·1°
$BaCl_2$	33·3	35·7	38·2	40·8	43·6	46·4	49·4	52·4	55·6	58·8	60·3.

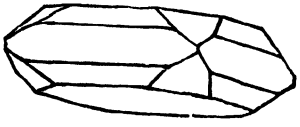


Fig. 160.

Barium chloride is less soluble in dilute hydrochloric acid than it is in water. It is almost insoluble in the concentrated acid, and also but slightly soluble in strong nitric acid, and for this reason these acids precipitate concentrated solutions of a barium salt. Absolute alcohol does not dissolve barium chloride, and addition of alcohol to its aqueous solutions precipitates the salt.

Crystallised barium chloride loses its water at a temperature of 113°, forming the anhydrous salt as a white powder of sp. gr. 3·856, which melts at 960° (Ruff and Plato) and on cooling solidifies to a translucent mass. On exposure to the air the chloride in a state of fusion parts with a small quantity of chlorine, baryta being formed. Hence the fused salt usually has an alkaline reaction. When heated in a current of steam it emits hydrochloric acid at a temperature below its fusing point. Barium chloride has an unpleasant bitter taste and acts as a powerful poison. Its chief use is for the preparation of the artificial sulphate or *permanent white*. It has also been

successfully employed for the prevention of incrustation in steam boilers when permanently hard waters are used. All the gypsum contained in solution is decomposed by barium chloride, whilst any calcium carbonate present in solution may be subsequently precipitated by milk of lime. The water thus softened forms no incrustation.

Barium Fluoride melts at 1280°, the *bromide* at 880°, and the *iodide* at 740° (Ruff and Plato).

Subhalogen Salts of Barium.—Like calcium and strontium, barium appears to form a series of halogen salts in which it is monovalent. The subchloride, BaCl, is formed at the cathode by the action of barium on the chloride during the electrolysis of the latter, and decomposes water readily. A series of crystalline double salts with the halogen salts of sodium can be obtained by heating the barium halogen salts with metallic sodium. The compound BaCl,NaCl, prepared in this way, decomposes water, loses metallic sodium at 700° *in vacuo*, and when treated with mercury yields barium amalgam.[1]

Barium Chlorate, $Ba(ClO_3)_2$, is obtained by adding barium chloride to a solution of sodium chlorate, double decomposition taking place:

$$2NaClO_3 + BaCl_2 = Ba(ClO_3)_2 + 2NaCl.$$

The solution on concentration deposits sodium chloride, which is fished out; the remaining solution is then evaporated and the barium chlorate purified by recrystallisation. It crystallises with one molecule of water in monoclinic prisms which readily dissolve in water and alcohol, the latter solution burning with a characteristic green flame. If a drop of sulphuric acid be brought on to a mixture of the salt and powdered sugar it takes fire and burns with a bright green flame, and if the chlorate in a state of fusion and strongly heated be plunged into an atmosphere of coal-gas, combustion also takes place, the oxygen of the chlorate combining with the carbon and hydrogen of the coal-gas. It is largely used for pyrotechnic purposes.

Barium Iodate, $Ba(IO_3)_2$.—This salt is employed for the preparation of iodic acid. It is obtained as a white granular precipitate by adding potassium iodate to barium chloride (Vol. I., p. 368). Barium iodate dissolves in about 4500 parts of cold and 500 parts of boiling water. It also dissolves in

[1] Guntz, *Compt. rend.*, 1903, **136**, 749; Haber and Tolloczko, *Zeit. anorg. Chem.*, 1904, **41**, 407.

hot nitric acid, from which solution it crystallises, on cooling, with one molecule of water in bright glittering monoclinic prisms; these are isomorphous with those of the chlorate and are decomposed by hydrochloric acid with evolution of iodine.

Barium and Sulphur.

276 *Barium Monosulphide*, BaS, is obtained when sulphuretted hydrogen is passed over heated baryta as long as water is formed. On the large scale it is prepared by roasting 20 parts of slack or pitch with 100 parts of heavy-spar. In order to assist the evolution of the carbon dioxide sawdust may be added to the mixture. It can be obtained crystalline [1] by fusing the amorphous salt in the electric furnace, and then has the sp. gr. 4·3. Barium sulphide decomposes in contact with water into barium hydroxide and barium hydrosulphide:

$$2BaS + 2H_2O = Ba(SH)_2 + Ba(OH)_2,$$

but these combine to form an additive compound $OH.Ba.SH,5H_2O$ which is obtained in colourless transparent six-sided tables when the solution is allowed to evaporate in vacuo. When these crystals are treated with a small quantity of water, barium hydrosulphide dissolves and barium hydroxide remains behind, but under no conditions can pure barium hydroxide be crystallised from a solution of the double salt.[2]

Barium Hydrosulphide, $Ba(SH)_2$, is prepared by saturating water with barium hydroxide in an atmosphere of hydrogen at 100°, and passing sulphuretted hydrogen free from oxygen through the solution heated to 60—70° for several days.[3] It crystallises with $4H_2O$ in aggregates of colourless, spear-shaped needles, which dissolve in water and lose sulphuretted hydrogen readily when heated, so long as water is also driven off, the sulphur then remaining only being given off at a red-heat.

Barium Tetrasulphide, BaS_4, is obtained by boiling aqueous solutions of the sulphide or hydrosulphide with sulphur, and forms red crystals, containing according to Schone $1H_2O$, and according to Veley, $2H_2O$. It dissolves in water, forming a deep red solution. A *barium trisulphide* and *pentasulphide* have also been described, but their existence is doubtful.

[1] Mourlot, *Compt. rend*, 1898, **126**, 643.
[2] Bruckner, *Zeit. Elektrochem.*, 1920, **26**, 1.
[3] Veley, *Journ. Chem. Soc.*, 1886, **49**, 369.

Bononian Phosphorus.—The Bononian phosphorus which has been already mentioned (Vol. I, p. 618) is best prepared by heating 5 parts of precipitated barium sulphate together with 1 part of powdered charcoal over an ordinary gas flame for 30 minutes, and then igniting it more strongly over a gas blowpipe for ten minutes. Whilst hot the mass must be filled into glass tubes and the tubes sealed. After exposure to sunlight or to the light of burning magnesium wire this mass phosphoresces in the dark with a bright orange-coloured light. The pure sulphide, like pure sulphide of calcium and of strontium, does not exhibit phosphorescence, but does so in the presence of small quantities of many metallic salts.[1]

Barium Sulphate, $BaSO_4$, is by far the commonest and most widely distributed of the barium compounds, and occurs as heavy-

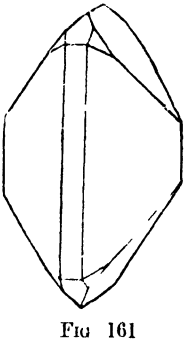


Fig 161

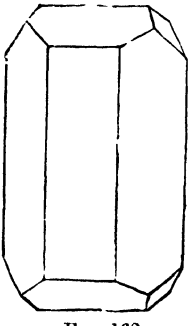


Fig 162

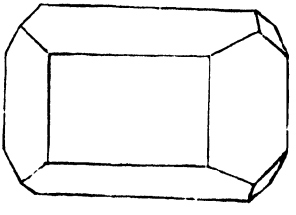


Fig 163

spar, which crystallises in the rhombic system, Figs. 161—163. If anhydrous baryta be brought into contact with fuming sulphuric acid, or even with sulphuric acid which contains a small quantity of water, combination takes place with such rapidity that the mass becomes incandescent. On the other hand, pure sulphuric acid which has the exact composition H_2SO_4, does not act upon baryta, but if the mixture be touched in one place with a hot iron or with a moistened glass-rod, combination begins and is at once propagated throughout the mass (Kuhlman). Sulphuric acid and its salts precipitate the sulphate from a solution of a soluble barium salt in the form of a crystalline powder. The pure mineral heavy-spar has a specific gravity of 4·486 (H. Rose), the precipitated salt at 4° having a specific gravity of 4·53 (Schröder). This salt is almost insoluble in water,

[1] Lenard and Klatt, *Ann. Phys.*, 1904, [4], **15**, 225, 425.

1 litre dissolving[1] only 0·0024 gram at 18·3°. The solubility is greatly influenced by the size of the particles of the solid salt.[2] It is somewhat more soluble in dilute acids and in the presence of many salts, *e.g.*, sodium thiosulphate. Barium sulphate is precipitated in a remarkable gelatinous form when dilute sulphuric acid is added to a solution of baryta in methyl alcohol, which when dried and heated forms hard masses resembling porcelain. A number of other salts of the alkaline earth metals can be obtained in a similar form.[3] If a salt of barium be heated with concentrated sulphuric acid, the sulphate dissolves to a certain extent and separates out on cooling in crystals having the composition $H_2SO_4,BaSO_4$; if the acid solution be exposed to moist air bright silky needles are formed having the composition $H_2SO_4,BaSO_4,2H_2O$.

The crude heavy-spar is prepared for use as a paint, either alone or along with white lead, by being finely ground, treated with sulphuric acid to remove salts of iron, washed and dried. Artificial barium sulphate is also manufactured on a large scale and is known as *permanent white*, or *blanc fixé*. This preparation is largely used as a pigment and is much to be preferred for this purpose to the finely ground mineral, inasmuch as the latter, with its denser structure, is transparent and has but little " body " or covering power. In order to prevent the formation of finely divided crystals a solution of barium chloride having a specific gravity of 1·19 is precipitated in the cold with dilute sulphuric acid having a specific gravity of 1·245. The precipitate is washed with cold water and sent to market in the moist state. In addition to its value as a paint, blanc fixé is largely used for giving weight to cards and paper.

Barium Disulphate, BaS_2O_7.—If powdered barium sulphate is intimately mixed with fuming sulphuric acid it dissolves, forming a syrup, which on heating to 150° deposits the disulphate in glistening granular crystals; these do not melt on heating but decompose at a dull red heat.

Barium Dithionate, $BaS_2O_6,2H_2O$.—This salt is prepared by decomposing the corresponding manganese salt with barium sulphide. On allowing the solution to evaporate in a warm place glittering rhombic crystals of the salt are deposited. It dissolves at 18° in 4·04, and at 100° in 1·1, parts of water. On

[1] Küster, *Zeit. anorg. Chem.*, 1896, **12**, 261.
[2] Hulett, *Zeit. physikal. Chem.*, 1901, **37**, 398.
[3] Neuberg and Neimann, *Biochem. Zeit.*, 1906, **1**, 166.

heating it is converted without change of form into barium sulphate.

Barium Persulphate, BaS_2O_8, is obtained by the action of barium hydroxide on ammonium persulphate, and crystallises in monoclinic prisms which are readily soluble in water, but gradually decompose on keeping, with formation of barium sulphate.

Barium and Nitrogen.

277 *Barium Nitride*, Ba_3N_2, is obtained by passing nitrogen over barium or barium amalgam heated to redness, but is best prepared by heating barium amide at 430° in a vacuum.[1] It forms a voluminous yellow powder, which volatilises slightly at 1,000° without melting. It is decomposed by water with formation of ammonia and barium hydroxide, and yields barium cyanide when heated in a current of carbonic oxide.[2]

Barium Azoimide, $Ba(N_3)_2$, obtained from ammonium nitride solution by boiling with baryta, forms hard, lustrous crystals which explode at 217°.

Barium Amide, $Ba(NH_2)_2$.—When ammonia is passed over cooled metallic barium a red mass and then a blue liquid is formed, which is regarded by Mentrel [3] as a solution of *barium ammonium*, $Ba,6NH_3$ in ammonia, but is more probably [4] a solution of metallic barium in liquid ammonia (see p. 392). At 200° ammonia is decomposed by barium with formation of the amide,[1] which is a greyish-white mass and melts at 280°.

Barium Nitrite, $Ba(NO_2)_2$, can be readily prepared by bringing a mixture of 360 grams of sodium nitrite and 610 grams of barium chloride into a boiling solution of 360 grams of sodium nitrite, filtering from the sodium chloride which is precipitated, cooling and recrystallising. It crystallises with $1H_2O$ in prisms, and serves as a convenient source for the preparation of the nitrites of other metals.[5]

Barium Nitrate, $Ba(NO_3)_2$.—This salt is prepared on the large scale either by decomposing the carbonate or sulphide by dilute nitric acid, or by mixing hot saturated solutions of sodium

[1] Guntz and Mentrel, *Bull. Soc chim.*, 1903, [3], **29**, 578.
[2] Maquenne, *Compt. rend.*, 1892, **114**, 25, 220.
[3] *Ibid.*, 1902, **135**, 740. [4] Ruff and Geisel, *Ber*, 1906, **39**, 828.
[5] Witt and Ludwig, *ibid.*, 1903, **36**, 4384. See also Arndt, *Zeit. anorg. Chem*, 1901, **27**, 341.

nitrate and barium chloride. On cooling, the larger portion of the barium nitrate crystallises out, and the remaining portion is obtained by evaporating the mother-liquors. Barium nitrate crystallises in combinations of the cube and octahedron, and in other more complicated forms of the regular system (Lewis). Its specific gravity is 3·2; it possesses an acrid taste and melts at a temperature of 593° (Carnelley). One hundred parts of water dissolve:

At	0°	10°	20°	50°	80°	100°	102°
$Ba(NO_3)_2$	5·0	7·0	9·2	17·1	27·0	32·2	34·8.

The salt is insoluble in concentrated nitric acid and in absolute alcohol, and dissolves only sparingly in these liquids diluted with water. Barium nitrate is largely used for pyrotechnic purposes, especially for the preparation of green fire, and for the manufacture of an explosive powder known as *saxifragin*, which consists of a mixture of 76 parts of nitrate of barium, 22 parts of carbon, and 2 parts of nitre.

Barium and Carbon.

278 *Barium Carbide*, BaC_2.—This substance is obtained by heating baryta with charcoal in an electric furnace, and closely resembles the corresponding calcium compound. Its behaviour on heating in nitrogen is, however, different from that of calcium, which forms calcium cyanamide. Barium carbide forms the cyanide:[1]

$$BaC_2 + N_2 = Ba(CN)_2.$$

Barium Carbonate, $BaCO_3$.—Barium carbonate occurs in nature as witherite. This mineral was discovered at Leadhills in Scotland by Withering in the year 1783. It crystallises in rhombic prisms and pyramids, is isomorphous with aragonite, and is chiefly found in England, one of its most celebrated localities being Fallowfield in Northumberland. It occurs also in Silesia, Hungary, Styria, Russia, Chili, and other places. Alstonite, $(Ba,Ca)CO_3$, is isomorphous with witherite, and contains the two metals in varying proportions. Baryto-calcite, on the other hand, has the formula $BaCO_3,CaCO_3$, and crystallises in the monoclinic system.

Artificial barium carbonate is a dense white powder of sp. gr.

[1] Erlwein, *Zeit. Elektrochem.*, 1903, **9**, 842.

4·275, obtained when a solution of chloride of barium is poured into an excess of a hot solution of ammonium carbonate. Barium carbonate appears to undergo a polymorphic change [1] at 811°, and does not melt below 1350° when heated in an atmosphere of carbon dioxide.[2] When heated in the air a basic carbonate, $BaO,BaCO_3$, appears to be formed, which melts below 980°. The dissociation pressure is 2·7 mm. of carbon dioxide at 1000° and 381 mm. at 1300°.

One litre of water dissolves only about 0·02 gram of barium carbonate at 18°, but it is more readily soluble in water containing carbonic acid. The artificial salt is employed in chemical analysis, and powdered witherite in the preparation of other barium salts and as a rat bane.

Barium Percarbonate, $BaCO_4$,[3] is prepared by passing carbon dioxide into cold water in which barium peroxide is suspended. It is insoluble in water, and in the dried condition slowly gives off oxygen, being converted into the carbonate.

Silicates of Barium.—It has been already stated that many of these salts occur as crystalline minerals. Barium silicate is also a constituent of baryta-glass, a flint glass in which the lead has been replaced by barium (p. 591).

Detection and Estimation of Barium.

279 The non-luminous gas-flame is coloured a yellowish-green tint when any volatile barium compound is brought into it. The barium compounds yield the most complicated of the spectra of the alkalis and alkaline earths. The spectrum is, however, at once distinguished by the green lines Baα and Baβ, which are by far the most distinct, appearing the first and continuing during the whole of the experiment. Baγ is not nearly so distinct, but is still a well-marked and characteristic line. As the spectrum of the barium compounds is more extended than the spectra of the compounds of the other metals, the reaction is not observed with so great a degree of delicacy, but it appears from Bunsen's experiments that about $\frac{1}{10000}$ of a milligram of barium salt may be detected with the greatest certainty. The chloride, bromide, iodide, and fluoride of barium, as well as the hydroxide, the sulphate, and carbonate, show the reaction

[1] Boeke, *Zeit. anorg. Chem.*, 1906, **50**, 1244.
[2] Finkelstein, *Ber.*, 1906, **39**, 1585.
[3] German Pat., 178019.

best. It may be obtained by simply heating any of these salts in the flame. Silicates containing barium which are decomposed by hydrochloric acid give the reaction, if a drop of hydrochloric acid is added to them before they are brought into the flame. Baryta-harmotome, treated in this way, gives the lines Caα and Caβ, together with the bands Baα and Baβ. Compounds of barium with fixed acids, giving no reaction either when alone or after addition of hydrochloric acid, should be fused with carbonate of sodium, as described under strontium, and the carbonate of barium thus obtained examined. If barium and strontium occur in small quantities together with large amounts of calcium, the carbonates obtained by fusion are dissolved in nitric acid and the dry salt extracted with alcohol; the residue contains only barium and strontium, both of which can almost always be detected. To test for very small traces of strontium or barium, the residual nitrates are converted into chlorides by ignition with sal-ammoniac, and the chloride of strontium is extracted by alcohol. Unless one or more of the bodies to be detected is present in very small quantities, the methods of separation just described are quite unnecessary. The detection of these three metals by the spectroscope is much facilitated by the use of a special burner in which a spray of the solution of the salts to be examined is brought into the flame.[1]

Soluble barium salts are distinguished from those of strontium and calcium, inasmuch as they are *immediately* precipitated by a solution of calcium sulphate. The qualitative separation of barium from strontium and calcium is usually effected by the addition of potassium chromate to a solution of the mixed salts containing acetic acid, barium chromate being precipitated. Barium and strontium may be separated by treating the mixed chlorides with absolute alcohol, or preferably by the action of amyl alcohol on the mixed bromides,[2] the barium salt being almost insoluble in both solvents. For quantitative estimation barium is almost always weighed as the sulphate, but in some special cases as the carbonate.

Atomic Weight of Barium.—The atomic weight of barium was determined by Marignac from the exact quantity of silver required to precipitate a known weight of crystallised barium chloride, and also from the weight of barium sulphate obtained

[1] Riesenfeld and Wohlers, *Ber.*, 1906, **39**, 2628.

[2] Browning, *Amer. J. Sci*, 1893, **44**, 459.

from the same salt, the number obtained being 136·15. Richards [1] subsequently redetermined the atomic weight by ascertaining the equivalent of both barium chloride and bromide to silver and silver chloride or bromide, and the results, which agree very closely, give the average number Ba 137·37, which is now (1922) adopted.

[1] *Zeit. anorg. Chem.*, 1892, **3**, 441; 1893, **6**, 89.

THE MAGNESIUM GROUP.

280 The elements of this sub-group differ from the metals of the alkaline earths more especially in the properties of the metals themselves, which are much more readily obtained in the free state and only undergo at most a slight superficial oxidation in the air at the ordinary temperature. At higher temperatures they combine with oxygen, forming the oxide corresponding to the divalent series of salts, and magnesium and zinc slowly decompose water at the boiling point. They are colourless and ductile metals, the melting and boiling points of which fall with increasing atomic weight, mercury being a liquid at the ordinary temperature, whilst it solidifies at a low temperature to a malleable solid. Most of the salts closely resemble the corresponding salts of the alkaline earth metals, except that they exhibit a greater tendency to form basic salts, and that the sulphates are readily soluble in water, and yield crystalline double salts. Mercuric sulphate forms an exception, as it is converted by water into an insoluble basic salt and a soluble acid salt, and mercury also differs from the other metals inasmuch as it forms a series of stable salts in which each atom of the metal replaces only one atom of hydrogen, in addition to the series common to all the members of the group, in which the metal is divalent. Some of the magnesium, zinc, and cadmium compounds combine with ammonia forming derivatives analogous to the ammoniacal copper compounds, mercury, in particular, yielding a large series of such derivatives.

GLUCINUM. Gl = 9·1. At. No. 4.

281 Vauquelin in 1798 was the first to detect the existence of the oxide of this metal in beryl, this mineral having formerly been regarded as a compound of silica with lime or alumina. The earth contained in beryl was shown by Vauquelin to be a distinct body, differing from both lime and alumina, inasmuch as it formed a soluble sulphate which was incapable of uniting with potassium sulphate to form an alum. Haüy had

previously observed that emerald was mineralogically identical with beryl, and on examining the former mineral Vauquelin found that it likewise contained the new earth. He did not give any special name to this new earth, but the editors of the *Annales de Chimie* gave it the name of glucina from γλυκύς sweet, because its salts possessed a peculiar sweet taste. As, however, there are other salts which possess the same property, the name beryllia, derived from the mineral, was given to it by the German chemists. The metal has likewise received two names, glucinum and beryllium, the former of which is to be preferred on historical grounds and is adopted here, although the latter is still employed by chemists in Germany.

Glucinum occurs in many minerals, especially in beryl, $Gl_3Al_2Si_6O_{18} = 3GlO,Al_2O_3,6SiO_2$, crystallising in hexagonal

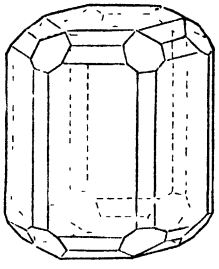


Fig 164.

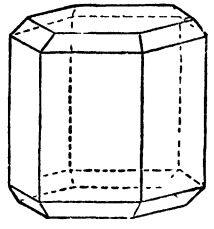


Fig. 165.

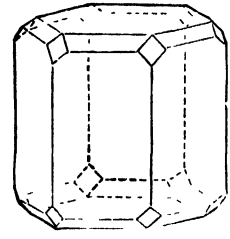


Fig. 166.

prisms, Figs. 164—166 (Class 27, p. 209), which usually have a green colour, colourless beryl being seldom met with. The transparent green-coloured varieties of beryl are known as emerald, those possessing a bluish-green tint being termed aquamarine; the green colour of emerald is probably due to traces of chromium. Beryl occurs also of a blue, yellow, grey, and rose-red tint. When the mineral is transparent it is termed precious beryl: when translucent or opaque it is known as common beryl. Glucinum also occurs in leucophane, $NaCaGlF(SiO_3)_2$; in phenacite, Gl_2SiO_4; euclase, $H_2O,2GlO,Al_2O_3,2SiO_2$; and chrysoberyl, GlO,Al_2O_3, as well as in other minerals.

Metallic Glucinum was first obtained by Wöhler in the year 1828 by fusing the chloride with potassium. Prepared in this way glucinum is a dark-grey powder, which under the burnisher assumes a bright metallic lustre.[1]

Debray first obtained the metal in a coherent state by placing

[1] *Ann. Chim. Phys*, 1855 [3], **44**, 5.

in a glass tube two or more boats made of a mixture of clay and lime, the first containing glucinum chloride and the others metallic sodium. The air having been replaced by dry hydrogen, the boats were heated, by which means the glucinum chloride was vaporised and then reduced by the melted sodium. Later, Nilson and Pettersson[1] prepared it by heating potassium glucinum fluoride with the calculated quantity of sodium in a steel crucible. Glucinum can also be prepared by the electrolysis of a fused mixture of the chloride with sodium chloride and ammonium chloride,[2] or of the fused double fluorides, $GlF_2,2NaF$, or GlF_2,NaF, the pure halogen salts offering too great a resistance to the current.[3] The metal has a specific gravity of 1·842,[4] and a specific heat of 0·4246 (Nilson and Pettersson), giving an atomic heat of 3·9 (see p. 19). It is a hard metal, possesses a bright silver-white colour,[5] melts at 1278° ± 5° [6] and when heated before the blowpipe becomes covered with a film of oxide which prevents further oxidation. In the finely powdered state, on the other hand, it takes fire when heated in the air and burns with great brilliancy. The powdered metal dissolves in dilute acids; the compact form is readily soluble in dilute hydrochloric acid, but dilute sulphuric acid dissolves it only when warm, whilst concentrated nitric acid does not attack it in the cold, and on heating does so only slowly. The metal does not decompose water even at a red heat (Debray). Ammonia does not act either on the powder or on the compact metal, but both forms dissolve readily in caustic potash with evolution of hydrogen.

GLUCINUM COMPOUNDS.

Glucinum and Oxygen.

282 *Glucinum Oxide, Glucina,* or *Beryllia,* BeO.—To obtain this earth from beryl the latter is fused with twice its weight of potassium carbonate and the melt treated with sulphuric acid; the excess of acid is evaporated off, water added, the silica

[1] *Ann. Phys. Chem.*, 1878, **4**, 554.

[2] Borchers, *Journ. Chem. Soc.*, 1896, **70**, ii., 521.

[3] Lebeau, *Compt. rend.*, 1898, **126**, 744. Compare Warren, *Chem. News*, 1895, **72**, 310.

[4] Fichter and Gablczynski, *Ber.*, 1913, **46**, 1604.

[5] Compare on this point Kahlbaum and Sturm, *Zeit. anorg. Chem.*, 1905, **46**, 237.

[6] Oesterheld, *ibid.*, 1916, **97**, 1.

removed by filtration and the solution concentrated. Almost the whole of the aluminium separates out on cooling as alum, and the mother-liquor then contains chiefly the sulphates of glucinum and iron with small quantities of alum. To separate the glucinum, advantage is taken of the solubility of glucinum hydroxide and carbonate in an excess of ammonium carbonate solution, the iron and alumina being left for the most part undissolved. In carrying out the separation the mother-liquor is poured into a concentrated solution of ammonium carbonate, the liquid allowed to stand for several days, and the precipitated iron and aluminium salts filtered off. The filtrate on boiling deposits a basic glucinum carbonate together with a little ferric hydroxide.[1]

To prepare pure glucina from this precipitate, it is redissolved in ammonium carbonate solution, and a strong current of steam blown through the liquid, which precipitates the glucina; this process is repeated several times, and the final precipitate is dissolved in hydrochloric acid, precipitated with ammonia, washed, and dried.[2] According to Krüss [3] it then still contains a small quantity of impurity, which is removed by redissolving in ammonium carbonate solution, adding a little ammonium sulphide, and allowing it to stand for several days. A slight black precipitate is formed, and the filtered solution yields pure glucina.

A more convenient method [4] consists in heating powdered beryl with twice its weight of sodium silicofluoride at 850° for 30—40 minutes. Aluminium and glucinum fluorides are formed and combine with the excess of sodium fluoride, and on extraction with hot water sodium glucinum fluoride dissolves with but little alumina and silica. Addition of caustic soda precipitates the hydroxides, which are collected, washed, and dissolved in sulphuric acid. On concentrating the solution about 90 per cent. of the glucinum originally present in the beryl crystallises as the sulphate.

According to Gibson the best method of preparing glucina from beryl is as follows:—Coarsely powdered beryl is heated with 6 parts of ammonium hydrogen fluoride for 10—12 hours at a heat not exceeding dull redness. The aluminium is thus almost completely converted into insoluble aluminium fluoride,

[1] Joy, *Amer. J. Sci.*, 1863, [2], **6**, 83.
[2] Humpidge, *Proc. Roy. Soc.*, 1886, **39**, 1.
[3] *Ber.*, 1890, **23**, 727.
[4] Copaux, *Compt. rend.*, 1919, **168**, 610.

and the residue on treatment with water yields a solution containing chiefly glucinum and iron fluorides. This is evaporated to dryness, and heated with strong sulphuric acid until the ferric sulphate formed commences to decompose, fluorine and silicon being thus completely removed. The solution obtained on adding water is boiled with nitric acid to oxidise the iron to the ferric state, and the filtered liquid poured into an excess of concentrated ammonium carbonate solution. The bulk of the iron separates on addition of an equal volume of hot water, and the filtrate is then mixed with an excess of mercuric chloride and precipitated with ammonium sulphide, the whole of the iron coming down together with the mercuric sulphide, whereas it is only partially precipitated if no mercuric chloride be first added. The filtered solution is boiled to precipitate the basic glucinum carbonate, which on ignition yields pure glucina, any traces of ammonium and mercury salts being volatilised with the carbon dioxide.[1]

To prepare glucina from leucophane, the latter, after separation from admixed tourmaline, is heated with sulphuric acid to remove fluorine, the excess of acid boiled off, the residue boiled with water, and the filtered extract added to an excess of ammonium carbonate solution. After ten days the solution is filtered, the filtrate boiled, and the precipitated crude basic glucinum carbonate treated in the manner already described.[2]

A method for the extraction of glucina from gadolinite has also been described.[3]

Glucina is a white amorphous powder having a specific gravity of 3·016, which when heated to the highest temperature of a wind furnace assumes the form of microscopic prisms resembling corundum (Rose). It may be easily obtained in this form by the ignition of a mixture of glucinum and potassium sulphates (Debray), and when fused in the electric arc forms a crystalline mass,[4] harder than ruby, which has the specific gravity 3·025. It is insoluble in water, and only dissolves in dilute acids when it has not been strongly ignited. Concentrated boiling sulphuric acid dissolves it easily, and if it be fused with an alkali, and the cold mass treated with water, the glucina goes into solution.

[1] *Journ. Chem. Soc.*, 1893, **63**, 909. Compare Lebeau, *Compt. rend.*, 1895, **121**, 641; Pollok, *Journ. Chem. Soc.*, 1904, **85**, 603.

[2] Kruss and Moraht, *Ber.*, 1890, **23**, 727.

[3] James and Perley, *J. Amer. Chem. Soc.*, 1916, **38**, 875.

[4] Lebeau, *Compt. rend.*, 1896, **123**, 818.

Glucinum Hydroxide, $Gl(OH)_2$.—This is thrown down as a gelatinous precipitate when a glucinum salt is precipitated with ammonia. This precipitate is soluble in acids, caustic alkalis, and alkali carbonates, but when heated with water or dilute ammonia, or when preserved dry, it gradually becomes much less soluble.[1] On drying it forms a voluminous white powder, which is converted into the oxide by ignition.

Salts of Glucinum.

283 *Glucinum Chloride*, $GlCl_2$, is obtained in the form of snow-white needle-shaped crystals when a mixture of the oxide and sugar charcoal is ignited in a current of dry chlorine or hydrochloric acid gas. It melts at 440° (Lebeau) and boils at about 520° (Nilson and Pettersson), and the specific gravity of its vapour[2] is 2·72, corresponding to the formula $GlCl_2$. In moist air it fumes as phosphorus pentachloride does. It is deliquescent, and dissolves in water with evolution of heat, the solution having an acid reaction, owing to hydrolysis. When the aqueous solution is allowed to evaporate over sulphuric acid, colourless crystals of the hydrated chloride, $GlCl_2,4H_2O$, separate out. A basic chloride is obtained by evaporating the solution to dryness. Glucinum chloride forms double salts with iodine trichloride,[3] platinum chloride, tin chloride, and mercuric chloride. Several basic chlorides have also been described; they are, however, not well defined.

The *iodide*, GlI_2, melts at about 510°, and its vapour burns in the air when strongly heated. The *bromide*, $GlBr_2$, sublimes without melting at 450°. The *fluoride*, GlF_2, melts at about 800°, and is converted by oxygen into the oxyfluoride.[4]

Sulphates of Glucinum.—The normal salt, $GlSO_4,4H_2O$, crystallises from a hot saturated solution in tetragonal pyramids which dissolve at the ordinary temperature in their own weight of water, possess a sweet taste, and effloresce on exposure to the air. When heated they first melt in their water of crystallisation, leaving the anhydrous salt on further heating, which

[1] Hahn and van Oordt, *Zeit. anorg. Chem.*, 1904, **38**, 377; van Oordt, German Patent, 165488 (19/12/03).

[2] Humpidge, *Proc. Roy. Soc.*, 1885, **38**, 188; Nilson and Pettersson, *Ber.*, 1884, **17**, 987.

[3] Weinland and Schlegelmilch, *Zeit. anorg. Chem.*, 1902, **30**, 134.

[4] Lebeau, *Compt. rend.*, 1898, **126**, 1272, 1418.

decomposes at a red-heat, glucina remaining behind. In contact with a saturated solution this hydrate passes at about 112° into the dihydrate, which is stable in dry air and melts at 158°, yielding the monohydrate, which loses all its water at 220°; a hexahydrate also exists.[1] The sulphate does not form mixed crystals with the sulphates of copper, nickel, iron, etc., and differs in this respect from the sulphates of the magnesium group of metals.[2]

Glucinum readily forms basic sulphates, which are obtained by boiling the normal sulphate with glucinum carbonate or hydroxide; they form gelatinous or gum-like masses, and are probably not definite compounds, but solid solutions of the hydroxide and sulphate.

Glucinum Nitrate, $Gl(NO_3)_2,3H_2O$, crystallises with difficulty. It is extremely deliquescent, and is easily soluble in alcohol. When heated for twenty hours on the water-bath a thick mass of the basic salt, $Gl(OH)NO_3,H_2O$, is obtained, which is readily soluble in water. On heating to 200° the oxide is produced.

Triglucinum Orthophosphate, $Gl_3P_2O_8,6H_2O$, is precipitated by the action of disodium phosphate on glucinum salts in aqueous solution in presence of acetic acid and *monoglucinum orthophosphate* is obtained in hygroscopic leaflets by the action of phosphoric acid on glucinum hydroxide. Other phosphates, and the phosphite and hypophosphite are known.[3]

Glucinum Carbide, GlC_2, is obtained by heating glucina with sugar charcoal, and a little oil, to a very high temperature in the electric furnace. It forms transparent yellowish-brown microscopic crystals, which are slowly decomposed by water and dilute acids with evolution of pure methane.[4]

Glucinum Borocarbide, $C_4B_6Gl_6$, is produced when glucina is heated with boron in a carbon boat in the electric furnace. It forms a hard crystalline mass, which is not attacked by water, and is only superficially oxidised when heated in oxygen.[5]

Carbonates of Glucinum.—The normal carbonate, $GlCO_3,4H_2O$, is obtained by passing carbon dioxide for a considerable time through water containing basic carbonate of glucinum in suspension. The solution is allowed to evaporate over sul-

[1] Levi-Malvano, *Zeit. anorg. Chem.*, 1906, **48**, 446; Parsons, *J. Amer. Chem. Soc.*, 1904, **26**, 1433.

[2] Retgers, *Zeit. physikal. Chem.*, 1896, **20**, 481.

[3] Bleyer and Muller, *Zeit. anorg. Chem*, 1912, **79**, 263.

[4] Lebeau, *Compt. rend.*, 1895, **121**, 496; Henry, *ibid.*, 600.

[5] Lebeau, *ibid.*, 1898, **126**, 1347.

phuric acid in an atmosphere of carbon dioxide. Crystals are then formed which readily decompose with evolution of carbon dioxide.

When a solution of a glucinum salt is added to an alkali carbonate, or when a solution of the oxide in ammonium carbonate is boiled, a basic carbonate of varying composition separates out as a white powder.

Detection and Estimation of Glucinum.

284 The salts of this metal do not impart any tint to the non-luminous gas-flame. The glucinum spark spectrum contains two characteristic bright lines in the blue, having a wave-length of 4573 and 4489 (Kirchhoff and Thalén). These lines are, however, not seen when the chloride is volatilised in the electric arc (Bunsen).

Glucinum may be readily separated from all other metals by the fact that its oxide is soluble in ammonium carbonate solution. In the process of analysis it is precipitated together with alumina, and it may be separated from this earth by treatment with ammonium carbonate. For quantitative estimation and for separation from alumina and ferric oxide the method proposed by Joy may be employed. The precipitate is treated with ammonium carbonate, the filtrate boiled, and the precipitated basic carbonate of glucinum converted by ignition into the oxide, which is weighed. The metal can also be separated from aluminium by boiling the neutral solution with sodium thiosulphate, which precipitates aluminium hydroxide.[1]

Another method depends on the fact that basic glucinum acetate readily sublimes at 160—170° at 19 mm., whilst basic acetates of iron and aluminium are non-volatile.[2]

Glucinum can be quantitatively precipitated as hydroxide by ammonia or by a boiling solution of iodate and iodide of potassium (Glassmann).

The Atomic Weight of glucinum has been determined by Nilson and Pettersson [3] by analysis of the sulphate, and found to be 9·04, whilst Krüss and Moraht [4] by the same method found it to be 8·99. Parsons,[5] by the analysis of certain organic

[1] Glassmann, *Ber.*, 1906, **39**, 3366.

[2] Kling and Gelin, *Bull. Soc. chim.*, 1914, [4], **15**, 205.

[3] *Ber.*, 1880, **13**, 1451.

[4] *Ibid.*, 1890, **23**, 2556.

[5] *J. Amer. Chem. Soc.*, 1904, **26**, 721; *Zeit. anorg. Chem.*, 1905, **46**, 215.

derivatives, the acetylacetonate and the basic acetate, has obtained the number 9·1 (O = 16), which is now (1922) adopted as the most probable value.

MAGNESIUM. Mg = 24·32. At. No. 12.

285 Nehemiah Grew, a London physician living in the seventeenth century and for some time secretary of the Royal Society, published in the year 1695 an account of a peculiar salt found in the well-known mineral spring at Epsom under the title "*De salis carthartici in aquis Ebshamensibus et alius contenti natura et usu.*" The medicinal value of this salt soon afterwards became widely celebrated, and the salt was known in England as Epsom-salts, and on the continent as English-salt. The presence of the same substance was soon afterwards detected in other English mineral springs, and George and Francis Moult in the year 1700 established a large manufactory of the salt near London, obtaining it from a spring at Shooter's Hill. In 1710 Hoy discovered that the same salt could be obtained by crystallisation from the mother-liquors of sea-water after addition of green vitriol (ferrous sulphate). The same salt was subsequently shown by Fr. Hoffmann to exist in the Seidlitz mineral water. Another compound of magnesium having medicinal value was also discovered at the beginning of the eighteenth century by a Roman ecclesiastic, and termed by him *magnesia alba.* Why this name was given to it in contrast to *magnesia nigra*—as black oxide of manganese was then called—is not known. The mode of preparation of this substance was for some years kept secret, until in the year 1707 Valentini, of Giessen, pointed out that magnesia alba could be obtained by boiling down the mother-liquors from the preparation of nitre and igniting the residual products. Shortly afterwards, in 1709, Slevogt, of Jena, prepared the same substance by the precipitation of saltpetre mother-liquors with a fixed alkali. The substance thus obtained was a mixture of calcium carbonate and magnesium carbonate in varying proportions; hence its medicinal action was very variable, and a satisfactory discrimination between lime and magnesia was rendered more difficult. The distinction between these two earths was first clearly pointed out by Black in the year 1755. He showed that white magnesia was a compound of fixed air with a peculiar earth, which differed from lime in yielding a soluble sulphate. The properties of the new earth

were subsequently more completely investigated by Bergman in 1775, but Black retained for it the name of magnesia. When Davy proved that this earth was the oxide of a metal, the name of *magnium* was given by him to this metal, the name *magnesium* or *manganesium* being at that time used to designate the metal contained in pyrolusite. This confusion was terminated by the general adoption of the name magnesium for the metal contained in magnesia alba, and of manganese for that contained in pyrolusite.

Magnesium is a metal widely distributed in nature. It is found as magnesite, $MgCO_3$; dolomite, $MgCa(CO_3)_2$; kieserite, $MgSO_4,H_2O$; epsomite, $MgSO_4,7H_2O$; kainite, $MgSO_4,K_2SO_4$, $MgCl_2,6H_2O$; carnallite, $MgCl_2,KCl,6H_2O$; spinel, MgO,Al_2O_3; asbestos, $CaMg_3(SiO_3)_4$; talc, $H_2Mg_3(SiO_3)_4$; meerschaum, $H_2Mg_2(SiO_3)_3,H_2O$, and as the chief constituent of many silicates, such as augite, olivine, tourmaline, and serpentine, while it is contained in smaller quantities in most of the other silicates.

Magnesium sulphate, $MgSO_4$, is a chief constituent of certain saline springs, whilst the chloride, $MgCl_2$, occurs in salterns and in sea-water. Magnesium is also found in the animal and vegetable worlds. The bones of animals and the seeds of the cereals contain small quantities of magnesium phosphate, and ammonium magnesium phosphate separates out from urine on standing, thus giving rise to many urinary deposits as well as to gravel and stone. The same salt likewise occurs in guano.

286 *Preparation of Metallic Magnesium.*—Davy was the first to prepare metallic magnesium, but he did not obtain it in the pure state. It was first obtained as a coherent metal by Bussy,[1] who fused the anhydrous chloride of magnesium with potassium. Bunsen afterwards obtained it by the electrolysis of magnesium chloride, which for this purpose was fused in a porcelain crucible[2] (Fig. 167); the carbon of the negative pole was cut so as to form pockets, as shown in Fig. 168, inside which the metal was deposited: unless this precaution was taken, the metal, being lighter than the fused chloride, rose to the surface and burned. As it is difficult to prepare the pure chloride, Matthiessen employed a mixture of the chlorides of potassium and magnesium in the ratio of 3 molecules of potassium chloride to 4 of magnesium chloride.[3]

[1] *Journale de Chimie Medicale Ann.*, 1830, 141.
[2] *Annalen*, 1852, **82**, 137. [3] *Journ. Chem. Soc.*, 1856, **8**, 107.

The manufacture of magnesium on the large scale was first effected by Sonstadt and Mellor. The process employed was essentially that of Caron and Deville,[1] which consisted in heating together magnesium chloride, fluor-spar, and sodium. Wöhler suggested the use of the fused double chloride of magnesium and sodium instead of anhydrous magnesium chloride, whilst Sonstadt introduced the use of fused carnallite. An important improvement was the distillation of the crude metal, as this usually contains carbon, silicon, and nitrogen. The fact that magnesium can be readily distilled was indeed discovered by Deville and Caron, but first technically employed by Sonstadt. For this purpose the crude magnesium was placed in an iron crucible having an iron tube passing through from the bottom to within an inch of the lid. The crucible was filled with the crude

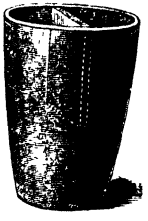


FIG 167.

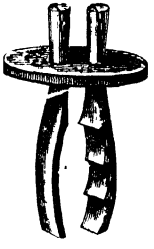


FIG 168.

metal to the level of the mouth of the tube, the lid carefully screwed and luted down, and the air displaced by a current of hydrogen or coal-gas. As the crucible became heated the magnesium distilled over, passing through the upright tube into a box placed below, where, on the completion of the operation, it was found in the form of a coherent mass which was subsequently melted and cast into ingots or any other form that might be required.

Magnesium is now mainly manufactured by the electrolysis of fused carnallite, which gives up its water of crystallisation and forms a clear fluid below 700° C. The electrolysis is conducted in a closed electric furnace, and a current of coal-gas or hydrogen is passed through during the process to remove all oxygen and to carry off the chlorine which is evolved, and thus prevent its action on the metallic magnesium which is set free and floats on the surface of the fused electrolyte. A current

[1] *Ann. Chim. Phys.*, 1863, [3], **67**, 347.

density of 0·15 ampere per square centimetre of cathode area is required. The metal is usually pressed when in a semi-fluid state into wire of varying thickness and of any required length; this is afterwards flattened into ribbon, in which form it usually occurs in commerce. It is also marketed in ingot form for alloying purposes.

The magnesium industry is quite small, although the increased use of "magnalium" alloys has given it an impetus. These alloys[1] consist of aluminium and magnesium. As now manufactured they seldom contain more than 2 per cent. of magnesium and generally contain small quantities of copper or nickel. They have been used instead of brass for the manufacture of scientific instruments.

287 *Properties.*—Magnesium is a brilliant white metal, which melts at 650°, and boils at about 1100°. It has a specific gravity of 1·75, and a granular crystalline fracture, and is sometimes obtained in hexagonal crystals isomorphous with those of cadmium and zinc. It preserves its lustre in dry air, but in moist air becomes covered with a film of oxide; when a piece of ribbon is held in the flame of a candle it burns with an intensely white light, forming a mixture of magnesia and magnesium nitride. The heated metal readily decomposes steam, hydrogen being evolved and magnesia produced. Magnesium also burns readily in carbon dioxide, carbon being deposited. It dissolves easily in dilute acids, and begins to decompose concentrated sulphuric acid at 215°.[2] It is not acted on by alkalis. When the metal is brought into a solution of one of its salts, it slowly dissolves, hydrogen being evolved and the hydroxide or a basic salt being produced.[3] It brings about a similar decomposition in many other salt solutions, producing for example in a solution of copper sulphate a precipitate of copper and cuprous oxide, and an evolution of hydrogen.[4] Alloys of magnesium and lead containing from 5—50 per cent. of magnesium are very reactive and readily absorb the whole of the oxygen from moist air: the two

[1] *Eng. and Min. Journal*, 1899, **68**, 664.

[2] Adie, *Proc. Chem. Soc.*, 1899, 133.

[3] Kippenberger, *Chem. Zeit.*, 1895, **19**, 269; Vitali, *L'Orosi*, 1895, **18**, 289; Lemoine, *Compt. rend*, 1899, **129**, 291; Bryant, *Chem. News*, 1899, **79**, 75; Kahlenberg, *J. Amer. Chem. Soc.*, 1903, **25**, 380; Roberts and Brown, *ibid.*, 801.

[4] Commaille, *Compt. rend.*, 1866, **63**, 556; Clowes and Caven, *Proc. Chem. Soc*, 1897, **13**, 221; Divers, *ibid.*, 1898, **14**, 57; Tommasi, *Bull. Soc. chim.*, 1899, [3], **21**, 885.

metals form a compound, Mg_2Pb, which is the most active alloy of the series.[1]

Magnesium has been obtained by the electrical method (p. 82) in the form of an olive-green, unstable colloidal solution in ether.[2]

The light from burning magnesium wire is rich in chemically active rays, so that it is possible to photograph by means of it. Bunsen and Roscoe have determined the actinic value of this light compared with that of the sun.[3] They showed that a burning surface of magnesium wire, which seen from a point at sea level has an apparent magnitude equal to that of the sun, effects, at that point, the same chemical action as the sun would do if shining from a cloudless sky at the height of 9° 53′ above the horizon. On comparing the visible brightness of these two sources of light it was found that the brightness of the sun's disc as measured by the eye is 524·7 times as great as that of burning magnesium when the sun's zenith-distance is 67° 22′, whilst at the same zenith-distance the sun's *chemical brightness* was only 36·6 times as great. Hence the value of this light as a source of chemically active rays for photographic purposes becomes at once apparent. The light from burning magnesium has been employed for signalling, and for military and naval purposes, and it is especially employed in pyrotechny. Magnesium powder mixed with an oxidising agent, such as potassium chlorate or a peroxide, is much used for the production of flash-lights for photographic purposes.

Metallic magnesium combines with nitrogen on heating, forming the nitride, and has been used for the separation of the argon group of gases from atmospheric nitrogen; it is also made use of in chemical analysis, and in toxicological investigations, where, as it is perfectly free from arsenic, it may be used with advantage in Marsh's apparatus instead of zinc. It may be used also in the estimation of nitrates and nitrites in drinking water, and in other cases, as a reducing agent. In the form of powder it reduces most metals from their oxides when heated with the latter, and is used for the preparation of several elements such as silicon and boron.[4] It is also added as a deoxidiser to molten nickel before casting.

[1] Ashcroft, *Trans. Faraday Soc.*, 1919, **14**, 271.
[2] Svedberg, *Ber.*, 1905, **38**, 3616.
[3] *Phil. Trans.*, 1859, **149**, 920.
[4] Winkler, *Ber.*, 1890, **23**, 44, 120.

MAGNESIUM COMPOUNDS.

Magnesium and Oxygen.

288 The only stable oxide of magnesium is the monoxide, MgO, with which correspond the salts of the metal. The peroxide, MgO_2, has not been obtained pure, and the existence of the suboxide, Mg_8O_5, is doubtful.[1]

Magnesium Oxide or Magnesia, MgO.—This substance, which occurs as the mineral periclase, is formed when the metal burns in the air, and is also produced by the ignition of the magnesium salt of any volatile oxy-acid. It is prepared on the large scale by igniting the carbonate, magnesia alba, and is known as *magnesia usta* or *calcined magnesia*. Two varieties of this are prepared from the corresponding varieties of the basic carbonate (p. 658), and they are known as light and heavy magnesia, the volumes occupied by equal weights being in the ratio of 3·5 to 1. When brought into water, combination takes place and the hydroxide is formed,[2] but the rate at which this combination occurs varies greatly with samples of the oxide which have been prepared by different methods. Thus the oxide prepared by gently heating the native carbonate or the nitrate sets with water to a firm mass, whilst the light and heavy oxides combine rapidly but do not set, and crystals of the oxide are scarcely attacked by water.[3] It is tasteless, but in the moist state turns red litmus paper blue. When heated in an electric furnace it forms transparent crystals, melts at about 2250°, and finally volatilises, though less readily than lime. Reduction to magnesium and magnesium carbide takes place when the oxide and carbon are heated in the electric furnace.[4] When magnesia is ignited in a current of hydrogen chloride it is obtained in the form of regular cubes and octahedra, and if a mixture of magnesia and ferric oxide is treated in this way black octahedra of magnoferrite, MgO,Fe_2O_3, are formed, together with those of MgO containing a little ferric oxide; these are of a yellow colour, identical with

[1] Baborovsky, *Ber*, 1903, **36**, 2719; *Zeit Elektrochem.*, 1905, **11**, 465. See also Frary and Berman, *Trans. Amer. Electrochem. Soc*, 1915, **27**, 209.

[2] Rose, *Pogg. Ann.*, 1851, **83**, 450.

[3] See also Anderson, *Journ. Chem. Soc.*, 1905, **87**, 257. Parravano and Mazzetti, *Atti. R. accad. Lincei*, 1921, **30**, 1, 63.

[4] Lebeau, *Compt. rend*, 1907, **144**, 799.

periclase, a mineral found at Monte Somma, near Naples. Crystals resembling those of periclase are also formed when the hydroxide is heated to redness with caustic potash.[1]

Magnesia is employed as a medicine, as a refractory lining in furnaces, " magnesite " bricks being of great importance in basic steel furnaces and in basic lined copper converters, for the manufacture of crucibles and cupels,[2] and in certain processes for the regeneration of chlorine from ammonium chloride.

Magnesium Hydroxide, $Mg(OH)_2$, is obtained as a white precipitate when aqueous potassium or sodium hydroxide is added to a solution of a magnesium salt, and occurs in nature as the mineral brucite, which is found embedded in serpentine with other magnesium minerals. It has been found by the conductivity method that it dissolves in 115,000 parts of water at 18° (8·7 milligrams per litre), but direct determinations give higher numbers.[3] The hydroxide can be dried at 100° without loss of water, but is converted into the oxide at a low red heat. The hydroxide is not precipitated from solutions of magnesium salts by ammonia in presence of ammonium salts, this being probably due to the fact that the presence of these salts greatly diminishes the dissociation of the molecules of $NH_4{\cdot}OH$ present in aqueous ammonia (p. 145).[4]

Magnesium Peroxide.—When caustic soda is added to a solution of magnesium sulphate containing hydrogen peroxide, the precipitate contains a peroxide of magnesium, which has, however, not been prepared pure. The material obtained gradually loses oxygen when preserved, and after drying appears to contain about equal molecular proportions of the oxide and peroxide.[5] The commercial product usually contains about 8 per cent. of available oxygen.[6] Carrasco[7] has obtained the following peroxides by successive addition of an ethereal solution of hydrogen peroxide to magnesia: $5MgO,2MgO_2,3H_2O$; $3MgO,2MgO_2,3H_2O$, and $2MgO,2MgO_2,3H_2O$. They are light powders which explode violently when heated.

[1] de Schulten, *Bull. Soc. Fran. Min.*, 1898, **21**, 87.

[2] See *Chem. Zeit*, 1906, **30**, 211, 329.

[3] Dupré, junr., and Bialas, *Zeit angew. Chem*, 1903, **16**, 54.

[4] Lovén, *Zeit. anorg Chem.*, 1896, **11**, 404; Treadwell, *ibid.*, 1904, **37**, 326.

[5] Ruff and Geisel, *Ber.*, 1904, **37**, 3683.

[6] Foregger and Philipp, *J. Soc Chem. Ind*, 1906, **25**, 298. See also German Patent, No. 168271 (27/7/1901).

[7] *Gazz.*, 1909, **39**, ii.,'47.

Magnesium and the Halogens.

289 *Magnesium Fluoride*, MgF_2, occurs as the mineral sellaite in colourless tetragonal crystals, found at Montiers in Savoy. When pure magnesia is evaporated to dryness with an excess of aqueous hydrofluoric acid, this same compound is obtained as an amorphous mass almost insoluble in water. When this is fused with common salt and the mass gradually cooled, it is deposited in crystals which, after washing with water, exhibit the same form as sellaïte (Cossa).

Magnesium Chloride, $MgCl_2$, is contained in sea-water, in many brine springs, and in various salt beds, and is at present prepared in large quantities at Stassfurt. It forms several crystalline hydrates, the limits of stability of which in contact with a saturated solution are as follows: $12H_2O$ from $-33{\cdot}6°$ to $-16{\cdot}8°$, the melting point being $-16{\cdot}4°$; $8H_2O(\alpha)$ from $-16{\cdot}8°$ to $-3{\cdot}4°$; $6H_2O$ from $-3{\cdot}4°$ to $116{\cdot}7°$; $4H_2O$ from $116{\cdot}7°$ to $181{\cdot}5°$; above this temperature $2H_2O$. In addition to these an isomeric labile hydrate with $8H_2O$ (β) is known.[1] One hundred parts of water dissolve 53·5 parts of anhydrous salt at 10°, 73 parts at 100°, and 128 parts at 186°. The hydrate with $6H_2O$, which is deposited when a hot concentrated solution cools, crystallises in deliquescent needles, and is decomposed on heating above 186°, water and hydrochloric acid being given off, and magnesia remaining. The anhydrous salt can be obtained by heating this hydrate to 175° in a vacuum[2] or by adding ammonium chloride to the solution, evaporating to dryness, carefully heating and finally igniting. It may also be obtained by evaporating the solution in a current of hydrochloric acid gas (Hempel), and forms a laminated crystalline solid, which dissolves in water with evolution of heat. It possesses a bitter saline taste, and is now largely used for the purpose of dressing cotton goods. Magnesium chloride forms crystalline double salts with other chlorides, especially with those of the alkaline earths. Of these the following are the most important:

Potassium Magnesium Chloride or Carnallite, $MgCl_2,KCl,6H_2O$. —This compound crystallises in rhombic prisms which deliquesce on exposure to the air, leaving a residue of potassium chloride.

[1] van't Hoff and Dawson, *Zeit. physikal. Chem.*, 1897, **22**, 598; van't Hoff and Meyerhoffer, *ibid.*, 1898, **27**, 75; Bogorodsky, *J. Russ. Chem. Phys. Soc.*, 1898, **30**, 735.

[2] German Patent, 161662 (7/3/03).

Ammonium Magnesium Chloride, $MgCl_2,NH_4Cl,6H_2O$, is deposited from solution in small rhombic crystals which dissolve in six parts of water.

Calcium Magnesium Chloride, $2MgCl_2,CaCl_2,12H_2O$, or tachhydrite, occurs at Stassfurt in yellowish rounded masses which deliquesce on exposure to the air. It can readily be prepared by dissolving the constituent salts in a liquid containing 1000 molecular proportions of water, 44 of magnesium chloride, and 106 of calcium chloride, and cooling to 25°.[1]

Oxychlorides of Magnesium.—If strongly-ignited magnesia be brought into contact with a concentrated solution of the chloride, the mixture after standing for some hours solidifies to a mass so hard that it is capable of being polished (Sorel). A mass of this kind which had been exposed for six months to the air gave results on analysis which render it probable that it is a mixture of magnesium carbonate and the compound

$$MgCl_2,5MgO,17H_2O, \text{ or } 2Mg\begin{cases}Cl\\OH\end{cases},4Mg(OH)_2,12H_2O.$$

This substance loses water on heating, but does not give off hydrogen chloride, and chloride of magnesium may be withdrawn from it by repeatedly boiling with water, leaving a residue of magnesium hydroxide as a hard non-crystalline mass resembling brucite.[2] If a solution of magnesium sulphate to which ammonia and sal-ammoniac have been added (a mixture frequently used in the laboratory) is allowed to stand for some time, a crystalline precipitate having the composition

$$2Mg\begin{cases}OH\\Cl\end{cases},4Mg(OH)_2,8H_2O \text{ is sometimes formed (J. Davis).}$$

Magnesium Bromide, $MgBr_2$, occurs in sea-water and in many brine springs. The anhydrous salt is obtained by heating magnesium in bromine vapour, or by leading bromine vapour over an ignited mixture of magnesia and sugar charcoal. It forms a white crystalline mass which hisses and evolves heat when brought into contact with water, and crystallises from a hot concentrated solution in needles, having the composition $MgBr_2,6H_2O$. At 18° the saturated solution contains 103·4 parts of the anhydrous salt dissolved in 100 of water.[3] On heating the crystals, hydrobromic acid is given off and magnesia

[1] van't Hoff, *Zeit. anorg. Chem.*, 1905, **47**, 271.

[2] Bender, *Annalen*, 1871, **159**, 341.

[3] Mylius and Funk, *Ber.*, 1897, **30**, 1716.

is left behind.[1] The bromide, like the chloride, forms many double salts,[2] and also combines with many organic substances.

Magnesium Iodide, MgI_2, is found together with the bromide in sea-water and brine springs. It can be prepared by dissolving magnesia in hydriodic acid. On evaporation, hygroscopic crystals of the hydrate, $MgI_2,8H_2O$, are deposited, which readily undergo decomposition with liberation of iodine. The solution saturated at 18° contains 148 parts of the anhydrous salt dissolved in 100 of water (Mylius and Funk).

Magnesium and Sulphur.

290 *Magnesium Sulphide*, MgS.—This substance is not formed in the wet way, but is obtained when a mixture of magnesium filings and sulphur is heated to dull redness in a current of sulphur vapour[3] or sulphuretted hydrogen. The product is a brown, coherent, hard, and brittle coke-like mass, mixed with a small quantity of magnesium oxide and some unchanged metal. On exposure for some time to the air the difficultly fusible sulphide slowly tarnishes, and evolves sulphuretted hydrogen, and the granular and bright steel-grey fracture becomes dull and coated with a grey oxide. When heated in the electric furnace[4] it forms cubical crystals of sp. gr. 1·85. It is slightly soluble in water, yielding a straw-yellow solution, but on exposure to the light it deposits sulphur and becomes colourless. This solution doubtless contains magnesium hydrosulphide, $Mg(SH)_2$, which may also be obtained by passing sulphuretted hydrogen into water containing magnesia in suspension.[5] It is an extremely unstable compound, and on exposure to the air, or when heated, gives off sulphuretted hydrogen, leaving magnesia behind. A solution of this substance has been proposed as a source of sulphuretted hydrogen for laboratory purposes.

Magnesium Sulphate, $MgSO_4$, occurs in nature as *kieserite*, $MgSO_4,H_2O$, and *Epsom salts* or *epsomite*, $MgSO_4,7H_2O$. These two compounds can be readily distinguished by the action of water on them. Epsom salts is readily soluble in water, whilst kieserite is as sparingly soluble as gypsum. Kieserite occurs crystallised in rhombic prisms, but is more commonly found in

[1] See Kreider, *Amer. J. Sci.*, 1905, [4], **20**, 97.
[2] de Schulten, *Bull. Soc. chim.*, 1897, [3], **17**, 167.
[3] Parkinson, *Journ. Chem. Soc.*, 1867, **20**, 127.
[4] Mourlot, *Compt. rend*, 1898, **127**, 180.
[5] Berzelius, *Pogg. Ann.*, 1825, **6**, 443.

granular masses which dissolve slowly when allowed to remain in contact with water, being gradually converted into Epsom salts. Epsom salts occur in many mineral waters. The same compound is found as epsomite or hair-salt in silky fibres and fibrous crusts at Idria in Carniola, in the gypsum quarries of Montmartre near Paris, and in various other localities. The floors of the limestone caves in Kentucky, Tennessee, and Indiana are in many instances covered with minute crystals of epsomite mingled with earth. In the Mammoth cave in Kentucky it adheres in loose masses like snowballs (Dana).

The manufacture of magnesium sulphate from the upper layers of salt (*Abraumsalz*) at Stassfurt is carried out on the large scale. The crude kieserite is placed in sieves in water. The magnesium chloride and finely divided chloride of sodium dissolve, whilst the kieserite falls through the meshes of the net in small powder, and larger pieces of rock-salt, anhydrite, and earthy impurities remain behind. The powder is then brought into conical wooden moulds in which it is allowed to remain, and in which it soon becomes a hard coherent mass, inasmuch as a portion of the salt combines with water to form the heptahydrate, which binds together the remaining powder of the kieserite. This kieserite-stone is then dried and powdered, and contains 80 to 90 per cent. of magnesium sulphate, and from 1 to 2 per cent. of common salt. It is either brought into the market in this form, or worked up into Epsom salts. Sulphate of magnesium was formerly produced in considerable quantity by treating either native magnesium carbonate or dolomite with sulphuric acid; the gypsum formed in the latter case, being much less soluble than magnesium sulphate, is easily separated from it. Formerly, also, dolomite was burnt, the lime dissolved out by crude pyroligneous acid, and the residual magnesia treated with sulphuric acid (Henry).

Magnesium sulphate forms a large number of hydrates, but the curve of equilibrium with a saturated solution has not been very accurately determined. The ordinary heptahydrate (Epsom salts) is stable in contact with a saturated solution from 1·8° to 0·48°, at which temperature it passes into the hydrate with $6H_2O$, which in its turn passes into kieserite at 68°. The heptahydrate crystallises from a hot concentrated solution in four-sided rhombic prisms (Class 6, p. 209), shown in Fig. 169, and is isomorphous with the corresponding sulphates of zinc and nickel. As a rule, the commercial salt occurs in the powdery

form consisting of minute delicate needles obtained by quick crystallisation of a concentrated solution. The crystals are not deliquescent, but the commercial salt sometimes becomes moist in contact with air in consequence of the presence of traces of magnesium chloride. The crystals possess an unpleasant saline bitter taste, and have a specific gravity of 1·685 (Schiff). On heating, they melt in their water of crystallisation, and lose six molecules at 150°, the last molecule being termed by Graham *constitutional water*, because it is not driven off until a temperature of 200° is reached. The solution saturated in contact with this hydrate at 10° contains 30·9 parts of anhydrous salt in 100 of water, and at 40°, 45·6 parts.

When a boiling and concentrated solution of magnesium sulphate is placed in a closed vessel it remains supersaturated when cold. Such a solution may stand for weeks or months without solidification, but milk-white crystals of the hexahydrate are sometimes deposited, and, sometimes, monoclinic tablets of a labile heptahydrate. From this it is seen that the heptahydrate is dimorphous; this is shown also by the fact that it crystallises as an isomorphous constituent with monoclinic ferrous sulphate, $FeSO_4,7H_2O$. Magnesium sulphate is insoluble in absolute alcohol.

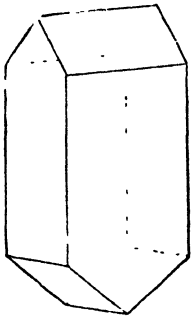


Fig. 169.

Epsom salts is largely used as a purgative, and, like the chloride, is employed as a dressing for cotton goods. It is also used in dyeing with aniline colours, as goods thus dyed are found to stand the action of soap better, this being probably due to the formation of an insoluble magnesia soap.

Magnesium sulphate forms a series of characteristic double salts with the sulphates of the alkali metals. These have the general formula $MgSO_4,M^I_2SO_4,6H_2O$, and crystallise in well-developed monoclinic prisms.[1] It also forms a large number of other double salts, many of which occur as minerals. When the anhydrous sulphate is dissolved in hot concentrated sulphuric acid, the solution on standing deposits the compound $MgSO_4,H_2SO_4$, in six-sided tablets, which soon absorb moisture from the air and are thereby decomposed.[2]

[1] See Tutton, *Journ. Chem. Soc*, 1896, **69**, 355, 1905, **87**, 1123.

[2] Schiff, *Annalen*, 1861, **118**, 365.

Magnesium and Nitrogen, Phosphorus and Arsenic.

291 *Magnesium Nitride*, Mg_3N_2.—Deville and Caron, when preparing magnesium, observed that the distilled metal sometimes appeared covered with small transparent needles,[1] which decomposed in moist air with formation of ammonia and magnesia, and therefore contained a nitride of magnesium. This compound was obtained in the amorphous state by Briegleb and Geuther,[2] by igniting magnesium in ammonia or in nitrogen gas. The nitride of magnesium thus prepared is a greenish-yellow amorphous mass, which when heated in dry oxygen gas is converted, with bright incandescence, into magnesia. The nitride is, however, produced when compressed magnesium turnings are burnt in the air, and is covered by a layer of oxide.[3] On exposure to the air, or when treated with water, it is quickly decomposed into ammonia and magnesia, so much heat being evolved in the latter case that the water boils. When heated in a current of sulphuretted hydrogen gas ammonium sulphide and magnesium sulphide are formed.

Magnesium Nitrate, $Mg(NO_3)_2$.—This salt occurs in the mother-liquors from the saltpetre manufacture, and in the surface water of towns, having been first detected by Berzelius in the well-water of Stockholm. It is prepared by dissolving magnesia alba in nitric acid. It forms several hydrates,[4] that with $9H_2O$ being stable in contact with a saturated solution from $-29°$ to $-18°$, at which temperature it passes into the hexahydrate, which crystallises in prisms and needles and melts at 90°. The solution saturated at 18° contains 73·4 parts of the anhydrous salt in 100 parts of water. The hexahydrate dissolves in nine parts of alcohol of specific gravity 0·84, but is less soluble in pure alcohol.

Magnesium Phosphide, Mg_3P_2, is formed in small, dark-coloured crystals, when magnesium is heated in hydrogen containing phosphorus vapour. It is decomposed by water with formation of magnesium hydroxide and pure phosphine, and burns in oxygen, forming magnesium phosphate.[5]

Phosphates of Magnesium.—The Normal Orthophosphate, $Mg_3(PO_4)_2$, occurs in small quantities in the seeds of the cereals and in bones. It is obtained in the form of a hydrated white

[1] *Ann. Chim. Phys.*, 1863, [3], **67**, 348.
[2] *Annalen*, 1862, **123**, 228; see also Merz, *Ber.*, 1891, **24**, 3940.
[3] Kirchner, *Chem. Zeit.*, 1901, **25**, 395.
[4] Funk, *Ber.*, 1899, **32**, 96; Mylius and Funk, *ibid.*, 1897, **30**, 1716.
[5] Gautier, *Compt. rend.*, 1899, **128**, 1167.

precipitate when a solution of normal sodium orthophosphate is added to a solution of Epsom salts.[1] One part of the salt dissolves in 5,000 parts of water. A phosphato-fluoride of magnesium having the formula $2Mg_3(PO_4)_2,MgF_2$ occurs in nature as *wagnerite.*

Hydrogen Magnesium Orthophosphate, $HMgPO_4$, is obtained when a solution of Epsom salts is mixed with one of common sodium phosphate; on standing, hexagonal needles of the acid salt containing seven molecules of water are deposited. These dissolve in 322 parts of cold water. If this solution is heated it becomes milky owing to the separation of the insoluble normal salt, a tetra-hydrogen phosphate, $H_4Mg(PO_4)_2$, remaining in solution; this latter compound, however, has not been obtained in the pure state. A hydrate with $3H_2O$ has also been described.[2]

Magnesium Ammonium Orthophosphate, $Mg(NH_4)PO_4,6H_2O$. —This salt, a frequent constituent of urinary calculi, was discovered by Fourcroy. It is produced in the putrefaction of urine, and large crystals of it have been found in some varieties of guano. It is formed when an ammoniacal solution of sal-ammoniac is mixed with a solution of magnesium sulphate, and a soluble orthophosphate then added. If the solution be dilute, the precipitate takes some time to form, and deposits in small crystals which attach themselves to the sides of the vessel, especially upon points presenting any roughness or inequality, as where the beaker-glass has been scratched. It separates in this way from extremely dilute solutions, affording a very delicate test either for magnesium or for phosphoric acid. According to Graham the best mode of obtaining it in distinct crystals is to mix 600 parts of hot water with four parts of strong ammonia; then add seven parts of crystallised sodium phosphate, two parts of sal-ammoniac, and four parts of magnesium sulphate. The crystals which are thus deposited are transparent tetragonal prisms. One part of the salt dissolves in 15,000 parts of water at 15°, and in 44,000 parts of ammoniacal water, whilst in presence of ammonium chloride it is somewhat more readily soluble. When heated the salt gradually loses the whole of the water and ammonia, pyrophosphate of magnesium, $Mg_2P_2O_7$, remaining behind.[3]

[1] See de Schulten, *Bull. Soc. chim.*, 1903, [iii], **29**, 724; *Bull. Soc. Fran. Min.*, 1903, **26**, 81.

[2] Struve, *Zeit. anal. Chem.*, 1897, **36**, 289.

[3] Compare Struve, *ibid.*, 1898, **37**, 485.

If a solution of magnesium chloride is added slowly to a 10 per cent. solution of dipotassium hydrogen phosphate, *magnesium potassium phosphate*, $MgKPO_4,6H_2O$, is precipitated.[1] The rubidium salt may be similarly obtained.

The Arsenates of Magnesium closely correspond to the phosphates.

Magnesium and Carbon and Silicon.

292 *Carbides of Magnesium.*—Two carbides of magnesium, MgC_2 and MgC_3, exist. The first yields acetylene when treated with water, and the second allylene. They have not been prepared pure.[2]

Carbonates of Magnesium.—Normal Magnesium Carbonate, $MgCO_3$, occurs in nature as magnesite, a mineral isomorphous with calc-spar. The same mineral frequently occurs in compact or granular masses, and is found in large quantities in various localities, especially in the island of Eubœa and in India. The normal carbonate is also formed by the action of magnesium chloride on calcium carbonate (Marignac). It has a specific gravity of 3·056, is not easily soluble in dilute acid, and is not affected by being boiled with water or alkali carbonates.

A second variety of the normal carbonate is obtained by heating magnesium ammonium carbonate in dry air at 130°. It differs remarkably from magnesite in its properties, as it is very hygroscopic, and when treated with water sets like plaster of Paris to a hard mass [3] consisting of the hydroxycarbonate. Magnesium carbonate readily dissolves in carbonic acid, but the solution is only stable in presence of excess of carbon dioxide.[4] The amount dissolved increases with the pressure of the carbon dioxide and diminishes with rise of temperature.

According to Engel,[5] 1,000 parts of water at 12° contain the following amounts of magnesium carbonate in the form of bicarbonate when saturated under varying pressures of carbon dioxide:

Pressure of CO_2 . .	0·5	1	1·5	2	2·5	3	6	atmospheres.
Parts of $MgCO_3$ as $Mg(CO_3H)_2$ . .	20·5	26 5	31	34·2	36·4	42·8	50·6	

[1] Balareff, *Zeit. anorg. Chem.*, 1918, **102**, 241.
[2] Novák, *Zeit. physikal. Chem.*, 1910, **73**, 513.
[3] Engel, *Compt. rend.*, 1889, **129**, 598.
[4] Treadwell and Reuter, *Zeit. anorg. Chem.*, 1898, **17**, 170
[5] *Compt. rend.*, 1888, **100**, 444.

The solution has an alkaline reaction and a bitter taste. If it be placed in a partially closed flask at 50°, crystals of the empirical formula $MgCO_3,3H_2O$ separate out, and a similar change occurs when the solution is heated. This substance is probably the *hydroxycarbonate*, $HO{\cdot}Mg{\cdot}CO_3H,2H_2O$, for it loses $2H_2O$ at 100°, but does not begin to lose carbon dioxide or the remaining molecule of water until 125° is reached. Crystals of the empirical formula $MgCO_3,5H_2O$ are deposited at a lower temperature, and these lose $2H_2O$ at 16°. The anhydrous compound, $HO{\cdot}Mg{\cdot}CO_3H$, can also be obtained by boiling the crystals containing $2H_2O$ with xylene. The hydrate is slowly decomposed by boiling water with formation of a mixture of the anhydrous compound and magnesium hydroxide,[1] the composition of which depends on the time of boiling. The hydrated hydroxycarbonate is also formed when a solution of a magnesium salt is precipitated with an equivalent amount of sodium carbonate in the cold. It appears probable that a mixed carbonate [2] of magnesium and sodium is first formed:

$$2Na_2CO_3 + MgSO_4 = Mg(CO_3Na)_2 + Na_2SO_4.$$

This then immediately undergoes partial hydrolysis into the hydroxycarbonate or a mixture of this and the hydroxide, and the various so-called basic carbonates of magnesium [3] are all to be regarded as mixtures of this kind (Davis). The *magnesia alba* of the shops is a product of variable composition. The "light" variety is prepared by precipitating a dilute solution of Epsom salts in the cold with sodium carbonate, washing with boiling water, and drying at 100°. The "heavy" variety is obtained by adding sodium carbonate solution to a boiling concentrated solution of Epsom salts, evaporating to dryness, digesting with water, filtering and washing, and finally drying at 100°.

When evaporated to dryness, the solution of the carbonate in carbonic acid yields a crystalline powder, which, examined under the microscope, is found to consist of crystals having the form of aragonite;[4] but if the solution is heated to 300° in a vessel closed by a porous stopper through which the car-

[1] Davis, *J. Soc. Chem. Ind.*, 1906, **25**, 788.

[2] See Reynolds, *Journ. Chem. Soc.*, 1898, **73**, 264; von Knorre, *Zeit. anorg. Chem.*, 1903, **34**, 260.

[3] Brill, *Zeit. anorg. Chem.*, 1905, **45**, 275; Anderson, *Journ. Chem. Soc.*, 1905, **87**, 261.

[4] Rose, *Pogg. Ann.*, 1837, **42**, 366.

bonic acid can slowly escape, microscopic rhombohedra of the form of native magnesite are deposited.[1] Magnesium carbonate is, therefore, isodimorphous with calcium carbonate.

Another method of preparing magnesium carbonate is that patented by Pattinson, which consists in igniting dolomite and then treating it with water and carbon dioxide under pressure, when the carbonate of magnesium dissolves in the carbonic acid more readily than the carbonate of calcium; the solution of bicarbonate of magnesium which is formed is decanted from the insoluble carbonate of calcium and decomposed by a current of steam. The salt thus obtained is very white and of a loose texture.

The mineral termed *hydromagnesite*, possessing a similar composition to magnesia alba, occurs in small white monoclinic crystals.

Magnesia alba is almost insoluble in water. It dissolves, however, readily in solutions of ammoniacal salts, owing to the formation of ammonium carbonate, and soluble double carbonates of magnesium and ammonium. For this reason ammonium carbonate does not precipitate a magnesium salt completely, and no precipitate occurs in the presence of ammonium chloride.

Magnesium Calcium Carbonate or Dolomite, $MgCO_3,CaCO_3$, occurs as a mineral in the massive state, forming whole mountain ranges. It was at one time considered to be an isomorphous mixture of the two constituent carbonates, but it has been found that it possesses a lower degree of crystalline symmetry (Class 15, p. 209) than calcite, and that its properties are not the mean of those of its constituents.

Magnesium Silicide.—This compound was obtained by Wohler as a by-product in the preparation of metallic magnesium, by fusing together a mixture of sodium, magnesium chloride, and sodium silicofluoride, and was prepared by Geuther by heating sodium chloride, sodium silicofluoride and magnesium to a high temperature in a Hessian crucible.[2] It is most readily obtained by heating 1 part of quartz sand and 1·5 parts of magnesium powder, and then forms a bluish half-fused mass,[3] but when obtained by Geuther's method it forms crystals having a metallic lustre. It has probably the formula Mg_2Si, although Wöhler found the composition Mg_4Si_3, and Geuther Mg_5Si_3. This variation in the results is probably due to the fact that the

[1] Sénarmont, *Ann. Chim. Phys.*, 1850, [3], **30**, 129.
[2] *J. pr. Chem.*, 1865, **95**, 424. [3] Gattermann, *Ber.*, 1889, **22**, 186.

product readily loses magnesium on ignition,[1] or the substances may be mixtures of Mg_2Si and MgSi. In favour of the latter view is the fact that when the silicide is treated with hydrochloric acid, spontaneously inflammable silicon hydride is evolved, and silicoformic anhydride produced (Vol. I., p. 911), the decompositions being represented thus:

(1) $Mg_2Si + 4HCl = 2MgCl_2 + SiH_4$.
(2) $2MgSi + 3H_2O + 4HCl = 2MgCl_2 + Si_2H_2O_3 + 4H_2$.

The silicide obtained by heating together 48 parts of magnesium and 28 of silicon [2] yields a certain proportion of the silicon hydride, Si_2H_6, when treated with hydrochloric acid, and therefore probably contains a silicide of the formula Mg_3Si_2.

Magnesium Silicates.—As already mentioned (p. 644), magnesium occurs as a constituent of a very large number of silicates, many of which have received important technical applications. For a description of these various minerals reference must be made to works on mineralogy.[3]

Detection and Estimation of Magnesium.

293 Magnesium and its compounds do not impart any tint to the non-luminous gas-flame. The spark spectrum of magnesium is, however, very characteristic (Bunsen, Kirchhoff, Thalén), giving lines in the green coincident with Fraunhofer's *b*. The brightest of these lines is situated very close to an air-line, and for this reason it is better to observe the magnesium spark in an atmosphere of hydrogen, or in one of coal-gas, than in the air (Bunsen).

In the course of ordinary qualitative analysis, magnesium is obtained together with the alkali metals, as it is not precipitated by ammonium carbonate in presence of ammonium chloride. The presence of magnesium is readily detected by the addition of sodium phosphate to a portion of the solution, as on standing for a short time a crystalline precipitate of $Mg(NH_4)PO_4,6H_2O$ is deposited. The formation of this precipitate is greatly accelerated by stirring the solution with a glass rod, when the crystals are deposited where the rod has scratched the glass.

Magnesium is usually estimated by precipitation as mag-

[1] Winkler, *Ber.*, 1890, **23**, 2642.
[2] Moissan and Smiles, *Compt. rend.*, 1902, **134**, 569.
[3] See Miers, *Mineralogy*, Sections XV. and XVI. (London, Macmillan & Co.)

nesium ammonium phosphate by means of sodium phosphate in the presence of ammonia and ammonium chloride. The precipitate is washed with dilute ammonia, in which it is less soluble than in pure water, and is then converted by ignition into the pyrophosphate, which is weighed. The quantitative separation of magnesium from the alkalis is accomplished by the method proposed by Berzelius. The solution, which must contain the metals in the form of chlorides, as is indeed always the case in the analysis of silicates, etc., is evaporated to dryness, and the residue ignited in order to volatilise the ammoniacal salts. The fixed residue is then warmed with a small quantity of water, and a little finely divided oxide of mercury added, the mixture again evaporated to dryness on a water-bath, and the residue ignited in order to expel the mercuric chloride and excess of oxide. The residue contains the magnesium in the form of the insoluble oxide, whilst the alkali metals remain as chlorides, which are extracted by water and estimated. The precipitation of the magnesia can also be effected by means of baryta water, the excess of baryta being subsequently removed by treatment with carbon dioxide. The magnesia, after having been well washed, is dissolved in hydrochloric acid, and precipitated as the ammonium magnesium phosphate.

The Atomic Weight of magnesium was very carefully determined by Marignac [1] by the analysis and synthesis of magnesium sulphate, the average number obtained being 24·20. Burton and Vorce,[2] by converting a known weight of pure magnesium into magnesia, obtained the number 24·10, whilst Richards and Parker,[3] by the analysis of the anhydrous chloride, prepared by heating ammonium magnesium chloride, $NH_4Cl,MgCl_2$, in dry hydrogen chloride, obtained the value 24·32, which is at present (1922) accepted.

ZINC. Zn = 65·37. At. No. 30.

294 The ancients were acquainted with the alloy of zinc and copper which we term brass, but they were not aware that it contained any other metal besides copper, and it was only after some time that a more accurate examination of brass and the ores which were employed for its production led to the recogni-

[1] *Jahresb.*, 1883, 42. [2] *Amer. Chem. J.*, 1892, **12**, 219.
[3] *Zeit. anorg. Chem*, 1896, **13**, 81.

tion of zinc as an elementary body. Aristotle, in the fourth century B.C., mentions the preparation of brass under the name of Mossinœcian copper, which he describes as being bright and light-coloured, not produced by the addition of tin, but by its having been melted with a peculiar earth found on the shores of the Black Sea. The early use of brass is clearly proved by the following analysis by Tookey, quoted by Percy, of an undoubtedly genuine Greek coin of Trajan struck in Caria A.D. 110:

Copper	77·59
Zinc	20·70
Tin	0·39
Iron	0·27
	98·95.

This ore, by means of which copper could be coloured yellow, was termed Καδμεία or *cadmia*, by Dioscorides and Pliny. The same word is also used by the latter author to designate the sublimate, consisting of impure oxide of zinc, found in the brassfounders' furnaces. It has already been stated in the Historical Introduction that the older alchemists were acquainted with the means of turning copper a yellow colour. The material by which this change was brought about was termed in the Latin translation of their works *tutia*. Agricola believed that brass was a mixture of copper and earth termed galmei or calamine, and he describes the employment of cadmia in the place of the natural ore as follows: "Sunt qui in cadmiæ fossilis locum cadmiam fornacum substituunt."

The word zinc is first found in the writings of Paracelsus, who also pointed out that zinc was a metal. He says in his treatise on minerals: "There is another metal called the *zinken*, which is unknown to the fraternity, and is a metal of a very singular kind." In other places he describes it as a bastard or semi-metal. The word zinc occurs in many subsequent authors, and sometimes it is employed to denote the metal, at other times the ore from which the metal is obtained. Libavius was the first to investigate the properties of zinc more exactly, although he was not aware that the metal was derived from the ore known as calamine. He states that a peculiar kind of tin is found in the East Indies called calaëm. Some of this was brought to Holland, and came into his hands. He describes its outward

appearance and general properties minutely, and compares them with those of the other metals, laying very particular stress upon the fact that when heated in the air this metal takes fire and burns. The exact nature of zinc and its ores continued doubtful during the seventeenth century. Glauber, it is true, stated that calamine was an ore of zinc, but Lemery so late as 1675 believed that zinc was identical with bismuth, and Boyle often employed the names zinc and bismuth indiscriminately for the same substance, also using the word spiauter (our English spelter), a name apparently of Eastern origin. In general it was believed that the brass which was obtained from copper and calamine contained the latter substance as such. The view that brass is an alloy was first put forward by Kunkel at the end of the seventeenth century. He says in his *Laboratorium*, "I have already remarked in my annotations that calamine allows its mercurial (metallic) part to pass into the copper and form brass. For thou wilt never believe that as a *sal* it could tinge copper; as a *terra* it cannot enter it, since it would make the copper brittle, and moreover could not tinge it." Stahl afterwards gave it as his opinion that calamine could turn copper into brass by being first converted into zinc.

According to W. Hommel,[1] the name zinc is erroneously attributed to Basil Valentine and the discovery of the metal to Paracelsus, for the identification of zinc as the metal from blende was only accomplished by Homberg in 1695.

The preparation of zinc on the large scale appears to have been first carried out in England. According to Bishop Watson, zinc works were first established at Bristol about the year 1743. "In about the year 1766 Watson visited Mr. Champion's works near Bristol and saw the process of making zinc, which at that time was kept rigidly secret. Many years afterwards he published an accurate description of this process, which is the same as that hereafter described as the English process" (Percy).[2] The first continental zinc works were erected in 1807 at Liége.

Zinc is said to have been found in the native state near Melbourne, in Australia, but it occurs chiefly as zinc blende or zinc sulphide, ZnS, which, when of a yellow colour, is known as rosin-blende, and when of a dark colour as black-jack. It is found in England, in many districts in Europe and America, and also in New South Wales, Rhodesia, and Burma. Zinc

[1] *Chem. Zeit.*, 1912, **36**, 905. [2] *Metallurgy*, i., 521.

blende is usually associated with other mineral sulphides, galena and iron pyrites being almost invariably present. Another ore which was formerly of chief importance is calamine, smithsonite or zinc-spar, $ZnCO_3$, found near Altenberg, in the neighbourhood of Aix-la-Chapelle, at Wiesloch, in Belgium, Spain, Siberia, and North America, as well as at Alston Moor, Lead Hills, Donegal, and Matlock in Great Britain and Ireland. It also occurs as siliceous or electric calamine, or hemimorphite, Zn_2SiO_4,H_2O, found together with zinc-spar.

Other ores of zinc are franklinite, $(Zn,Fe,Mn)O,(Fe,Mn)_2O_3$; red zinc ore, or oxide of zinc, which derives its peculiar colour from the presence of oxide of manganese; hydrozincite, $ZnCO_3,2Zn(OH)_2$; aurichalcite, $2(Cu,Zn)CO_3,3(Cu,Zn)(OH)_2$; zinc sulphate or goslarite, $ZnSO_4,7H_2O$, and gahnite or zinc-spinel, ZnO,Al_2O_3, etc. Zinc has been found in the ashes of the yellow pansy (*Viola calarminaris*), and of many other plants growing in soil which contains zinc.[1]

295 *Smelting of Zinc.*—In former times calamine was the only ore of zinc from which the metal was extracted, but at the present time large quantities of zinc silicate, a mineral occurring with the carbonate, are employed for the preparation of zinc, whilst zinc blende is the chief source. In America the metal is extracted from franklinite and from the red zinc ore. The first process in the preparation of zinc consists in the roasting of the ore in order to drive off the carbonic acid and water which it contains, and, in the case of zinc blende, to convert the sulphide into oxide. In roasting the latter ore, unless a wet method of extraction is to be used, great care has to be taken to prevent the formation of zinc sulphate, which requires a very high temperature for its decomposition, and, if not decomposed, would be again converted, in the process of reduction which follows, into sulphide, and thus cause a considerable loss.

For sulphides this roasting may take place in large mechanical furnaces, these being either long-bedded furnaces with mechanical stirrers, or muffle furnaces, also worked mechanically. Considerable success has been met with in Australia by finishing the roast in a blast-roasting machine; the product is particularly suitable for subsequent furnace treatment.

The reduction of the zinc ores was formerly carried on in England by a process termed distillation *per descensum*. The mixture of ore and coal was heated in crucibles closed at

[1] See also Javillier, *Bull. Sci. Pharm.*, 1908, **15**, 559.

the top, but having a pipe leading from the bottom stopped by a wooden plug. The latter was quickly carbonised, thus becoming porous and allowing the vapour of the reduced zinc to pass down the tube, where it was condensed. This plan necessitated a large consumption of fuel, and has therefore been abandoned.

In the Belgian process, tube-shaped retorts made of refractory fire-clay are employed. These may be either circular or elliptical in cross-section, and vary from 3 feet 3 inches to 5 feet in length, the circular retorts being about 6 to 10 inches in

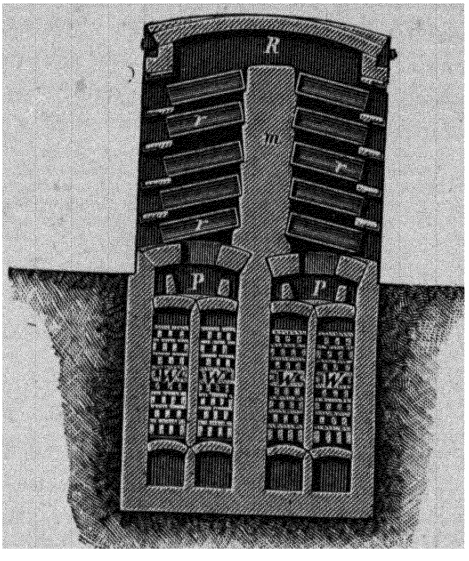


Fig. 170.

diameter, and the elliptical retorts about 7 inches by 9 inches. To the open end a conical clay tube is luted, about 16 inches in length, and having a diameter of 6 inches at one end and 3 inches at the other, and to this adapter is fitted a sheet-iron condenser or nozzle which serves to condense zinc fume. The furnaces in which these retorts are heated were formerly fired with coal, but now gas-fired regenerative furnaces are used of the type shown in Fig. 170.

The number of retorts per furnace varies considerably. In coal-fired furnaces from 6 to 9 rows are used, and each furnace may have 48 or more retorts. In gas-fired furnaces 4 to 6 rows only are used, but these are much longer and may have from

56 to 72 retorts in each row. The retorts are fixed in a slightly slanting direction to facilitate withdrawal of the spent charge.

A mixture of 2 parts of ground roasted ore and 1 part of coal dust is brought into the retorts, each holding about 40 lb. of the mixture. As soon as the temperature has risen high enough, the reduction begins, and carbon monoxide is evolved and burns from the end of the clay adapter with a blue flame. After a while the flame becomes much more brilliant, showing that the metal is beginning to volatilise; the iron condenser is then placed on to the end of the clay adapter, and the metallic vapours are thus condensed. After about three hours the iron condenser is taken away and the oxide knocked out. A ladle is then held under the mouth of the clay adapter, and the melted zinc which has accumulated therein is scraped out. The iron receiver is then again fixed in its place, and after a

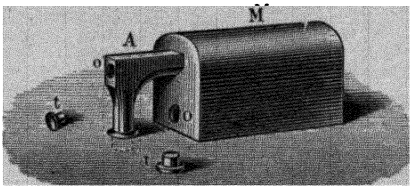


FIG. 171.

further period of four hours the operation is repeated. It is completed in about twenty hours. The exhausted charge is then removed from the retort and a fresh one introduced. In this way one charge is worked off from each retort in twenty-four hours.

In the *Silesian process*, clay retorts or muffles (Fig. 171) about 1 metre long are arranged side by side in the horizontal bed of a reverberatory furnace (Fig. 172). No fewer than 30 or 40 muffles are thus arranged, and these may contain 1,500 to 2,000 kilos. of the mixture of coal and roasted ore. This mixture is introduced through a luted clay door in the muffle or retort. When the temperature has risen sufficiently high, the vapour of the reduced zinc passes out of the retort by a bent clay pipe (A, Fig. 171), and condenses in an iron tube, falling down into an iron tray placed in a closed recess (o, Fig. 172), in the furnace. In this process a considerable quantity of zinc is burnt, producing zinc oxide, known as Silesian zinc-flowers.

A combination of the Belgian and Silesian methods is being

largely employed in the Belgo-Silesian furnace (Fig. 173). One modification of this consists of a furnace, having three rows of muffles, the bottom row being supported throughout their whole

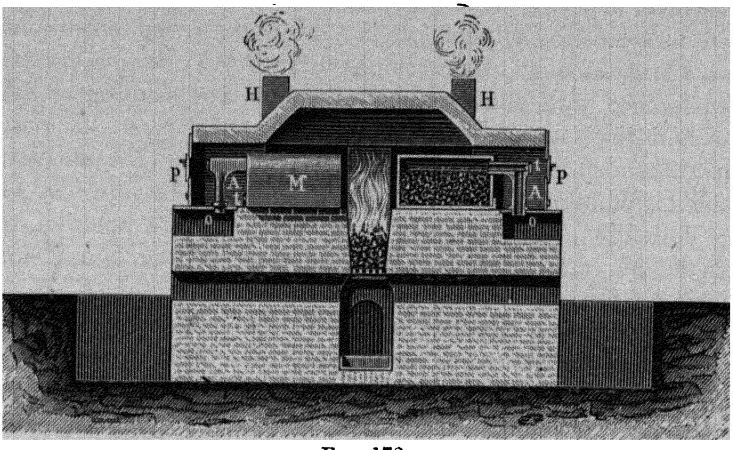


FIG. 172.

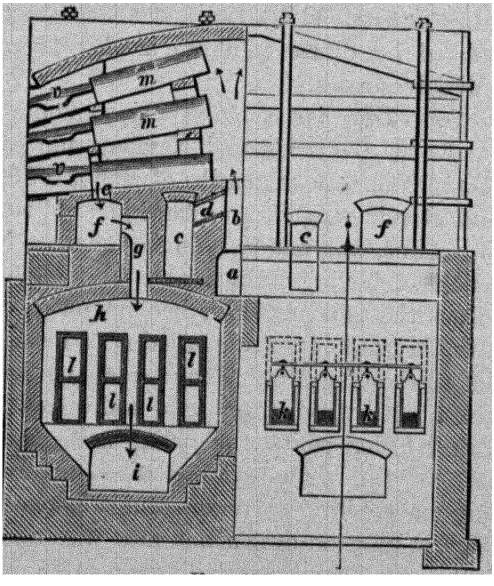


FIG. 173.

length upon the hearth, while the upper rows are supported at their ends only, as in Belgian furnaces. These furnaces are generally gas-fired, with recuperative heating of the air required for combustion.

Electric furnaces are now applied to the smelting of zinc ores in districts where electric current is cheap and coal is dear, and within recent years large plants have been equipped for the production of zinc by wet extraction and electro-deposition. In these processes the sulphide ore is roasted under such conditions that a large amount of zinc sulphate is formed; the material is then leached with dilute sulphuric acid for the solution of the zinc and the solution is carefully purified. This is the most important step in the process, as small quantities of impurities, including minute traces of cobalt, are found to be injurious to the deposition. The slightly acid zinc sulphate solution is then submitted to electrolysis and the spent solution is used for leaching a further quantity of roasted ore.

Commercial zinc obtained by distillation methods is impure. It almost always contains small quantities of lead, iron, and carbon, and frequently silver, cadmium, and small traces of arsenic, antimony, and other metals are present. The metal obtained by the electrolytic method is much purer, approaching 99·9 per cent. of zinc. The chemical purity of zinc may be readily ascertained by the fact that, when pure, it is scarcely attacked by dilute sulphuric acid, whereas common impure zinc dissolves readily.

296 *Properties.*—Zinc has a bluish-white colour, melts at a temperature of 419° (Heycock and Neville), and boils at 918° (D. Berthelot).[1] The vapour density of zinc is 2·36, so that its molecular and atomic weights are identical.[2] If zinc is heated to its melting point, but not to a higher temperature, poured out upon a non-conducting surface, and the molten metal then poured off from the portion which has solidified, the metal is obtained in the crystalline form, consisting of hexagonal prisms and pyramids or rhombohedra. Commercial zinc has a coarsely laminar texture. It is moderately hard and difficult to file, and when bent after fusion emits a crackling noise, not so loud as that emitted by tin. Zinc exhibits the greatest degree of ductility and malleability at temperatures between 100° and 150°, at which it may be drawn out into wire and rolled into plate.[3] On the other hand, it is so brittle at 205° that it may be powdered in a mortar. The specific gravity of zinc which

[1] *Compt. rend.*, 1900, **131**, 380; 1902, **134**, 705. Compare Le Chatelier, *ibid.*, 1895, **121**, 323.

[2] V. Meyer, *Ber.*, 1886, **19**, 3295. See also Biltz, *Journ. Chem. Soc.*, 1896, **70**, ii., 152.

[3] Hobson and Sylvestra, *Gilbert's Ann.*, 1806, **24**, 104.

has been distilled *in vacuo* is 6·9225 at 20°/4°, and this rises to 7·1272 when the metal is submitted to a pressure of 10,000 atmospheres.[1] It seems probable that the zinc used for the foregoing measurements was a practically pure sample of the stable form, whilst ordinary zinc is a mixture of this form with at least one other metastable allotrope.[2]

Zinc has been obtained by the electrical method in the colloidal state, forming a brown solution in ether,[3] and also as an unstable hydrosol.[4]

Zinc vapour readily burns in air, the combustion being shown by holding thin zinc turnings in the flame of a lamp, or, better still, by placing zinc in a white-hot crucible, and exposing the surface to the air or stirring it with an iron rod, when the metal burns with a bright white flame.

Pure zinc is very slowly dissolved by dilute sulphuric acid, whilst the impure metal readily dissolves with evolution of hydrogen. The inactivity of the former is due to the fact that a film of hydrogen forms on the surface of the zinc and prevents the further action of the acid; if, however, impurities are present, these form galvanic couples with the zinc, and as they are electro-negative to zinc the hydrogen is evolved from them, leaving the surface of the zinc continuously exposed to the action of the acid.[5] If a few drops of a solution of the sulphate of copper, cobalt, or nickel,[6] or of platinum chloride, be added to the acid in which the pure zinc is placed, hydrogen is rapidly evolved, because copper or platinum is deposited on the zinc, and acts in the manner above described. Zinc displaces many metals from their salts in aqueous solution, the action being rapid with copper: it has been shown that such reactions have a short period of induction and thereafter are first-order reactions until the deposition of the less electro-positive metal forms "local elements," after which the velocity of the action depends only on the rate of diffusion of the dissolved salt to the surface of the zinc.[7] When zinc is heated with concentrated sulphuric acid, sulphur dioxide is evolved, and no hydrogen sulphide is produced.[8] Zinc dissolves in hydrochloric acid with evolution of hydrogen and formation

[1] Kahlbaum, Roth, and Siedler, *Zeit. anorg. Chem.*, 1902, **29**, 177.

[2] Cohen and Heldermann, *Zeit. physikal. Chem.*, 1914, **87**, 409, 419, 426; Cohen, *ibid.*, 431.

[3] Svedberg, *Ber.*, 1905, **38**, 3616.

[4] Billitzer, *ibid.*, 1901, **35**, 1929.

[5] Weeren, *ibid.*, 1891, **24**, 1785.

[6] See Ball, *Journ Chem. Soc.*, 1897, **71**, 642.

[7] Centnerszwer and Drukker, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 528.

[8] Berthelot, *Ann. Chim. Phys.*, 1898, [7], **14**, 176; Adie, *Proc. Chem. Soc.*, 1899, **15**, 133.

of the chloride; and in nitric acid, with evolution of nitric oxide, nitrous oxide, or ammonia according to the conditions of the experiment, the last-named uniting with the excess of nitric acid to form ammonium nitrate. Zinc dissolves also in solutions of the alkalis with evolution of hydrogen, the zinc hydroxide first formed dissolving in the excess of alkali.

Zinc when exposed to the atmosphere is gradually attacked, a scale of basic carbonate being formed,[1] and it is also attacked and partially dissolved by water.[2]

Commercial zinc usually contains arsenic, which may be removed by adding 0·2 per cent. of metallic sodium to the fused metal, skimming off the surface layer and then granulating the metal by pouring it into cold water.[3]

About 60 per cent. of the zinc produced is used for galvanizing iron or steel as a protection against rusting: the articles after thorough cleaning, both mechanically and by pickling in acid, are immersed in a bath of molten zinc covered with a suitable flux. A similar but less robust coating is given in the "Sherardising" process by heating iron or steel to about 300°–350°C. in intimate contact with zinc dust. It is employed in the form of sheets for a variety of technical purposes, and is much used in the manufacture of brass, an alloy of the metal with copper. Zinc is also used for desilverising lead, in electrical batteries, for the precipitation of gold from its solution in potassium cyanide, and for a great number of other purposes. Metallic zinc in the form of fine dust is obtained in considerable quantity in the manufacture of the metal, mixed with a certain amount of oxide of zinc. This mixture, called *zinc dust* or *blue powder*, is a valuable reducing agent, often used for this purpose in organic chemistry, and also on a large scale for the reduction of indigo-blue: it is likewise employed as a paint for iron articles. In order to free the powder from oxide of zinc, it is only necessary to allow it to remain for some time in contact with very dilute hydrochloric acid. The residue is first washed with water and then with pure alcohol, after which it is dried and preserved. If exposed to the air in mass in a damp state, it is liable to ignite spontaneously.

[1] Moody, *Proc. Chem. Soc.*, 1903, **19**, 273.
[2] Davies, *J. Soc. Chem. Ind.*, 1899, **18**, 102.
[3] Hehner, *ibid.*, 1902, **21**, 675; Thorne and Jeffers, *Analyst*, 1906, **31**, 101.

Alloys of Zinc.

297 The most important alloys of zinc are those which it forms with copper, which, as already stated, were known long before metallic zinc had itself been isolated. Zinc also forms an important constituent of many aluminium alloys, of nickel silver, and of many antifriction alloys

The following table gives the composition of a variety of copper-zinc alloys:

	Gold-like alloy used by watch-makers	Aich's metal	Brass from			Tombac.		Roman coin of the reign of Titus
			Ocker	Stöll-berg	Eng-land	English	Viennese	
Copper ..	58 86	60·20	62·24	65 80	70·30	86·38	97·8	96 06
Zinc	40·22	38 10	37·27	33·80	29·30	13·61	2·2	2·71
Tin	—	—	0 12	0 25	0·17	—	—	—
Lead	1·90	—	0 59	0·28	0·28	—	—	—
Iron.....	—	1·60	0 12	—	—	—	—	0·85
	100·98	99 90	100 34	100 13	100·05	99 99	100 0	99·62

Brass, which has long been known, was always made up to the year 1780 by strongly heating copper together with calamine and charcoal or coal. The coal reduces the calamine to the metallic condition, and the zinc, instead of passing off as vapour, combines with the copper, and forms brass. At the present day, however, brass is prepared by adding the requisite quantity of metallic zinc to molten copper. The composition of brass varies considerably; common brass, sometimes termed English brass, contains about two parts of copper to one of zinc. When more copper is added the colour becomes reddish. That containing about 80 per cent. of copper is termed German or Dutch brass or tombac. On the other hand, an additional proportion of zinc yields a light yellow metal known as Muntz metal, an alloy which was first prepared by Muntz, in the year 1832, and has since been very largely used for the sheathing of ships. Another such alloy, named Aich's metal from its inventor, is malleable when hot.

Brass and the other copper-zinc alloys are all harder than copper; they are malleable, and can be hammered and rolled into thin plates and drawn out to fine wire; they can also be

readily worked in the lathe. These properties, as well as their beautiful colour, bright lustre, and cheapness, render them most useful in the arts and manufactures.

COMPOUNDS OF ZINC.

Zinc and Oxygen.

298 *Zinc Oxide*, ZnO.—This compound occurs as the mineral zincite or red zinc ore, which consists of a mixture of zinc oxide with 0·7 to 12 per cent. of red oxide of manganese. It occurs, especially in New Jersey, in red or orange-yellow hexagonal crystals or in a granular mass. Zinc oxide is also occasionally found in the crystalline state in brass-melting furnaces, as well as in the zinc furnaces. It has already been mentioned that the finely divided oxide was known to the ancients as tutia, pompholyx or flowers of zinc, and Dioscorides states that if too much cadmia is employed in the manufacture of brass, pompholyx is formed like tufts of wool,[1] whence the name *Lana philosophica* was given to this substance by the alchemists. The similarity between the oxide of zinc obtained by combustion and flakes of snow led the alchemists to term it *nix alba*; this was translated into German as "weisses Nichts," and retranslated into Latin as "nihilum album."

Zinc oxide is known in commerce as "zinc white," and is prepared on the large scale and used as a paint and as a "filler" in the rubber industry. It is obtained by the distillation of zinc in earthenware retorts, the burning vapours of the zinc being brought into chambers through which a current of air is passed and the oxide allowed to deposit in a second chamber. The preparation of zinc white directly from the ore has been carried on at Liége.[2]

Zinc oxide is prepared for pharmaceutical purposes by precipitating a solution of zinc sulphate with sodium carbonate and igniting the basic carbonate thus thrown down. As the commercial zinc sulphate frequently contains Epsom salts (magnesium sulphate) as an impurity, it is best, in order to obtain the pure compound, to dissolve zinc in dilute sulphuric acid, and then either to treat the solution with sulphuretted hydrogen, or to allow the solution to remain for some time in contact

[1] πομφόλυξ ἐρίων τολύπαις ἀφομοιοῦται.

[2] See Hofmann's *Ber. Entw. Chem. Ind.*, i., 919.

with metallic zinc, in order to precipitate the cadmium, copper, arsenic, and other metals. To the filtrate a small quantity of an alkaline solution of sodium hypochlorite is added, in order to throw down the iron, manganese, etc.; the solution is then filtered, and poured in a thin stream into a boiling solution of pure sodium carbonate. The precipitate is washed with boiling water, and, after drying, it is gently ignited in a glass flask or platinum basin.

Zinc oxide has a specific gravity of 5·6; when hot it possesses a lemon-yellow colour, but on cooling it becomes white.[1] When heated in the oxy-hydrogen flame it emits a brilliant white light, and after being thus heated, phosphoresces for some time in the dark. It evaporates at an appreciable rate at 1400° and rapidly volatilises in the electric furnace, the vapour condensing in long, transparent crystals.[2] It is probable that the oxide undergoes polymerisation when heated, a small amount of heat being evolved in the process. The anhydrous oxide gradually takes up water from the air.[3]

The reduction of zinc oxide by carbon in an atmosphere of nitrogen begins at 800°, and increases rapidly with rise of temperature. Its reduction by carbon monoxide begins at 600°, and also increases rapidly with rise of temperature.[4]

It readily dissolves in acids, forming the corresponding zinc salts, which are colourless, unless the acid be coloured. The normal soluble salts redden litmus solution; they possess a disagreeable metallic taste, and act as poisons and emetics.

Zinc Hydroxide, $Zn(OH)_2$, is obtained as a white powder, when caustic potash, caustic soda, or ammonia is added to a solution of a zinc salt, but when prepared in this way it usually contains small amounts of a basic zinc salt. It is very soluble in an excess of these reagents, zinc oxide acting as an acid-forming oxide towards the strong alkalis, and it is upon this fact that the solution of zinc in alkalis with evolution of hydrogen depends. The reaction takes place especially quickly in presence of metallic iron. If metallic zinc is allowed to remain under the surface of a solution of ammonia in contact with iron or copper, zinc hydroxide crystallises from the solution in colourless, transparent rhombic prisms (Runge); and if a saturated solution

[1] Compare Schüpphaus, *J. Soc. Chem. Ind.*, 1899, **18**, 987.

[2] Moissan, *Compt. rend.*, 1892, **115**, 1034.

[3] de Forcrand, *Compt. rend.*, 1902, **134**, 1426; **135**, 36; *Ann. Chim. Phys.*, 1902, [vii], **27**, 26.

[4] Doeltz and Graumann, *Metallurgie*, 1907, **4**, 290.

of the hydroxide in caustic potash is allowed to stand, regular octahedra of the compound, $Zn(OH)_2,H_2O$, are formed (Bödeker).

The crystalline hydroxide is stable up to 85° in the air, but loses all its water at 130–140°, except a trace which is driven off only at a red heat. The amorphous hydroxide, on the other hand, loses its water gradually as the temperature rises (de Forcrand). The hydroxide is soluble in about 190,000 parts of water at 18°.[1] It is readily soluble in caustic alkalis and in ammonia, but is insoluble in dimethylamine.[2]

In its behaviour to alkalis it may be regarded as a weak acid, H_2ZnO_2, but the salt formed is very largely hydrolysed, the amount of the hydroxide dissolved by an alkali being a function of the concentration of the latter.[3] A study of the equilibrium between zinc oxide and sodium hydroxide solution has established[4] the existence of a stable compound, $Na_2O,ZnO,4H_2O$. Freshly precipitated zinc hydroxide requires nearly 7 molecular proportions of caustic soda in concentrated solution to dissolve it completely, and the solution thus formed is not permanent, zinc hydroxide being gradually precipitated from it in a less soluble form. Only a very small amount of a sodium zincate is ever present in the solution, the greater part of the dissolved hydroxide being probably present in the colloidal state.[5] When the hydroxide dissolves in ammonia, on the other hand, a complex hydroxide, the formula of which is still unsettled, is probably formed.[6]

Zinc Peroxide, ZnO_2.—A product containing zinc peroxide is formed by the action of hydrogen peroxide on the hydroxide,[7] and by the electrolysis of a solution of zinc chloride with a porous diaphragm, hydrogen peroxide being added to the cathode compartment.[8] It forms a yellowish powder containing variable amounts of zinc hydroxide and water.[9] Zinc peroxide

[1] Dupré, jun., and Bialas, *Zeit. angew. Chem.*, 1903, **16**, 54.

[2] Herz, *Zeit. anorg. Chem.*, 1901, **26**, 90.

[3] Rubenbauer, *Zeit. anorg. Chem.*, 1902, **30**, 331; Moir, *Proc. Chem. Soc.*, 1905, **21**, 310. See also Kuriloff, *Zeit. Elektrochem.*, 1906, **12**, 209; *Bull. Acad. St. Pétersbourg*, 1901, **1**, 95.

[4] Goudriaan, *Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 179.

[5] Hantzsch, *Zeit. anorg. Chem.*, 1902, **30**, 289.

[6] Dawson and McCrae, *Journ. Chem. Soc.*, 1900, **77**, 1239; Euler, *Ber.*, 1903, **36**, 3400; Bonsdorff, *Zeit. anorg. Chem.*, 1904, **41**, 132.

[7] Kuriloff, *Compt. rend.*, 1903, **137**, 618; de Forcrand, *ibid.*, 1902, **134**, 601; **135**, 103.

[8] Foregger and Philipp, *J. Soc. Chem. Ind.*, 1906, **25**, 398.

[9] Hinz, German Patent, 151129.

may also be formed by the action of 30 per cent. hydrogen peroxide solution on potassium, sodium, or ammonium zinc-oxide.[1]

Zinc and the Halogens.

299 *Zinc Chloride*, $ZnCl_2$.—Impure chloride of zinc was first prepared by Glauber. He describes in his *De furnis novis philosophicis*, published in 1648, an *oleum lapidis calaminaris*, "obtained by dissolving calamine in spirit of salt, and heating the solution, when a thick *oleum* remains as unctuous as olive-oil, and not particularly corrosive, for the spirit of salt has itself been weakened by corroding the calamine and thus lost its acrimony. This oil must be well preserved against the action of the air, otherwise in a few days it attracts so much air to it that it becomes a watery liquid." In 1735 Hellot prepared "butter of zinc," by distilling flowers of zinc with sal-ammoniac; and Pott, in 1741, obtained the same substance by distilling zinc with corrosive sublimate. Gallisch, in 1782, noticed that zinc deliquesced when exposed to the action of dephlogisticated muriatic acid gas (chlorine), and Westrumb, in 1790, observed that when finely divided zinc was dropped into the gas, the metal took fire. This historical sketch serves to show the methods by which the anhydrous chloride may be obtained. The same substance is formed when a mixture of anhydrous zinc sulphate and calcium chloride is distilled (Persoz).

Zinc chloride is a white or usually greyish-white mass of sp. gr. 2·907 at 25°/4°, soft, like wax, at the ordinary temperature, melting when heated a little above 100° (H. Davy), and subliming at a higher temperature in white, needle-shaped crystals. It is very deliquescent, is soluble in alcohol, and boils at 730°, its vapour density being 1·6, corresponding to the normal formula. It also has the normal molecular weight when dissolved in urethane, as determined by the freezing point method (Castoro).[2]

A concentrated solution of zinc chloride is best obtained by dissolving zinc, its oxide, or carbonate, in hydrochloric acid, and evaporating the solution to the consistency of a syrup. On the addition of a little concentrated hydrochloric acid to this syrupy solution, small, deliquescent octahedra separate out, having the

[1] Kazanecky, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1452; see also Carrasco, *Gazz.*, 1911, **41**, i., 16; Teletoff, *J. Russ. Phys Chem. Soc.*, 1911, **43**, 131; Rosenfeld and Nottebohm, *Zeit. anorg. Chem.*, 1914, **89**, 405; **90**, 150; and Sjöström, *ibid.*, 1917, **100**, 237.

[2] *Gazz.*, 1898, **28**, ii., 317.

composition $ZnCl_2,H_2O$. In addition to this, hydrates with 1·5, 2·5, 3, and $4H_2O$ are known, the curve of equilibrium for zinc chloride and water being one of great complexity.[1] Zinc chloride is used in surgery as a caustic, and is employed in the laboratory for the purpose of separating the elements of water from many organic substances. It is used as a preservative of timber, for vulcanising paper fibre and as a flux for soldering operations. It is also employed on a large scale, as is magnesium chloride, for weighting cotton goods. When its solution is evaporated, hydrochloric acid is evolved and basic salts are formed; these may also be obtained by diluting the aqueous solution, and by boiling the solution of the chloride with zinc oxide and adding water, when precipitates are formed consisting of mixtures of Zn(OH)Cl and $Zn(OH)_2$ in varying proportions. The oxychlorides, $ZnCl_2,4ZnO,6H_2O$ and $2ZnCl_2,2ZnO,3H_2O$, have been described by Driot.[2] When a solution having a specific gravity of 1·7 is boiled with an excess of oxide, a liquid is formed which has the property of dissolving silk, and this is used for separating silk fibres from those of wool, or of cotton or linen, whilst all of these dissolve in a solution of normal zinc chloride.

Zinc chloride forms double salts with 2 and 3 molecules of ammonium chloride;[3] the products obtained by the crystallisation of solutions containing chloride of zinc and the chlorides of sodium, potassium, ammonium, and lithium at temperatures between 20° and 100° have been examined by Ephraim.[4]

Zinc Bromide, $ZnBr_2$, is formed when bromine vapour is passed over the metal heated to redness. It corresponds closely to the chloride in its properties, and on heating sublimes in the form of white needles. It melts at 394°, and boils at 650°. The products of crystallisation of solutions containing bromide of zinc and the bromides of sodium, potassium, ammonium, and lithium at temperatures between 20° and 100° have been examined by Ephraim.[4]

Zinc Iodide, ZnI_2.—Zinc and iodine readily unite when they are heated together to form a colourless mass which melts at 446°, and sublimes in four-sided needles. An aqueous solution can be easily obtained by warming metallic zinc and iodine

[1] Dietz, *Ber.*, 1899, **32**, 90; Mylius and Dietz, *ibid.*, 1905, **38**, 921.
[2] *Compt. rend.*, 1910, **150**, 1426.
[3] Meerburg, *Zeit. anorg. Chem.*, 1903, **37**, 199.
[4] *Zeit. anorg. Chem.*, 1908, **59**, 56; see also Ephraim and Model, *ibid.*, 1910, **67**, 379.

together with water. On evaporating the solution, the anhydrous compound separates out in the form of regular octahedra, which when exposed to the air first absorb water and deliquesce, and then take up oxygen and lose iodine.

Zinc and Sulphur.

300 *Zinc Sulphide*, ZnS, is found as *blende*, which crystallises in the regular system, frequently in hemihedral forms (Class 31, p. 209). Its specific gravity varies from 3·5 to 4·2. In the pure state it is transparent, and has a light yellow colour; usually, however, it contains iron and other metals which impart to it a red, brown, or black tint. The same compound is more rarely found as wurtzite in hexagonal crystals. When ammonium sulphide is added to a solution of a zinc salt, a white amorphous precipitate of zinc sulphide is formed; this is soluble in dilute acids, with the exception of acetic acid, with evolution of hydrogen sulphide. When this precipitate is heated in a current of hydrogen, or fused at 1800°—1900° under a pressure of 100--150 atmospheres,[1] or when zinc oxide is ignited in an atmosphere of sulphuretted hydrogen, zinc sulphide is obtained in crystals which have the form of wurtzite. Natural crystals of zinc sulphide have the property of phosphorescing after exposure to light, and the phosphorescent sulphide may be artificially prepared by heating precipitated zinc sulphide to whiteness in a covered crucible (Sidot). Pure zinc sulphide remains non-phosphorescent, but if the material contains small amounts of alkali chlorides and the sulphides of other metals, such as bismuth, copper, or manganese, a brilliant phosphorescence is obtainable.[2] The phosphorescent sulphide glows when exposed to X-rays, Becquerel rays, or the α-radiation from radium, and when placed in ozonised oxygen.[3] For the action of the Röntgen rays on a crystal of zinc sulphide see p. 217.

Zinc Sulphate, $ZnSO_4$.—This salt, long known under the name of white vitriol, is thus described in the first book of Basil Valentine's *Last Testament*—"Behold the ▽ (water) of Goslar, how a fine white and red vitriol is found there." The name vitriol was applied to all the salts of the common metals

[1] Tiede and Schleede, *Ber.*, 1920, **53B**, 1717.

[2] Grune, *Ber.*, 1904, **37**, 3076; Hofmann and Ducca, *ibid.*, 3407; Jorissen and Ringer, *Chem. Centr.*, 1906, **1**, 644.

[3] Schenck and Mihr, *Ber.*, 1904, **37**, 3464.

possessing a vitreous lustre,[1] and to this day iron sulphate is known as green vitriol, and copper sulphate as blue vitriol.

White vitriol was prepared on the large scale at Goslar, in the Harz, in the sixteenth century. It was obtained by lixiviating the roasted ore, but its composition remained long unknown. Thus, in Lemery's *Cours de Chymie*, published in 1675, we read, "Le vitriol blanc est le plus dépuré de substance metallique." It was, indeed, soon discovered that this salt might be obtained by dissolving calamine in sulphuric acid, but as this ore always contains iron, green vitriol was obtained at the same time. In addition to this, the fact that both green vitriol and blue vitriol when heated become white through loss of water of crystallisation led to still further confusion between these compounds. It was not until 1735 that Neumann suggested that the base of white vitriol consisted of zinc or calamine, and this view was confirmed by Hellot, inasmuch as he obtained the salt by dissolving zinc in dilute sulphuric acid, whilst Brandt showed that brass was obtained from white vitriol by calcining it and heating it with charcoal and copper.

Zinc sulphate occurs not infrequently in zinc mines, where it is formed by the oxidation of blende. It is, however, usually obtained on the large scale by roasting ores containing sulphide of zinc, afterwards exhausting with water, and evaporating the solution to the crystallising point, when the hydrate $ZnSO_4,7H_2O$, isomorphous with Epsom salts, separates out. These crystals on heating fuse readily in their water of crystallisation. Commercial zinc vitriol is made to assume the shape of a sugar-loaf by stirring this fused mass in wooden troughs with wooden shovels till crystallisation takes place, and subsequently pressing the mass into moulds. The aqueous solution has an acid reaction (p. 111), 0·03 per cent. of the salt being hydrolysed in a 1/16 normal solution.[2]

Zinc sulphate forms several hydrates. The heptahydrate is stable in contact with water up to 39°, and then passes into the hexahydrate, which at 70° is converted into a lower hydrate, probably the monohydrate.[3]

[1] "Atramentum candidum potissimum stiriæ figura reperitur Goslariæ, translucidum cristalli instar; nec cæruleum nec viride caret perspicuitate; unde superior ætas atramento sutorio vitrioli nomen imposuit."—AGRICOLA, *De Natura Fossilium*, Lib. III., ed. 1657.

[2] Ley, *Ber.*, 1897, **30**, 2192.

[3] See Landolt-Börnstein-Roth, *Physikalisch chemische Tabellen.*

One hundred parts of water dissolve :

	At 0°	15°	39°	50°	70°	100°
$ZnSO_4$	41·9	50·88	70·06	76·84	89	78·5

The heptahydrate has the specific gravity 1·95 : it effloresces slowly in the air, and on heating to 100° loses six molecules of water, the last molecule being evolved only at a moderate red-heat. The hexahydrate, isomorphous with the corresponding magnesium salt, separates out when a solution of the sulphate is evaporated above 50°.

The anhydrous salt forms a friable mass having a specific gravity of 3·4. When heated more strongly, sulphur dioxide and oxygen are evolved, and a basic salt remains behind, which is formed also when zinc sulphate and zinc oxide are boiled together. On cooling the hot saturated solution, glistening scales separate out having the formula $SO_2(O{\cdot}Zn{\cdot}O{\cdot}Zn)_2O,2H_2O$. At a white heat all the zinc sulphates are completely decomposed, leaving a residue of zinc oxide. Besides these, several other basic zinc sulphates are known, and also characteristic double salts with the alkali sulphates, having the general formula $ZnSO_4,M_2SO_4,6H_2O$.[1]

Zinc sulphate is employed in medicine, in dyeing, and in the manufacture of lithopone.

Zinc Thiosulphate, ZnS_2O_3, is prepared by treating a mixture of zinc dust and water at 45–50° with a rapid stream of sulphur dioxide until the metal has entirely dissolved; a large excess of sulphur dioxide must be avoided, as this reacts with zinc thiosulphate, forming polythionic acids. The viscid, greyish-yellow mass produced, when cooled to the ordinary temperature, sets to a stiff paste which is drained in an inert atmosphere.[2]

Zinc and Nitrogen and Phosphorus.

301 *Zinc Nitride*, Zn_3N_2, is formed when zincamide is heated to dull redness :

$$3Zn(NH_2)_2 = Zn_3N_2 + 4NH_3,$$

and is also produced to some extent when zinc is heated at 600° in a current of ammonia.[3] It is a green powder which is decom-

[1] Tutton, *Journ. Chem. Soc.*, 1904, **85**, 1123; Koppel, *Zeit. physikal. Chem*, 1905, **52**, 385. See also Mallet, *Journ. Chem. Soc.*, 1900, **77**, 220.

[2] Gränau, Landshoff and Meyer, D. R. Patent, 184564.

[3] White and Kirschbraun, *J. Amer. Chem. Soc.*, 1906, **28**, 1343.

posed by water with such energy that the mass when moistened becomes incandescent:

$$Zn_3N_2 + 3H_2O = 3ZnO + 2NH_3.$$

Zincamide or *Zinc Diamine*, $Zn(NH_2)_2$, is formed by the action of dry ammonia on zinc ethyl:

$$Zn(C_2H_5)_2 + 2NH_3 = Zn(NH_2)_2 + 2C_2H_6.$$

It is a white amorphous powder and is decomposed by water with evolution of heat as follows:

$$Zn(NH_2)_2 + 2H_2O = Zn(OH)_2 + 2NH_3.$$

Zinc Hydrazide, ZnN_2H_2, is formed by the interaction of zinc ethyl, dissolved in dry ether, and hydrazine. It may also be prepared from zincamide and anhydrous hydrazine in ethereal suspension.[1]

Zinc Nitrate, $Zn(NO_3)_2$.—The hexahydrate crystallises from a very concentrated solution of zinc in nitric acid, in striated colourless pointed four-sided prisms. These are very deliquescent, and are soluble in alcohol. It melts at 36·4°, and passes at about 35°, and at a concentration of 65 per cent. of anhydrous salt, into the trihydrate, which melts at 45·5°. A hydrate with $9H_2O$ also exists below −17°.[2] When heated for some time at 100°, the salt loses water and nitric acid and a basic nitrite remains, which is also formed by boiling the solution with zinc oxide. Hydrates with 2, 4, and 6 molecules of water are also known, and the interactions between these have been investigated by Vasilieff.[3]

Zinc Phosphide, Zn_3P_2, is obtained as a grey mass by heating finely divided zinc in the vapour of phosphorus (Schrotter).[4] Zinc phosphide is employed in medicine.

Zinc Phosphates. An investigation of the equilibrium between zinc oxide, phosphoric oxide and water[5] has proved that at 25° the following phosphates exist: $Zn_3(PO_4)_2,4H_2O$; $ZnHPO_4,3H_2O$; and $Zn(H_2PO_4)_2,2H_2O$: and that at 37° a lower hydrate of the second phosphate, $ZnHPO_4,H_2O$, is formed.

[1] Ebler and Krause, *Ber.*, 1910, **43**, 1690.

[2] Funk, *Zeit. anorg. Chem.*, 1899, **20**, 400.

[3] *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 748.

[4] See also Vigier, *Bull. Soc. chim.*, 1861, **3**, 5, and Jolibois, *Compt. rend.*, 1908, **147**, 801.

[5] Eberly, Gross and Crowell, *J. Amer. Chem. Soc.*, 1920, **42**, 1433.

Zinc and Carbon.

302 *Carbonates of Zinc.—Normal Zinc Carbonate*, $ZnCO_3$ occurs as zinc-spar or calamine, crystallising in rhombohedra having a specific gravity of 4·42. Zinc-spar is found sometimes in the pure state, but, in general, more or less of the zinc is found to be replaced by magnesium, cadmium, iron, and other isomorphous metals. When a solution of zinc vitriol is precipitated by the addition of an alkali carbonate or bicarbonate, the first product is the amorphous normal carbonate, which passes into the hydrated crystalline carbonate, $ZnCO_3,H_2O$, or into the basic carbonate, $5ZnO,2CO_2,4H_2O$, or into a mixture of these, according to the concentration of the solutions and the temperature. The basic carbonate may be obtained pure by dissolving zinc carbonate or oxide or metallic zinc in water containing carbon dioxide and boiling the solution. When boiled with an excess of sodium carbonate it is finally converted into anhydrous zinc oxide.[1]

Zinc Cyanide, $Zn(CN)_2$, is a snow-white powder used in medicine, and prepared by precipitating zinc acetate with aqueous hydrocyanic acid. It is insoluble in water and in alcohol, but dissolves in solutions of cyanide of ammonium and potassium, forming double salts [2] such as $K_2Zn(CN)_4$.

Ammoniacal Derivatives of Zinc.

303 These compounds closely resemble the corresponding derivatives of the cupric salts (p. 457). *Zincammonium chloride*, $ZnCl_2,4NH_3,H_2O$, is obtained by adding ammonia to a solution of zinc chloride until the precipitate first formed redissolves, and on the evaporation of the solution crystallises out in nacreous plates. When heated to 149° it is converted into $ZnCl_2,2NH_3$, which crystallises in rhombic prisms, and on further heating loses ammonia, forming the compound $ZnCl_2,NH_3$; the latter is an amber-coloured mass which distils at a red-heat without decomposition.[3]

Zinc sulphate also yields crystalline ammonia derivatives, having the composition: $ZnSO_4,2NH_3,H_2O$; $ZnSO_4,4NH_3,4H_2O$. The anhydrous sulphate also combines directly with ammonia,

[1] Kraut, *Zeit. anorg. Chem.*, 1896, **13**, 1.
[2] Sharwood, *J. Amer. Chem. Soc.*, 1903, **25**, 570.
[3] Kane, *Ann. Chim. Phys.*, 1839, **72**, 290.

forming the compound $ZnSO_4,5NH_3$, which is a white powder and is decomposed by water with separation of zinc hydroxide.

When zinc sulphate solution is treated with excess of ammonia, the clear solution probably contains the complex salt, $Zn(NH_3)_4SO_4$ (Dawson and McCrae).

Detection and Estimation of Zinc.

304 The salts of zinc do not, as a rule, impart any tint to the non-luminous gas-flame, but a few of the salts formed from volatile acids, such as the nitrate, produce a green coloration. The spark spectrum of zinc, however, is characteristic, and can be well shown by volatilising a small piece of the metal in the lower carbon pole of the electric lamp. Amongst the more prominent zinc lines are 6363 and 6102 in the red, and 4926 and 4911 in the blue.

The most characteristic compound of zinc is the white sulphide insoluble in water, in acetic acid, and in the alkalis. In the ordinary course of qualitative analysis zinc is thrown down together with the other metals precipitated by ammonium sulphide, such as cobalt, nickel, iron, manganese, chromium, and aluminum, the first four being precipitated as sulphides, the last two as hydroxides. The well-washed precipitate is treated with dilute hydrochloric acid, which leaves nickel and cobalt sulphides undissolved; the filtrate is boiled and a little potassium chlorate is added to remove sulphuretted hydrogen and oxidise the iron to the ferric state; ammonia is then added, which precipitates the iron, chromium, and aluminium, as hydroxides. The filtrate is acidified, mixed with an excess of sodium acetate, and sulphuretted hydrogen passed through the solution; zinc is thus precipitated as the sulphide, manganese remaining in solution. When a zinc compound is ignited on charcoal before the blowpipe, and the heated mass is moistened with a solution of cobalt nitrate and again ignited, a beautiful green mass, known as Rinmann's green, is obtained. Zinc compounds heated in the blowpipe flame on charcoal with sodium carbonate yield an incrustation of zinc oxide, which when hot is yellow, but on cooling becomes white.

Small traces of zinc can be readily and accurately detected by *Bunsen's method of flame-reactions*. This depends upon the fact that the more volatile metals, such as zinc, mercury, and arsenic, are reduced from their compounds when these are heated on a

thread of asbestos held in the upper reducing flame of the Bunsen burner. If a small porcelain basin, filled with cold water, be held just above the substance to be examined, the volatilised metal condenses on the outside of the cold basin as a metallic film, and in a few seconds the reaction is complete. A square centimetre of filter paper is moistened with nitric acid, and this rubbed over the surface of the basin so as to dissolve the metallic film; the paper is then rolled up, placed in a coil of thin platinum wire, and burned in the upper oxidising flame at as low a temperature as possible, when the colour of the ash is seen to be yellow when hot, but white on cooling. The ash is next moistened with a drop of dilute cobalt solution, and heated in the flame, when the mass attains a green colour.

For the quantitative estimation of zinc, the solution is precipitated with a boiling solution of sodium carbonate, the basic carbonate washed and dried and converted by ignition into zinc oxide, which is then weighed. Zinc may also be estimated gravimetrically by the electrolysis of an alkaline solution of the hydroxide, and volumetrically by titration with a standardised solution of sodium sulphide or potassium ferrocyanide, a solution of ammonium molybdate or uranium acetate being used as indicator when ferrocyanide is employed.

Atomic Weight of Zinc.—This was determined by Marignac [1] from the quantity of zinc and chlorine contained in potassium zinc chloride, K_2ZnCl_4, his results giving an average value of 65·25, whilst Baubigny [2] by analysis of the sulphate obtained the number 65·40. Morse and Burton,[3] from the amount of zinc oxide yielded by pure zinc, the metal being converted into the nitrate and this decomposed by heating, arrived at the number 65·26; they, however, neglected the amount of oxygen and nitrogen occluded by zinc oxide under these circumstances, and a repetition [4] of their experiments, in which allowance was made for this source of error, gave the value 65·45. Gladstone and Hibbert [5] found the ratio of the equivalents of zinc and silver as determined by comparing the quantity of zinc dissolved and silver precipitated by the same current to be 3·298, from which, taking silver as 107·88, the atomic weight of zinc is found to be 65·41. Finally, Richards and Rogers,[6] by the

[1] *Jahresb.*, 1883, 42. [2] *Compt. rend*, 1883, **97**, 908.
[3] *Amer. Chem. J.*, 1888, **10**, 311.
[4] Morse and Arbuckle, *Amer. Chem. J.*, 1898, **20**, 195.
[5] *Journ. Chem. Soc.*, 1889, **55**, 443. [6] *Zeit. anorg. Chem.*, 1895, **10**, 1.

analysis of zinc bromide prepared from pure zinc oxide or electrolytic zinc, found the atomic weight to be 65·38. The value which is at present (1922) accepted is 65·37.

CADMIUM. Cd=112·40. At. No. 48.

305 This metal was discovered in the year 1817 by Stromeyer. He observed that a sample of zinc carbonate obtained from the zinc works at Salzgitter yielded an oxide which, although it did not contain any iron, possessed a yellow colour, and he found that this was due to the presence of the oxide of a new metal, which he soon afterwards detected in other samples of the oxide of zinc, as well as in metallic zinc itself. Whilst Stromeyer was engaged on these experiments, Hermann, in Schonebeck, also discovered the new metal in a sample of zinc oxide which was employed for pharmaceutical purposes, and which had been confiscated in Magdeburg, inasmuch as the acid solution yielded a yellow precipitate with sulphuretted hydrogen; this was supposed to be caused by the presence of arsenic. Hermann showed that this supposition was not correct, and ascertained that a new metal was present. Soon afterwards Meissner and Karsten also observed the existence of the same substance. In 1818 Stromeyer published a complete investigation of the metal, giving to it the name which it now bears, from *cadmia fornacum*, because the metal was chiefly found in the zinc flowers of the zinc furnaces.

Cadmium not only occurs as a constituent of zinc ores, but likewise as sulphide in the mineral greenockite, a somewhat rare substance found at Greenock, Bishopstown, and Kilpatrick in Scotland, as well as in Bohemia and Pennsylvania. The quantity of cadmium contained in the various samples of calamine and blende varies considerably and averages less than 0·5 per cent.

In the process of zinc smelting the more volatile vapour of cadmium comes off with the first portions of the zinc, and these vapours burn in the air with formation of the oxides of cadmium and zinc. The cadmium is extracted from the first portion of dust which is condensed in the iron cones or other dust chambers used in connection with the adapters of the zinc furnaces, when sufficiently rich. This dust may contain from 1 to 6 per cent. of cadmium, and is mixed with a suitable proportion of coal and again distilled at a low red head from retorts

having long sheet-iron cones as adapters; the enriched distillate thus obtained may contain over 20 per cent. of cadmium. This product is now mixed with charcoal and distilled in small cast-iron or clay retorts, and the resulting metallic cadmium is cast into rods or ingots.

Cadmium compounds are obtained during the purification of zinc sulphate solutions for the electro-extraction of zinc.

An electrolytic method is sometimes used in the refining of the metal, the cadmium being deposited on platinum electrodes and then distilled in vacuo.

Cadmium possesses a tin-white colour and a fibrous fracture, and takes a high polish. It can be easily obtained crystallised in regular octahedra by sublimation in a current of hydrogen (Kämmerer). The pure metal obtained by electrolysing the sulphate and subliming the product in a vacuum forms flat needles or silvery six-sided plates.[1] It is somewhat harder than tin, but may be cut with a knife. It can be easily rolled out to foil and drawn into wire, but when heated to 80° it becomes brittle. When bent it emits a crackling sound, as does tin when similarly treated. The specific gravity of the cast metal is 8·546, but after hammering it attains a specific gravity of 8·667 (Schroder).[2] It melts at 321·7°[3] and boils at 778°.[4] Its vapour has a dark yellow colour and a disagreeable smell, producing headache when inhaled. The density of cadmium vapour is 3·94, and the molecule of cadmium in the gaseous state is therefore monatomic.[5] Dilatometric measurements indicate that ordinary cadmium consists of two or more allotropic forms.[6]

Cadmium has been obtained in the form of a deep brown-coloured colloidal solution in water by the electrical method[7] (p. 82). In its behaviour towards acids cadmium resembles zinc.

Cadmium is employed in the preparation of certain alloys of low melting point, such as Lipowitz' metal, which consists of eight parts of lead, fifteen of bismuth, four of tin, and three of cadmium, and melts at 60°. An amalgam of cadmium was

[1] Mylius and Funk, *Zeit. anorg. Chem.*, 1896, **13**, 157.

[2] See also Kahlbaum and Sturm, *Zeit. anorg. Chem.*, 1905, **46**, 217.

[3] Holborn and Day, *Ann. Physik*, 1900, [iv], **2**, 505.

[4] D. Berthelot, *Compt. rend.*, 1902, **134**, 705.

[5] Deville and Troost, *Compt. rend.*, 1859, **49**, 239. Compare Biltz, *Chem. Centr.*, 1895, i., 770.

[6] Cohen and Helderman, *Zeit. physikal. Chem.*, 1914, **87**, 409, 419, 426; Cohen, *ibid.*, 431.

[7] Bredig, *Zeit. physikal. Chem.*, 1900, **32**, 127.

formerly used as a stopping for teeth, but is no longer employed, as it turns the dentine yellow. Cadmium is also employed in the construction of cells of standard electromotive force.

CADMIUM COMPOUNDS.

Cadmium Oxygen.

Cadmous Oxide, Cd_2O, may best be prepared by heating cadmium oxalate at 300° in a rapid stream of carbon dioxide. The green product thus obtained approximates closely to a composition of Cd_4O and was formerly believed to be a definite suboxide of that formula.[1] On heating this product *in vacuo*, the free cadmium may be distilled off, leaving Cd_2O as a homogeneous green mass.[2] If the product of the reaction of cadmium on cadmic chloride (*vide infra*) is treated with water, lustrous transparent crystals first separate, which soon fall to a white amorphous powder of cadmous hydroxide, CdOH. This, when gently heated, yields cadmous oxide as a yellow microcrystalline powder.[3] When heated more strongly cadmous oxide decomposes into cadmic oxide and metallic cadmium.

306 *Cadmic Oxide*, CdO.—This substance forms the brown blaze of the zinc smelters. The metal cadmium burns with a bright flame when heated in the air, forming a brown oxide, which may also be obtained by passing a mixture of steam and cadmium vapour through a red-hot tube. When the metal is heated to whiteness in a current of oxygen, the oxide sublimes in dark red, probably cubic, crystals, and may be obtained in the form of a dark blue-black powder, consisting of microscopic octahedra, by igniting the nitrate. It also occurs as a mineral[4] in octahedra possessing a specific gravity of 6·15. It does not melt at a white-heat, but is easily reduced at a moderate red-heat on charcoal before the blowpipe; the metal, however, volatilises and burns, and the oxide is deposited as a brown incrustation on the charcoal. The oxide formed by the combustion of the metal contains a trace of peroxide.[5] The reduction of cadmium oxide by carbon in nitrogen commences at 580°.[6]

[1] Tanatar, *Zeit. anorg. Chem.*, 1901, **27**, 432; Tanatar and Lævin, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 495.

[2] Denham, *Trans. Chem. Soc.*, 1919, **115**, 556.

[3] Morse and Jones, *Amer. Chem. J.*, 1890, **12**, 488; Denham, *loc. cit.*; compare Canzoneri, *Gazz.*, 1897, **27**, ii, 486.

[4] Neumann and Wittich, *Chem. Zeit.*, 1901, **25**, 561.

[5] Manchot, *Ber.*, 1906, **39**, 1170.

[6] Doeltz and Graumann, *Metallurgie*, 1907, **4**, 419.

Cadmic Hydroxide, $Cd(OH)_2$, is obtained as a white precipitate by the addition of a soluble salt of cadmium to caustic potash. The hydroxide absorbs carbon dioxide from the air, and at 300° is resolved into the oxide and water. It is soluble in a solution of ammonia, a complex hydroxide probably being formed,[1] as in the case of zinc hydroxide.

This oxide and hydroxide correspond to the only series of cadmium salts definitely known, which are for the most part colourless salts closely resembling those of zinc. The soluble ones have a disagreeable metallic taste, and act as emetics. A series of cadmous salts appears, however, to exist, as the cadmic halogen compounds when heated with cadmium yield salts having strongly reducing properties. These have not been obtained pure, the products appearing to consist of mixtures of cadmous and cadmic salts.

Cadmic Salts.

307 *Cadmium Chloride*, $CdCl_2$.—This salt is obtained by evaporating a solution of the metal or oxide in hydrochloric acid. The hydrated chloride, $CdCl_2,2\frac{1}{2}H_2O$, is deposited in the form of rectangular prisms which readily effloresce on exposure to the air, and on heating lose water and melt at 590° (Ruff and Plato). The transparent pearly mass of the anhydrous chloride sublimes at a higher temperature in transparent micaceous laminæ. Its specific gravity at 25°/4° is 4·047.[2]

Hydrates with 5, 4, $2\frac{1}{2}$, 2 and 1 mol. H_2O have been described, but the existence of those with 5 and $2H_2O$ is doubtful (Dietz). The hydrate with $4H_2O$ passes into that with $2\frac{1}{2}H_2O$ at −5°, and the latter is converted into the monohydrate at 34°. The saturated solution contains in 100 parts of water [3]:

At	0°	30°	60°	80°	100°
$CdCl_2$	90	128·6	136·8	140·4	147.

Cadmium chloride combines with ammonia to form the unstable compound $CdCl_2,6NH_3$, a bulky powder, which passes at about 62° into $CdCl_2,2NH_3$; this may also be obtained by evaporating a solution of the chloride in aqueous ammonia [4]

[1] Euler, *Ber.*, 1903, **36**, 3400; Dawson and McCrae, *Journ. Chem. Soc*, 1900, **77**, 1239; Bonsdorff *Zeit. anorg. Chem.*, 1904, **44**, 132.

[2] Baxter and Hines, *Amer. Chem. J.*, 1904, **31**, 220.

[3] Dietz, *Zeit. anorg. Chem.*, 1899, **20**, 257.

[4] Lang and Rigaut, *Journ. Chem. Soc.*, 1899, **75**, 883.

or of the hydroxide in ammonium chloride.[1] It is inodorous, and is stable up to 210°.

Cadmium Iodide, CdI_2, is obtained by dissolving the metal in hydriodic acid, or by digesting it with iodine and water. It crystallises in large transparent six-sided anhydrous tablets, which do not undergo alteration on exposure to the air. It melts at 350° (Ruff and Plato), and gives off iodine when heated to a higher temperature. It dissolves readily in water and alcohol. Its specific gravity is 5·61–5·73.[2] One hundred parts of water dissolve (Dietz):

At	18°	50°	100°
CdI_2	85·3	97·4	127·6.

Iodide of cadmium is used in photography, being one of the few iodides soluble in alcohol.

Cadmium Sulphide, CdS.—Cadmium sulphide occurs in yellow hexagonal glittering crystals as greenockite. It is obtained as a fine yellow precipitate when a cadmium salt is precipitated with sulphuretted hydrogen, this precipitate being employed as a pigment. It melts at a white heat, and forms on cooling a lemon-yellow, micaceous mass, having a specific gravity of 4·86. Heated in the electric furnace, it yields crystals of greenockite.[3] It is soluble in strong hydrochloric and nitric acids, and in boiling dilute sulphuric acid.

According to Buchner,[4] two modifications of cadmium sulphide exist; the α variety is precipitated in a fairly acid solution by means of sulphuretted hydrogen, and the β variety, which resembles red lead, is precipitated in very acid solutions. This modification changes to the α form when heated.

Cadmium Sulphate, $CdSO_4$.—A concentrated solution of cadmium sulphate, when allowed to evaporate spontaneously, deposits large monoclinic crystals, having the composition $3CdSO_4,8H_2O$. This hydrate is stable in contact with its saturated solution up to 74°, at which temperature it passes into the monohydrate, a microcrystalline powder, the solubility of which diminishes with rise of temperature. A metastable hydrate with $7H_2O$ is also known.[5] The normal

[1] Grossmann, *Zeit. anorg. Chem.*, 1902, **33**, 149.

[2] Compare Snell, *J. Amer. Chem. Soc.*, 1907, **29**, 1288.

[3] Mourlot, *Compt. rend.*, 1896, **123**, 54; cf. Tiede and Schleede, *Ber.*, 1920, **53B**, 1717.

[4] *Chem. Zeit.*, 1891, **15**, 329.

[5] Mylius and Funk, *Ber.*, 1897, **30**, 824.

salt when heated yields a basic compound, $SO_2[OCd(OH)]_2$, sparingly soluble in water, and crystallising in pearly scales. One hundred parts of water at 23° dissolve 59 parts of the anhydrous normal salt, and at the boiling point a somewhat larger quantity. Crystallised cadmium sulphate is used in diseases of the eye and in the "normal cadmium cell." Stable crystalline compounds of the composition $3CdSO_4,4H_2O,4HCl$ and $3CdSO_4,8HCl$ have been described.[1]

Cadmium Amide, $Cd(NH_2)_2$, is prepared by the action of excess of cadmium thiocyanate or potassium cadmium cyanide upon potassamide in liquid ammonia solution. It is a white powder which reacts violently with water, explodes on heating suddenly giving metallic cadmium, and heated at 180° in a vacuum loses ammonia to form the *nitride*, Cd_3N_2, a black amorphous powder which explodes in contact with water. If in the above preparation excess of potassamide is used, potassium ammonocadmiate, $Cd(NHK)_2,2NH_3$, is formed.[2]

Cadmium Nitrite, $Cd(NO_2)_2$, prepared from cadmium chloride and silver nitrite forms bright pale yellow crystals which decompose slowly at 150° forming cadmium oxide and nitrate and nitric oxide.[3]

Cadmium Nitrate, $Cd(NO_3)_2,4H_2O$, crystallises in fibrous needles, which melt at 59·5°, deliquesce in the air, and are soluble in alcohol.[4]

Cadmium Carbonates.—Minute rhombohedral crystals of the *normal carbonate*, having the sp. gr. 4·96, can be obtained by adding excess of ammonium carbonate to a solution of cadmium chloride, and then just enough ammonia to dissolve the precipitate, and heating on the water-bath.[5] The white precipitate obtained by addition of an alkali carbonate to a soluble cadmium salt possesses a varying composition, according to the temperature at which the precipitation takes place and the amount of precipitant employed. With an excess of potassium carbonate in the cold the precipitate possesses nearly the composition of the normal salt.

[1] Baskerville and Harris, *J. Amer. Chem. Soc.*, 1901, **23**, 894.

[2] Bohart, *J. Physical Chem.*, 1915, **19**, 537.

[3] Rây, *Journ. Chem. Soc.*, 1917, **111**, 159.

[4] Funk, *Zeit. anorg. Chem.*, 1899, **20**, 414. See also Puschin, *J. Russ. Phys. Chem. Soc*, 1905, **37**, 382.

[5] de Schulten, *Bull. Soc. franç. Min.*, 1897, **20**, 195.

Detection and Estimation of Cadmium.

308 Cadmium salts do not impart any tint to the non-luminous gas-flame. The cadmium spectrum is well seen when the metal is volatilised in the electric arc; the most prominent lines being 6438 in the red, 5378 and 5338 in the green, and 5085, 4800, and 4677 in the blue.

The yellow sulphide of cadmium is the most characteristic compound of the metal. This is insoluble in dilute acids in the cold, and hence may be easily distinguished from zinc as well as from the other metals already described. Cadmium sulphide can easily be distinguished from other yellow sulphides, such as those of tin, antimony, and arsenic, by its insolubility in ammonium sulphide and in the caustic alkalis. The method of separating cadmium from the other metals precipitated by sulphuretted hydrogen will be discussed under these several metals. It may suffice here to remark that cadmium hydroxide, like the corresponding copper compound, is soluble in ammonia, and that these two metals are frequently obtained together in the process of analysis. In order to separate them, two methods may be employed. In the first place potassium cyanide may be added to the blue ammoniacal solution until this becomes colourless; sulphuretted hydrogen is then passed through, when the cadmium sulphide is completely precipitated. Or, in the second place, the metals may be both precipitated as sulphides, and the washed precipitate boiled with a mixture of five parts of water and one part of concentrated sulphuric acid, which dissolves the cadmium sulphide.

The quantitative estimation of cadmium is usually made by precipitating the carbonate from the boiling solution with sodium carbonate; this is then dried and converted by ignition into the oxide, preferably on an asbestos filter in a Gooch crucible, which is afterwards weighed. Cadmium may also be estimated as the sulphide, which is dried at 100° and then weighed.

Atomic Weight of Cadmium.—The atomic weight of cadmium was found by Huntingdon[1] from the analysis of the bromide to be 112·18. Morse and Jones obtained the number 112·07, but a repetition of the experiments,[2] in which allowance was made for the oxygen and nitrogen occluded by the oxide (compare Zinc,

[1] *Ber.*, 1882, **15**, 80.

[2] Morse and Arbuckle, *Amer. Chem. J.*, 1898, **20**, 536.

p. 683), led to the higher value 112·37. Baxter, Hines, and Freuert, by the analysis of the chloride [1] and bromide,[2] obtained the number 112·42. The determination of the atomic weight from the weight of metal electrolytically deposited from a solution of the oxide, chloride, or bromide [3] has led to the lower number 112·04, which is probably inaccurate, for Perdue and Hulett,[4] from electrolytic analyses of cadmium sulphate, conclude that the atomic weight is 112·3. Baxter and Hartmann [5] purified cadmium bromide by recrystallisation, converted to chloride and deposited cadmium electrolytically upon a mercury cathode, thus obtaining the value 112·417. The number at present (1922) accepted is 112·4.

MERCURY. Hg=200·6. At. No. 80.

309 We do not find this metal mentioned either in the books of Moses or in the writings of the older Greek authors. Theophrastus (B.C. 300) speaks of liquid silver or *quicksilver* (χυτὸς ἄργυρος), and says that it is obtained by rubbing cinnabar with vinegar in a copper vessel. Dioscorides, in the first century, mentions this body as ὑδράργυρος (from ὕδωρ, water, and ἄργυρος, silver), and states that it is obtained by subliming cinnabar and charcoal in an iron pot, upon which a cover is luted. Pliny, who named the material thus obtained *hydrargyrum*, in contradistinction to the native mercury, to which he gave the name of *argentum vivum*, was acquainted with the fact that all solid bodies, with the exception of gold, floated on the surface of the liquid metal. Isidorus, in the beginning of the seventh century, was also acquainted with the properties of mercury, as is seen from the following extract: "Argentum vivum servatur melius in vitreis vasis, nam cacteras materias perforat."

Mercury was known to the older alchemists, who were much interested in the examination of its properties, inasmuch as they believed this body, or some substance closely resembling it, to be one of the component parts of all metals. They were acquainted with the method of purifying it by distillation, and

[1] *Zeit. anorg. Chem.*, 1905, **44**, 158.

[2] *J. Amer. Chem. Soc.*, 1906, **28**, 770.

[3] Lorimer and Smith, *Zeit. anorg. Chem.*, 1891, **1**, 364; Hardin, *J. Amer. Chem. Soc.*, 1896, **18**, 990.

[4] *J. Physical Chem.*, 1911, **15**, 155. See also Richards, *J. Amer. Chem. Soc.*, 1911, **33**, 888.

[5] *J. Amer. Chem. Soc.*, 1915, **37**, 113; but see Hulett and Quinn, *ibid.*, 2046.

they knew how to prepare many of its compounds. During the epoch of iatro-chemistry, the properties of the mercury compounds were more minutely examined, especially with regard to their medicinal effects. Agricola regarded mercury as a metal, but Libavius placed it amongst those " quæ metallis sunt affinia," thus connecting it with bismuth, arsenic, galena, cinnabar, and other bodies. Even at a later date many chemists held similar views; thus Brandt in 1735 spoke of it as a semi-

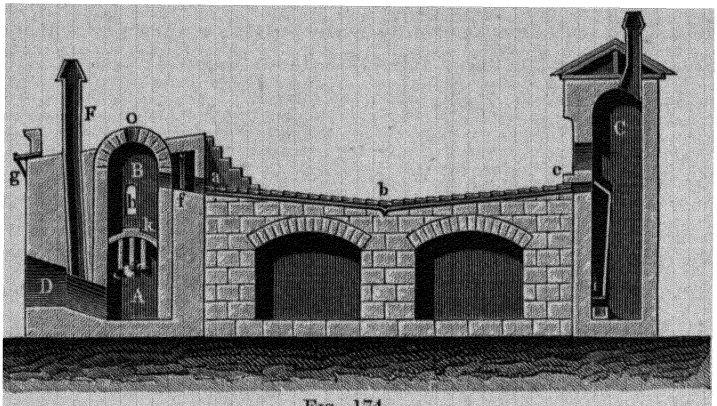


FIG. 174.

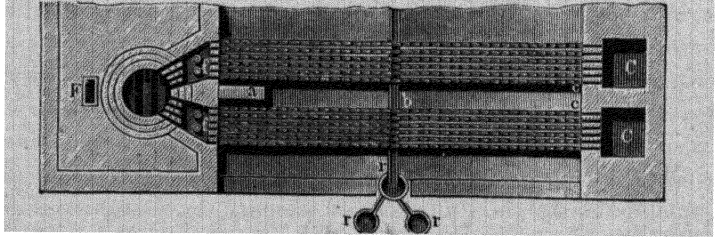


FIG. 175.

metal, and indeed it was not reckoned as a true metal until Braune, of St. Petersburg, in the winter of the year 1759, found that it solidified when exposed to a freezing mixture made of snow and nitric acid.

Mercury occurs in the native state, though in small quantity as compared with its other ores. It is found in globules disseminated through the native sulphide in the Palatinate, in Carniola, Hungary, Peru, California, Mexico, and other countries. It also occurs as silver- and gold-amalgam, as the iodide and chloride, and it is found occasionally in certain fahl-ores. The most important ore of mercury is the sulphide, or cinnabar.

The most celebrated mercury mines are found at Idria in Austria, Almaden in Spain, in California, especially the Pioneer Mine in Napa Valley, at Kweichow in China, Monte Amiata in Italy, in Texas and in Russia.

310 Most of the mercury of commerce is obtained by the treatment of cinnabar; and the chief method of extraction is roasting with an excess of air, by which means the sulphur is oxidised to sulphur dioxide, and the metallic mercury is driven off as vapour. This roasting process is carried out in shaft furnaces, reverberatory furnaces, or muffles, and the mercury vapour is condensed in earthenware pipes, water-cooled chambers of iron, or air-cooled chambers made of brick or wood and glass. A certain quantity of the mercury always condenses as a mercurial soot, which has to be re-treated for the extraction of the metal.

Of the older processes, in which the loss of mercury was excessive, sometimes amounting to 50 per cent., only the aludel furnace, used at Almaden, has survived. This furnace is shown

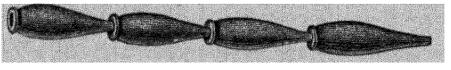


FIG. 176.

in Fig. 174, and consists of a shaft B, containing a perforated arch *k*, beneath which is the fireplace A. The air necessary for oxidation enters at the fire-door D. The mercurial vapours pass through a series of six openings *f*, into tubes made of earthenware, called aludels. These are open at both ends, and fit into one another in a similar way to the condensers employed in the manufacture of iodine. The aludels are arranged one behind the other, first in a descending, and then in an ascending position on arches of masonry (Figs. 174 and 175); the greater part of the mercury condenses in and runs from the aludels *a* (Fig. 175) into the channel *b*, and then into the cisterns *r r*. The shape and arrangement of the aludels is shown in Fig. 176. A small quantity of mercury vapour passes on into the chamber C, where it condenses, coming in contact with water contained in the vessel *i*.

The mercury thus obtained is filtered through linen, and exported, generally in iron bottles, but sometimes in leather bags.

For the treatment of finely divided ores the Granzita furnace,[1]

[1] *Eng. Min. Journ.*, 1885, 174.

Fig. 177, consisting of four shafts, with one fireplace (J) common to all, is used.

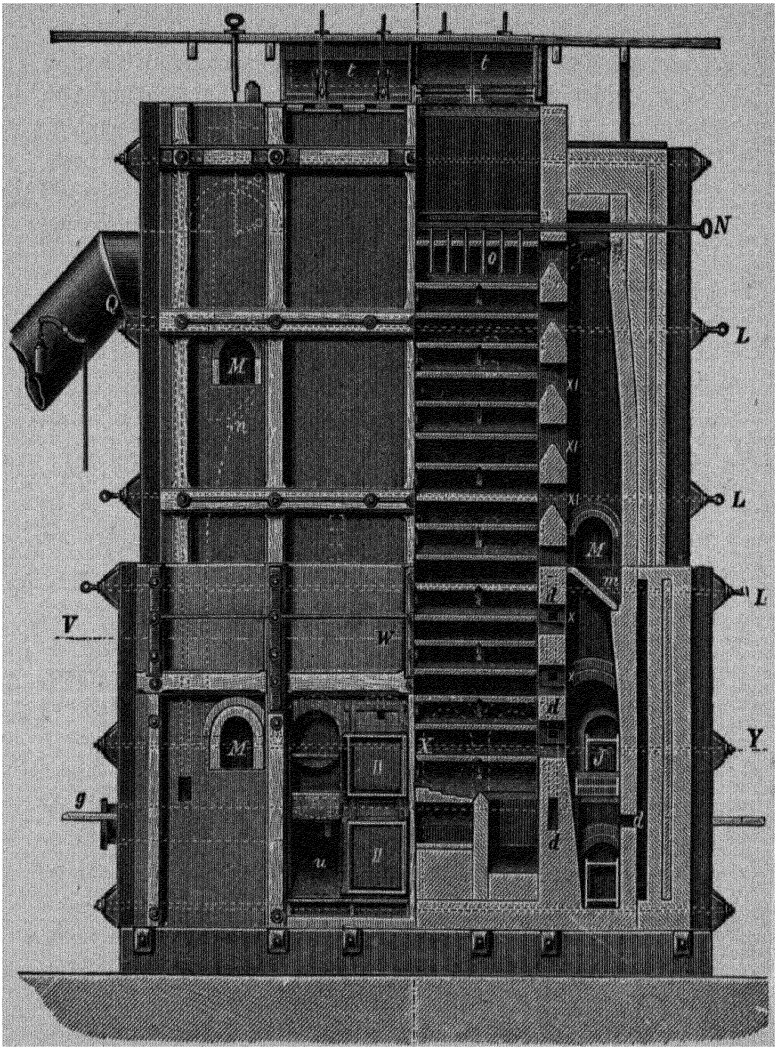


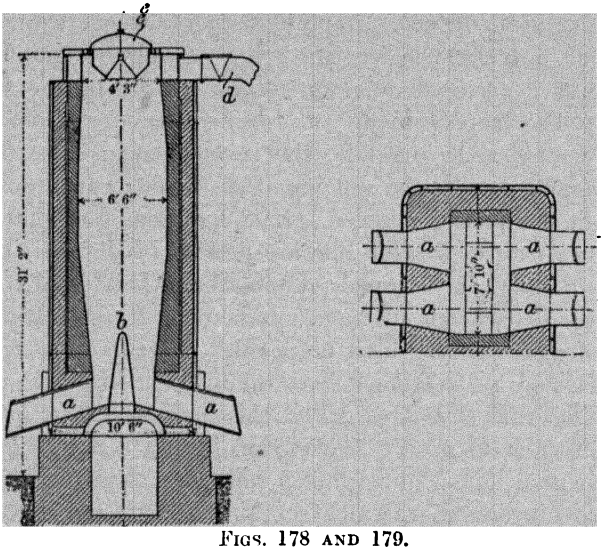
FIG. 177.

The shafts contain a number of inclined shelves, sloping at an angle of 45° in alternately opposite directions, to prevent the free fall of the ore. The flames from the fire, together with air, pass in the opposite direction to the ore and heat the shelves.

The distillation residues are removed from the furnace by means of eight openings (*u*) near the bottom, one ton being removed every 40 minutes, and a corresponding amount of fresh ore charged at the same time, by means of the hoppers (*t t*).

The mercurial vapours are condensed by passing through brick chambers, cooled by means of cast-iron water-backs let into the sides; these are followed by towers built of glass and wood, and from these the gases escape into a brick tower and are finally forced into a stack by means of a fan.

For the treatment of lump ore, true shaft furnaces, worked



FIGS. 178 AND 179.

continuously, are now largely used, in which the ore and fuel come into direct contact. One of the best examples of these modern furnaces is the Novak, shown in Figs. 178, 179, in which *a* are the openings for drawing out the residues, *b* is a ridge on the bottom, containing numerous holes, through which air passes into the furnace, *c* is the charging hopper, and *d* the pipe through which the gases and vapours escape. Charcoal is the fuel generally used, and is mixed with the ore before charging. The condensers usually employed consist of Y-shaped tubes of earthenware, cooled with water.

The following table shows the world's production of mercury in metric tons during the year 1919.[1]

[1] *Imperial Mineral Resources Bureau, Statistical Summary*, 1921.

Austria	980
Hungary	104
Italy	931
Spain	1351
Mexico	131
China	88
United States	800

311 The mercury of commerce usually contains a certain proportion of dissolved foreign metals, and these impurities give rise to the " tail " seen when the metal is allowed to run over a slightly inclined surface. Impure mercury, when shaken with air, yields a black powder consisting of minute globules of mercury each enclosed in a film of the oxides of the foreign metals. The surest mode of freeing mercury from these foreign metals is to distil it, the surface being covered with iron filings to prevent the spitting of the metal, which, however, cannot be completely avoided. It is a curious fact that when small quantities of lead or zinc are present in the mercury the rate of distillation is much diminished. The distillation is frequently carried out in vacuo, numerous forms of apparatus for this purpose having been proposed.[1] Mercury may be more easily purified by treating it with dilute nitric acid, the impurities being thus dissolved. For this purpose[2] the metal is allowed to flow in a very thin stream from a capillary opening in a drawn-out glass funnel into a wide glass tube 1·25 m. high and 5 cm. in diameter, which contains 5 per cent, nitric acid. A narrow tube is fastened to the bottom of this and bent upwards and then at right angles, from which the pure metal flows. The above operations may have to be repeated several times, and the metal, if pure, must leave no residue when dissolved in pure nitric acid, evaporated to dryness, and ignited. It may also be purified by being placed in a long, slightly inclined tube, through which air is drawn for several days, whereby the impurities are oxidised, and separate as a scum on the surface, or by drawing a rapid stream of air through mercury placed in a filter-flask and covered by a layer of 5 per cent. nitric acid.

Pure mercury possesses a silver-white colour. It is liquid at ordinary temperatures, and the globules retain a perfectly

[1] See Hulett, *Zeit. physikal. Chem.*, 1900, **33**, 611.
[2] L. Meyer, *Zeit. anal. Chem.*, 1863, **2**, 241.

spherical shape. The freezing point of mercury was first determined by Hutchins in 1783, at Fort Albany, in Hudson's Bay Territory, according to instructions received from Cavendish;[1] its melting point is —38·85°. In the act of freezing, mercury contracts considerably, giving rise to a solid, tin-white, ductile malleable mass, crystallising in octahedra, capable of being cut with a knife, and having a specific gravity of 14·1932 at its freezing point,[2] and of 14·383 at —188° (Dewar).

The liquid metal is transparent when in very thin films, and transmits violet-blue light (Melsens). When a powerful stream of water is poured from a height of a decimetre on a mass of from 15 to 20 kilos. of mercury, bubbles of the metal, of about 1 cm. in diameter, are seen swimming on the surface of the water. These consist of very thin films of mercury through which blue light is transmitted: they soon burst and leave behind a very small globule of the metal.

The specific gravity of mercury at 0°/4° is 13·59545,[3] at 100° 13·3522, and at 360° 12·7405.[4] The boiling point of mercury, according to Regnault's observations, is 357·25°. Baker[5] has shown that if the metal is dried for nine years over phosphorus pentoxide the boiling point is raised to 425°. The metal gives a colourless vapour, which has a specific gravity, according to the experiments of Dumas, of 6·976, or according to those of Bineau, of 6·7: the molecule of mercury in the gaseous condition is, therefore, like those of zinc and cadmium, monatomic. The critical temperature of mercury lies between 1500° and 1650°.[6] In spite of its high boiling point, mercury volatilises perceptibly at the ordinary temperature, both in a vacuum and in air, as proved by the "silvering" of gold-leaf kept for two months in a vessel over mercury (Faraday); and Merget has shown that even at — 44°, when mercury is solid, it still possesses a distinct vapour pressure. The vapour pressure of mercury, as determined by Ramsay and Young,[7] is given in the following table, the numbers below 220° being calculated by extrapolation:

[1] *Phil. Trans.*, 1783, **73**, 303. Consult Blagden, "History of the Congelation of Quicksilver," *ibid.*, 329.

[2] Mallet, *Proc. Roy. Soc.*, 1877, **26**, 77.

[3] Thiesen and Scheel, *Zeit. Instrumentenkunde*, 1898, **18**, 138.

[4] Landolt-Bornstein-Roth, *Physikalisch-Chemische Tabellen.*

[5] *Journ. Chem. Soc.*, 1922, **121**, 568.

[6] Bonomarov, *Zeit. anorg. Chem.*, 1914, **89**, 383.

[7] *Journ. Chem. Soc.*, 1886, **49**, 37. See also Herz, *Ann. Phys. Chem.*, 1882, **17**, 193; Morley, *Zeit. physikal. Chem.*, 1904, **49**, 95.

Temperature. C.	Pressure in mm.	Temperature. C.	Pressure in mm.
40° . . .	0·008	240° . . .	56·92
80 . . .	0·092	260 . . .	96·66
100 . . .	0·270	280 . . .	157·35
120 . . .	0·719	300 . . .	246·81
140 . . .	1·763	320 . . .	373·67
160 . . .	4·013	340 . . .	548·64
180 . . .	8·535	360 . . .	784·31
200 . . .	17·015	400 . . .	1495·60
220 . . .	31·957	450 . . .	2996·06

The vapour pressure at 0° C. probably does not exceed 0·0002 mm.

When mercury is contaminated with oxide or its halogen derivatives it adheres to glass, forming a bright mirror (Shenstone). When shaken with various liquids, or when triturated with sugar, sulphur, or other bodies, the liquid metal is obtained in a very finely divided state, being converted into a grey powder. This was formerly termed *Aethiops per se.* This act of fine division is termed the " extinction " or " deadening " of mercury. Grey mercurial ointment is formed by rubbing up mercury and fat together, and in this preparation the mercury is in the form of globules having a diameter of 0·002 to 0·004 mm. Mercury is not attacked by dilute hydrochloric or sulphuric acid, but is readily dissolved by nitric acid and by hot concentrated sulphuric acid. It is readily attacked by dry chlorine, bromine, or iodine.[1]

Mercury has been obtained in the colloidal form by the reduction of mercurous nitrate by stannous nitrate in the presence of ammonium citrate, as a black precipitate which forms a deep brown solution in water.[2]

Mercury is largely used in connection with the manufacture of physical and chemical apparatus, for collecting gases which are soluble in water, for the preparation of mirrors, for the amalgamation and extraction of silver and gold, for the preparation of the mercurial compounds, and in the electrolytic production of caustic soda.

Alloys of Mercury or Amalgams.

312 The general properties of these alloys have already been given on p. 97 of this volume.

[1] Shenstone, *Journ. Chem. Soc.*, 1897, **71**, 483.
[2] Lottermoser, *J. pr. Chem.*, 1898, [2], **57**, 484.

Sodium Amalgam.—Sodium combines violently with mercury, evolving light and emitting a hissing noise. One part of sodium in 100 parts of mercury forms an amalgam having an oily consistency, but with 80 of mercury to 1 of sodium a pasty mass is obtained, and with smaller quantities of mercury a hard and crystalline amalgam is formed.

The existence of many compounds of sodium and mercury has been deduced from the freezing-point curve of these two elements, and some of these have been separated and analysed (p. 98). The compound of highest melting point has the formula $NaHg_2$, and melts at 360°, the melting point being lowered by the addition of either mercury or sodium.[1]

The amalgams of the alkali metals decompose slowly on exposure to moist air and water, and amalgamate iron and platinum. Sodium amalgam is sometimes employed in the processes of extracting silver and gold, and frequently in organic chemistry as a reducing agent.

Potassium Amalgam.—Potassium combines with mercury with evolution of heat but without incandescence, forming a silver-white compound, which is liquid when it contains one part of potassium to about seventy parts of mercury, but becomes solid when it contains more potassium. The existence of several compounds of potassium and mercury has been deduced from the thermal diagram of these elements and some of these have been separated and analysed (p. 98). The compound KHg_2, which melts at 269·8°, is the amalgam of highest melting point formed by these two elements.[2]

Ammonium Amalgam.—This compound, discovered at the same time by Berzelius and Pontin,[3] and by Seebeck,[4] has already been described (p. 391).

The *Amalgams of the Alkaline Earth Metals* are easily formed by direct union of the elements, and have also been prepared by the electrolytic method (p. 98).

Magnesium Amalgam may be prepared by heating the two elements together. It decomposes water very energetically, and has been employed as a reducing agent in organic chemistry.

Copper Amalgam.—If copper foil is rubbed with a solution of nitrate of mercury it becomes covered with a bright, lustrous

[1] See Kurnakoff, *Zeit. anorg. Chem.*, 1900, **23**, 439; Kerp and Böttger, *ibid.*, 1900, **25**, 1; Schüller, *ibid.*, 1904, **40**, 385.

[2] Jänecke, *Zeit. physikal. Chem.*, 1907, **58**, 245.

[3] *Gilbert's Ann.*, **6**, 260. [4] Gehlen, *Neu. Allg. Journ. Chem.*, **5**, 482.

coating of the metal, and if a line be drawn with this solution on a piece of brass foil and the foil bent at this place, it can easily be broken, as the mercury very soon penetrates the metal and renders it brittle. Copper amalgam is obtained by rubbing a copper rod with the nitrate solution, and then allowing it to remain in contact with mercury under warm water. All the copper amalgams which contain from 25 to 33 per cent. of copper, when heated to 100°, become plastic when rubbed in a mortar. After from ten to twelve hours the amalgam loses its plasticity and assumes a granular, crystalline structure, and is hard enough to engrave upon tin. Its density is the same in the soft and hard states and, therefore, it does not expand or contract in hardening, and thus, when hard, fills cavities into which it has been pressed in the soft state. This amalgam is used for stopping teeth, but the copper which it contains renders it objectionable on account of its tendency to blacken. It is also used for sealing bottles, glass tubes, etc., when other plastic substances, such as cork, cannot be used, as well as for taking impressions of engraved metal work.

Silver Amalgam occurs as a mineral at Moschellandsberg, in the Palatinate, and crystallises in the regular system. It is artificially prepared as the silver tree (*arbor Dianæ*) by pouring mercury into a solution of silver nitrate. The composition of the product thus deposited as well as that of the natural amalgam varies considerably (p. 98).

COMPOUNDS OF MERCURY.

313 Mercury forms two chief series of compounds, the mercuric compounds, in which the metal is divalent, and the mercurous compounds, in which each atom of the metal replaces only one of hydrogen.

The *mercuric compounds* are obtained in many cases by the action of an excess of acid on metallic mercury. They are converted by reducing agents into mercurous salts, which are further reduced to metallic mercury in presence of an excess of the reducing agent. The soluble salts have a metallic taste, redden blue litmus, and are extremely poisonous.

The molecular weights of several of these salts have been determined by the vapour density method, and by the cryoscopic and ebullioscopic methods, and have been found to be normal, corresponding with the general formula $Hg_2X^I_2$.

Mercurous compounds are formed by the action of mercury or some other reducing agent on mercuric compounds, as well as in some cases by the action of acids on excess of mercury. They very readily dissociate in solution into metallic mercury and a mercuric compound,[1] this reaction being a reversible one and leading to a state of equilibrium between the mercurous and mercuric ions present. Thus, when excess of mercury is shaken with a faintly acid solution of mercuric nitrate at 25°, about 1/240 of the mercury in solution is finally present as mercuric salt and the remainder as mercurous salt, these two salts being about equally dissociated.[2]

The halogen derivatives with the exception of the fluoride are insoluble in water; the salts with oxy-acids dissolve only in presence of free acid, pure water converting them into soluble acid salts and insoluble basic salts. They have a metallic taste, and are poisonous, although less so than the mercuric salts.

The true molecular formula of the mercurous compounds has been the subject of much discussion, some authorities maintaining that these compounds have the general formula HgX^I, and others supporting the double formula, $Hg_2X^I_2$. In the former case mercury in these compounds must be supposed to act as a monad, in the latter it may be present as a dyad, as shown in the constitutional formula $X^I{\cdot}Hg{\cdot}Hg{\cdot}X^I$. The vapour density of mercurous chloride corresponds with the formula HgCl, but it has been shown by Harris and V. Meyer [3] that the vapour is a mixture of mercury and mercuric chloride, formed by dissociation from the mercurous chloride. If the vapour of calomel be passed through a porous tube, the mercury diffuses through the latter and condenses in globules, whilst the portion which finally condenses inside the tube contains an excess of mercuric chloride. Further, if solid potash be placed in the vapour, it is immediately coated with yellow mercuric oxide, and does not show even a momentary formation of the dark mercurous oxide. The vapour density, therefore, cannot be taken as a proof of the molecular formula HgCl.

Baker [4] has, however, found that very carefully dried mercurous

[1] Hada, *Journ. Chem. Soc.*, 1896, **69**, 1667.

[2] Abel, *Zeit. anorg. Chem.*, 1891, **26**, 361.

[3] *Ber.*, 1894, **27**, 1482; 1895, **28**, 364. See also Smith and Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 1541.

[4] *Journ. Chem. Soc.*, 1900, **77**, 646.

chloride volatilises without dissociation, yielding a vapour the density of which corresponds with the formula Hg_2Cl_2.

Beckmann,[1] by cryoscopic measurements, has shown that mercurous chloride, dissolved in fused mercuric chloride, has the formula Hg_2Cl_2.

The view that the mercurous compounds contain two atoms of divalent mercury in the molecule is also confirmed by the work of Ogg,[2] who has shown by a study of the equilibrium between mercury, mercurous nitrate, and silver nitrate, and from various properties of solutions of mercurous nitrate, that this salt in solution yields the divalent ion $\dot{H}g$–$\dot{H}g$, and therefore probably has the formula $Hg_2(NO_3)_2$.

Mercury and Oxygen.

314 These elements form three compounds:

Mercurous oxide, Hg_2O.
Mercuric oxide, HgO.
Mercury peroxide, HgO_2.

Mercurous Oxide, Hg_2O.—This compound, also called sub-oxide or grey oxide of mercury, is easily obtained by the action of caustic alkalis in excess on a mercurous salt. It is a blackish-brown powder, which by the action of light and a moderate temperature, as well as when brought in contact with different saline solutions, is decomposed into the metal and the monoxide; at 100° it unites with oxygen.[3] It corresponds with the series of *mercurous* salts.

Mercuric Oxide or *Mercury Monoxide*, HgO; commonly termed *Red Oxide of Mercury*, or *Red Precipitate*.—This compound was known to the Latin Geber, who obtained it by heating mercury in the air for a long time. It was afterwards known by the name of *mercurius præcipitatus per se*. The same compound is formed when a solution of mercury in nitric acid is evaporated, and the residue heated; the compound thus prepared was called by Raymond Lully *mercurius præcipitatus ruber*.

When mercury is exposed in a glass flask with a long neck for several weeks to a temperature somewhat below its boiling point, small red crystals of the oxide appear on the surface, and

[1] *Zeit. anorg. Chem.*, 1907, **55**, 175.
[2] *Zeit. physikal. Chem.*, 1898, **27**, 285.
[3] Colson, *Compt. rend.*, 1899, **128**, 1104.

this product, which has a dark-red colour and is highly crystalline, increases gradually in quantity. Mercuric oxide is prepared on the large scale by heating an intimate mixture of mercury and mercuric nitrate until no further red fumes are given off: in this way it is obtained in the form of bright brick-red, crystalline tablets, which have a specific gravity at 4° of 11·136 (Joule and Playfair).

When a solution of a mercuric salt is precipitated by caustic potash or soda, a yellow precipitate is obtained which, when dried in the air, consists of microscopic square tablets of the anhydrous oxide. The loss of weight at 175°, which led to the conclusion that this substance was a hydroxide,[1] is in reality due to partial decomposition of the oxide.[2] The yellow and red oxides are regarded by many chemists as differing only in the size of their particles,[3] but according to Schoch they possess different crystalline forms, and the dissociation pressure of the yellow oxide at 300° is considerably greater than that of the red oxide. When heated at 250—600° it is converted into the red oxide with simultaneous partial decomposition into mercury and oxygen. The yellow oxide has been employed as a standard in acidimetry,[4] as by treatment with potassium iodide it yields an equivalent quantity of pure potassium hydroxide.

Mercuric oxide is a powerful poison, it possesses an unpleasant metallic taste and an alkaline reaction, and is slightly soluble in water. When heated it first changes to a dark cinnabar-red colour, and afterwards assumes a black tint, but on cooling it resumes its original appearance. At a red heat it decomposes into its elementary constituents, and on cooling these partially recombine.

When the oxide is heated with sulphur explosions occur, and it is also decomposed when brought in contact with fused sodium, with evolution of light and heat.

Mercuric oxide is used in medicine, and is valuable for various purposes in chemical analysis.

Mercury peroxide, HgO_2, is prepared in small quantities by the catalytic decomposition of hydrogen peroxide by means of

[1] Carnelley and Walker, *Journ. Chem. Soc.*, 1888, **53**, 80.

[2] Schoch, *Amer. Chem. J.*, 1903, **29**, 319.

[3] Ostwald and Mark, *Zeit. physikal. Chem.*, 1895, **18**, 159; Ostwald, *ibid.*, 1900, **34**, 495; Koster and Stork, *Rec. trav. chim.*, 1901, ii., **20**, 394; Schick, *Zeit. physikal. Chem.*, 1902, **42**, 155. See also Cohen, *Proc. K. Akad. Wetensch. Amsterdam*, 1899, **2**, 273, 458.

[4] Incze, *Zeit. anal. chem.*, 1917, **56**, 177.

mercury;[1] it may be prepared also by the interaction of alcoholic mercuric chloride, hydrogen peroxide, and alcoholic potash.[2] The anhydrous peroxide is an amorphous, brick-red powder which is fairly stable in air. It is slowly decomposed by water.

Mercurous Salts.

315 *Mercurous Fluoride*, Hg_2F_2, is produced by the action of hydrofluoric acid on mercurous carbonate, or of silver fluoride on calomel.[3] It is a yellow, crystalline salt, blackened by light, and soluble in water.

Mercurous Chloride, Hg_2Cl_2, is commonly known as *calomel*. Calomel occurs as a mineral termed horn-quicksilver, found at Moschellandsberg, Idria, Almaden, and other places, crystallising in rhombic prisms. The artificial substance has been known for a long time, and it appears to have been used in the sixteenth century as a medicine, known by the name of *Draco mitigatus*, *Manna metallorum*, *Aquila alba*, or *Mercurius dulcis*. It afterwards received the name calomel, which it now bears, from καλομέλας, a fine black colour, because it turns black when acted upon by an alkali.

Mercurous chloride is formed by the direct union of its elements, and also by the action of hydrochloric acid or common salt solution on a dilute solution of mercurous nitrate. In order to prevent a basic nitrate being carried down with the insoluble chloride, an excess of hydrochloric acid or salt solution must be added, and the liquid must be warmed with the precipitate for some time. In this way it is obtained in the form of a yellowish-white, impalpable powder.

Calomel is commonly prepared by sublimation. For this purpose an intimate mixture of mercuric chloride (corrosive sublimate) and mercury in the right proportions is heated. Another, and now nearly obsolete process, is to rub up dry mercuric sulphate in a mortar with as much mercury as it already contains, and an equal quantity of common salt, until the globules disappear and a uniform mixture is produced. This is then sublimed, the vapour of calomel being carried into an atmosphere of steam or into a chamber containing air, where it is condensed in a finely-divided form; thus the

[1] Antropoff, *Zeit. Elektrochem.*, 1906, **12**, 585.
[2] Pellini, *Atti R. Accad. Lincei*, 1907, [v], **16**, ii., 408.
[3] Finkener, *Pogg. Ann.*, 1860, **110**, 142.

labour of powdering it is avoided. The following decomposition occurs :

$$HgSO_4 + Hg + 2NaCl = Hg_2Cl_2 + Na_2SO_4.$$

The sublimed powder thus obtained is well washed to free it from any traces of corrosive sublimate which it may contain, and dried ready for use. When dissolved in hot mercurous nitrate solution and allowed to cool, it separates out in yellowish-white, tetragonal plates.

Calomel has long been known and manufactured in China and Japan under the name of *keifun* (light powder). This product occurs as a light, bulky powder, consisting of very thin, minute scales, lustrous, transparent, and white or faintly cream-coloured. It is quite free from corrosive sublimate and is manufactured by heating balls of porous earth and salt, soaked in bittern (the mother-liquor of partially evaporated sea-water), along with mercury in iron pots lined with earth. The heat forms hydrochloric acid from the magnesium chloride in the bittern, the mercury sublimes into the clay covers of the pots, air enters by diffusion, and the following reaction occurs :

$$4Hg + 4HCl + O_2 = 2Hg_2Cl_2 + 2H_2O.$$

The cover thus becomes filled with a network of micaceous particles of calomel.[1]

Calomel is tasteless, and has a specific gravity of 6·56. It evaporates at a red heat without fusion, yielding a colourless vapour of specific gravity 8·21 (Deville and Troost). As already explained (p. 701), this vapour is a mixture of the vapours of mercury and mercuric chloride.

Calomel is also formed by the action of many reducing agents on solutions of mercuric chloride. It is partially decomposed by the action of concentrated solutions of chlorides, mercuric chloride passing into solution and mercury remaining undissolved.[2] The solubility of calomel [3] in water, as determined by the conductivity method, is about 0·4 mgrm. per litre at 20°.

Calomel is largely employed in medicine, the precipitated compound being more active in its medicinal properties than that prepared by sublimation, owing to its finer state of division. In certain cases abnormal poisonous effects have been produced

[1] Divers, *J. Soc. Chem. Ind.*, 1894, **13**, 108.
[2] Richards and Archibald, *Zeit. physikal. Chem.*, 1902, **40**, 385.
[3] Ley and Heimbucher, *Zeit. Elektrochem.*, 1904, **10**, 301.

by calomel, which have probably been caused by the presence of basic mercurous nitrate.

Mercurous Bromide, Hg_2Br_2, is obtained as a heavy, white precipitate by adding hydrobromic acid or potassium bromide to mercurous nitrate solution. It is obtained in white, nacreous, tetragonal plates of sp. gr. 7·037 by shaking a solution of mercurous nitrate with bromine water or an alcoholic solution of bromine. It sublimes at 340—350° without decomposition,[1] and slowly decomposes in the light. It is only sparingly soluble in water.

Mercurous Iodide, Hg_2I_2, is prepared by rubbing mercury with mercuric iodide or iodine in the requisite proportions, and then forms a greenish-coloured powder, which, however, is not pure. If an excess of iodine is boiled with a solution of mercurous nitrate containing a little nitric acid, mercurous iodide separates on cooling in transparent, yellow, tetragonal plates, which gradually blacken in the light. On heating, the colour changes successively to dark yellow, orange, and garnet-red, and on cooling the same colours are observed in the reverse order; it commences to sublime at 110—120°, and melts and decomposes at 290°.[2] It is partially decomposed by heat and by treatment with potassium iodide solution into mercury and mercuric iodide.[3] It dissolves slightly in oils, the best solvent being castor oil, which dissolves 2 per cent. In the form of powder it is used in medicine.

Mercurous Sulphide does not exist, a mixture of metallic mercury and mercuric sulphide being produced in cases in which its formation might be expected.

Mercurous Sulphate, Hg_2SO_4, is formed by heating concentrated or fuming sulphuric acid with an excess of mercury, or by precipitating mercurous nitrate with sulphuric acid, or by the electrolysis of sulphuric acid with a mercury anode.[4] It is a white, crystalline powder which when gently heated melts, and on cooling solidifies to a crystalline mass. It is precipitated almost completely by sulphuric acid from its solution in nitric acid. It is easily soluble in hot sulphuric acid; part of it separates out on cooling, and the remainder is precipitated on the addition of water. When heated with water at 25° it first

[1] Stroman, *Ber.*, 1887, **20**, 2822. [2] *Ibid*, 2818.

[3] François, *J. Pharm.*, 1899, [6], **10**, 16; *Compt. rend.*, 1895, **121**, 888; 1896, **122**, 190.

[4] Hulett, *Zeit. physikal. Chem.*, 1904, **49**, 494.

yields the basic salt, Hg_2SO_4,Hg_2O,H_2O, as a white powder, and with a larger amount of water is converted into the oxide (Cox).

Mercurous Nitrite, $Hg_2(NO_2)_2$, is the first product of the action of nitric acid on mercury, and may be prepared by the action of dilute nitric acid on excess of mercury. It forms yellow needles and is partially decomposed by water, forming mercury and mercuric nitrite, whilst part dissolves. It is slowly converted by dilute nitric acid into mercurous nitrate, or one of the basic salts derived from it.[1] The pure salt has a sp. gr. of 5·925.[2] When heated it decomposes, yielding nitric oxide, mercurous nitrate, mercury, and mercuric oxide.[3]

Mercurous Nitrate, $Hg_2(NO_3)_2$, is formed by the action of dilute nitric acid in the cold on mercury. Hot nitric acid, on the other hand, especially if an excess of acid be employed, forms mercuric nitrate. Bergman was the first to point out the difference between the two solutions thus obtained, the explanation, according to the then prevalent views, being that the solution of the metal in cold nitric acid contained less phlogiston than that in the hot acid. At a later period the same fact was explained by stating that in the former the mercury was less strongly oxidised than in the latter case.

Mercurous nitrate crystallises in monoclinic tablets or prisms of the formula $Hg_2(NO_3)_2,2H_2O$, which lose their water on exposure to dry air. The crystals melt at 70°, forming a clear liquid of sp. gr. 4·3.[4] The pure salt is at once decomposed by water (Hada), leaving a basic nitrate. It is easily soluble in dilute nitric acid, and this solution brought on to the skin colours it, first purple, and then a black tint.

A number of different basic nitrates are formed by the action of water on the nitrate under varying conditions of temperature, concentration, and acidity. Among those described[5] are $3Hg_2(NO_3)_2,Hg_2O,H_2O$, crystallising in long, thin prisms; $3Hg_2(NO_3)_2,2Hg_2O,2H_2O$, forming a white powder or hard, lustrous, triclinic prisms; $Hg_2(NO_3)_2,Hg_2O,H_2O$, a yellowish, crystalline mass; and $Hg_2(NO_3)_2,2Hg_2O,2H_2O$, a yellowish-green powder. As already mentioned (p. 702), mercurous nitrate in

[1] Rây, *Zeit. anorg. Chem.*, 1896, **12**, 365; *Journ. Chem. Soc*, 1897, **71**, 337.
[2] Rây, *Journ. Chem. Soc.*, 1908, **93**, 999.
[3] Rây and Sen, *Journ. Chem. Soc.*, 1903, **83**, 491.
[4] Retgers, *Jahrb. Min.*, 1896, II., 183.
[5] See Cox, *Zeit. anorg. Chem.*, 1904, **40**, 174.

solution dissociates partially into mercury and mercuric nitrate. When the salt is boiled with water, mercury slowly volatilises, and may be condensed in globules.[1]

Mercurous Carbonate, Hg_2CO_3, is obtained by precipitating the nitrate with potassium hydrogen carbonate. In order to remove a quantity of basic nitrate which is thrown down at the same time, the potassium carbonate is added in excess, and the solution is allowed to stand for some days. Mercurous carbonate is a yellow powder which decomposes at 130° into carbon dioxide, mercury, and mercuric oxide, and blackens on exposure to light (Lefort).

Mercuric Salts.

316 *Mercuric Fluoride*, $HgF_2,2H_2O$, is formed by the action of excess of hydrofluoric acid upon the oxide.[2] It is a white, crystalline mass which decomposes at 50°, with formation of the yellow *oxyfluoride*, HgF(OH), which is also obtained when an excess of mercuric oxide is treated with hydrofluoric acid. On slow evaporation it separates in dark yellow crystals. The fluoride is largely hydrolysed in aqueous solution, and is completely decomposed into oxide and hydrofluoric acid by a large amount of water at 25°, no basic salt being formed.[3]

Anhydrous mercuric fluoride, HgF_2, is obtained by heating mercurous fluoride in dry chlorine at 275° or dry bromine at 400° or by heating mercurous fluoride alone at 450° under 10 mm. pressure. It forms transparent octahedra, melting at 645° and boiling about 650°, is readily attacked and discoloured by traces of moisture, and attacks glass when vaporised in contact with it.[4]

Mercuric Chlorofluoride, HgClF, and *mercuric bromofluoride*, HgBrF, are obtained as pale yellow powders by the action of chlorine or bromine on mercurous fluoride at 100—120°.[4]

Mercuric Chloride, $HgCl_2$.—This salt is obtained when mercury is heated in chlorine. It was first obtained by the Latin Geber according to the following receipt: "Sublime *Argentvive* thus: Rc. of it *lib. j.* of *vitriol* rubified, *lib. ij.* of *rock-allum* calcined, *lib. j.* of *common salt*, *lib. semis.* and of *salt-petre* one fourth part. Incorporate all together, and sublime: and gather the *white*, *dense*, and *ponderous*, which shall be found about the *sides* of

[1] Hada, *Journ. Chem. Soc.*, 1896, **69**, 1667.
[2] Finkener, *Pogg. Ann.*, 1860, **110**, 628.
[3] Jaeger, *Zeit. anorg. Chem.*, 1901, **27**, 22; Cox, *ibid.*, 1904, **40**, 146.
[4] Ruff and Bahlau, *Ber.*, 1918, **51**, 1752.

the *vessel*, and keep it, as we have appointed of other things. But if, in the first *sublimation*, you shall find it turbid, or unclean (which may happen, by reason of your own negligence), again sublime it with the same *feces*, and reserve it for use." At a later date a somewhat similar method of preparation was employed on a large scale, and the product was termed *Corrosive sublimate* or *Mercurius sublimatus corrosivus*. For this purpose an intimate mixture of 3 parts of mercury, 2 of common salt, 2 of saltpetre, and 4 of calcined ferrous sulphate was heated:

$$Hg + 2NaCl + 2KNO_3 + Fe_2S_2O_9 = HgCl_2 + Na_2SO_4 + K_2SO_4 + Fe_2O_3 + 2NO_2.$$

The nitrogen peroxide which was given off was condensed in water, and the acid obtained was employed for the preparation of mercuric oxide. At the end of the sixteenth century, corrosive sublimate was a well-known commercial article. In the works of the so-called Basil Valentine the following statement occurs. He says: "Recipe mercurii sublimati, such as can be bought at the druggists, and has been sublimed with vitriol and salt; for the ☿ takes up in the sublimation the quintam essentiam salis. Then rub down the mercurium sublimatum very finely, lay it in the cellar in a thin layer on an iron plate, let it lie for some days and nights, when a fluid will be seen to flow from it, and the ☿ is revivified."

From its strongly corrosive properties, mercuric chloride was also termed *Draco*, and as it was capable of destroying the metallic lustre of several metals, it was called *mors* or *malleus metallorum*. The process which is now employed for the manufacture of corrosive sublimate, namely, that of subliming a mixture of mercuric sulphate and common salt, was first suggested by Kunkel, who in the year 1760 described this process in his *Laboratorium Chymicum* as follows: "The best *mercurius sublimatus* for use in chemistry and such as pleases me, is when I take an oleum vitrioli, which has been highly freed from all its phlegm, with merc. viv. ana, or if it has not been rectified so well, merc. one part and oleum one and a half parts, and distil off so much oleum until all the merc. is coagulated. The white Praecipitat sublimed with Sal communis ana gives a fine corrosive sublimate."

Mercuric chloride is obtained commercially by heating a mixture of equal parts of dry common salt and mercuric sulphate. As the latter salt can only with difficulty be got

free from mercurous salt, one-tenth of its weight of manganese dioxide is added to the mixture in order to prevent formation of calomel. The sublimation is carried on in large, flat, long-necked glass balloons, which are first placed in a sand-bath up to their necks, and gently heated in order to drive off all moisture. So much of the sand is then removed that only the lower half of the balloon is surrounded by sand, and then this is heated more strongly until the whole of the chloride is sublimed. On cooling, the balloon is broken and the cake of sublimate removed.

Mercuric chloride crystallises in needles belonging to the rhombic system,[1] the commercial article usually having the form of a semi-transparent, crystalline crust. According to the experiments of Poggiale, 100 parts of water dissolve the following:

At	10°	20°	50°	80°	100°
$HgCl_2$	6·57	7·39	11·34	24·3	53·96.

Mercuric chloride dissolves in about three parts of alcohol, crystallising from the solution in colourless, triclinic needles, and in four parts of ether, so that when this liquid is shaken up with the aqueous solution, the greater part of the salt is removed from the water. It crystallises by sublimation in a second triclinic form.[2] Mercuric chloride undergoes electrolytic dissociation in aqueous solution only to a very slight degree,[3] but is partially hydrolysed, so that its solution has an acid reaction to litmus.[4] The aqueous solutions decompose very slowly in the dark to form mercuric oxide, chlorine, and hydrochloric acid, but in the light to form only mercurous chloride and hydrochloric acid.[5] It is precipitated from its aqueous solution by sulphuric acid,[6] but dissolves without decomposition in concentrated sulphuric and nitric acids. Its specific gravity is 5·403 (Karsten), it melts at 288° and boils at 303°, the specific gravity of its vapour being 9·8 (Mitscherlich), corresponding with the normal molecular weight. Corrosive sublimate possesses a sharp, metallic taste, and is a violent poison; it is largely used, both

[1] Mitscherlich, *Pogg. Ann.*, 1833, **28**, 118; Luczizky, *Zeit. Kryst. Min.*, 1909, **46**, 297.

[2] von Lang, *Wien. Akad. Ber.*, 1862, **45**, 119.

[3] Grotrian, *Ann. Phys. Chem.*, 1883, **18**, 177. See also Luther, *Zeit. physikal. Chem*, 1904, **47**, 107.

[4] See Ley, *Ber.*, 1897, **30**, 2192.

[5] Verda, *Schweiz. Woch. Chem. Pharm*, 1907, **45**, 179.

[6] Viard, *Compt. rend.*, 1902, **135**, 242.

externally and internally, in medicine, especially in cases of syphilis. It is also used as an anti-putrescent for anatomical preparations, in dressing furs and skin, and especially as a bactericide in surgery. The dry salt or its solution is easily reduced, first to calomel and finally to metallic mercury, by arsenic, tin, zinc, etc., or by stannous chloride, oxalic acid, etc.[1]

Mercuric chloride has the power of forming crystallisable compounds with a number of other chlorides, especially with those of the alkali metals, giving rise to the following double chlorides, as well as to many others:

$KCl,HgCl_2,H_2O$	$NaCl,HgCl_2,2H_2O$
$2KCl,HgCl_2,H_2O$	$NH_4Cl,HgCl_2$
$KCl,2HgCl_2,2H_2O$	$2NH_4Cl,HgCl_2,H_2O$
$2NaCl,HgCl_2$	$2NH_4Cl,3HgCl_2,4H_2O$.

The fact that these salts dissolve in water more easily than mercuric chloride has long been known. The iatro-chemists prepared one of them by dissolving equal parts of corrosive sublimate and sal-ammoniac, and crystallising the solution. It was termed by them *Alembroth*. In many cases[2] the solutions of these double salts contain complex ions, such as $HgCl_4$, etc.

Mercuric chloride also unites with hydrochloric acid[3] to form the compounds $HgCl_2,HCl$ and $2HgCl_2,HCl$, and with phosphorus pentachloride, forming the compound $3HgCl_2,2PCl_5$, which can be sublimed in glistening needles. Compounds with hydroxylamine, acetone, and methyl alcohol have also been described.

Mercuric chloride forms also a series of basic salts, or *oxychlorides*, which are obtained by the action of mercuric oxide on mercuric chloride solution, or by adding potassium hydrogen carbonate or marble[4] to the latter. The best defined of these are $2HgCl_2,HgO$, which crystallises in red, monoclinic needles; $HgCl_2,2HgO$, which is a pitch-black, crystalline precipitate; and $HgCl_2,3HgO$, which forms glistening, golden-yellow scales, and occurs as the mineral kleinite in Texas. In addition to these several other oxychlorides are known,[5] containing a larger amount of oxygen.

[1] Oechsner de Coninck and Dautry, *Bull. Acad. roy. Belg.*, 1908, 55.

[2] See Sherrill, *Zeit. physikal. Chem.*, 1903, **43**, 705.

[3] John Davy, *Phil. Trans.*, 1822, **112**, 357.

[4] Tarugi, *Gazz.*, 1901, **31**, ii., 313; Arotowski, *Zeit. anorg. Chem.*, 1898, **12**, 353.

[5] Sachs, *Sitzungsber. K. Akad. Wiss., Berlin*, 1905, 1091.

Mercuric Bromide, $HgBr_2$.—Mercury combines with bromine with evolution of heat,[1] and the oxide dissolves in hot aqueous hydrobromic acid. The bromide dissolves to the extent of 0·4 part in 100 parts of cold water, and crystallises from aqueous solutions in glistening scales, melting at 235°,[2] and from alcoholic solution in rhombic needles or prisms, which can easily be sublimed. It forms, with sodium bromide and chloride, the compounds $HgBr_2$,2NaBr and $HgBr_2$,2NaCl, which are extremely soluble in water.[3] It closely resembles the chloride and, like it, forms a number of oxy-salts.[4]

Mercuric Iodide, HgI_2, is formed when the two elementary constituents are rubbed together in the proper proportions in a mortar with a small quantity of alcohol. It forms a scarlet, crystalline powder. It is also precipitated when a solution of potassium iodide is added to one of corrosive sublimate. In this case, however, the precipitate which first forms has a pale yellow colour, but soon becomes scarlet; it is easily soluble in an excess of either liquid. Mercuric iodide crystallises in tetragonal prisms and pyramids, from solution in hot, moderately concentrated solution of potassium iodide, in boiling alcohol, or in hot nitric acid.[5] It has the sp. gr. 6·26, melts at 253—254°, and volatilises without decomposition, the vapour having the density 15·6—16·2, corresponding with the formula HgI_2. It is very slightly soluble in water, but dissolves in many aqueous acids, ammoniacal salts, salts of mercury, and soluble iodides, with which it forms soluble double compounds.

Mercuric iodide is dimorphous, for on gently heating the red modification to a temperature of 126° the mass becomes yellow with absorption of heat.[6] This change also takes place when the red crystals are melted or sublimed, yellow, rhombic prisms of sp. gr. 6·06 being formed. These retain their form and colour when allowed to cool to the ordinary temperature, but readily pass into the red modification when touched or rubbed with a hard body, or even spontaneously, heat being evolved, and the red crystals retaining the form of the yellow.

Although the yellow form is stable only at and above 126°,

[1] Nernst, *Zeit. physikal. Chem.*, 1888, **2**, 20; Varet, *Compt. rend.*, 1895, **120**, 620.

[2] Guinchant, *Compt. rend.*, 1909, **149**, 479.

[3] Vicario, *J. Pharm. Chem.*, 1907, **26**, 145.

[4] Fischer and Wartenburg, *Chem. Zeit.*, 1902, **26**, 966.

[5] Luczizky, *Zeit. Kryst. Min.*, 1909, **46**, 297.

[6] Guinchant, *Compt. rend.*, 1907, **145**, 68.

mercuric iodide separates from nearly all organic solvents in this form at temperatures below 126°, even when crystallisation is induced by the addition of a crystal of the red form.[1] The vapour of mercuric iodide, moreover, always condenses in yellow crystals.[2]

When a cold solution of corrosive sublimate and then water are added to an alcoholic solution of potassium tri-iodide (KI_3) heated to 50°, a brown, crystalline precipitate is obtained of *mercury periodide*, HgI_6. If the solutions be mixed together hot, and allowed to cool slowly, rhombic tablets of mercury periodide are obtained mixed with the yellow and red iodide. Mercury periodide possesses in a high degree the peculiar optical properties of tourmaline, and readily loses iodine.

Mercuric iodide forms a very large number of double salts[3] and also combines with sulphuric acid, ammonia, pyridine, and other substances. With alkali iodides and ether it forms both crystalline and liquid compounds.[4]

Mercuric Perchlorate, $Hg(ClO_4)_2$, is a deliquescent salt, crystallising with $6H_2O$. When digested with excess of mercuric oxide it yields the basic salt $2Hg(ClO_4)_2,HgO,12H_2O$, which is converted by alcohol into the compound $Hg(ClO_4)_2,2HgO$; this explodes with great violence when heated.[5] A number of other explosive substances have been obtained by the action of organic compounds on the perchlorate and chlorate.[6]

317 *Mercuric Sulphide* or *Cinnabar*, HgS, usually occurs in beds in slate rocks and shales, and more rarely in granite or porphyry. It is found in Idria, Almaden, in the Palatinate, in Carinthia, Translyvania, Tuscany, in the Urals and Altai, in China abundantly, and in Japan, Mexico, and Southern Peru. Extensive mines of cinnabar exist in California in the coast ranges at different points, from Clear Lake in the North to San Louis Obispo in the South, the principal mines in which region are at New Almaden and in the vicinity of Santa Clara Co., about sixty miles S.S.E. of San Francisco.

[1] Kastle and Clark, *Amer. Chem. J.*, 1899, **22**, 473; Kastle and Reed, *Amer. Chem J.*, 1902, **27**, 209; Gernez, *Compt. rend.*, 1903, **136**, 889, 1322; Mascarelli, *Atti R. Accad. Lincei*, 1906, [5], **15**, ii., 192. See also Sulc, *Zeit. anorg. Chem.*, 1900, **25**, 399.

[2] Gernez, *Compt. rend.*, 1899, **128**, 1516.

[3] Compare Dubois, *Ann. Chim. Phys.*, 1909, [8], **16**, 258.

[4] Marsh, *Journ. Chem. Soc.*, 1910, **97**, 2297.

[5] Chikashigé, *Journ. Chem. Soc.*, 1895, **67**, 1013; 1905, **87**, 822.

[6] Hofmann, *Ber.*, 1905, **38** 1999.

Cinnabar is found in rhombohedral crystals (Class 18, p. 209), which, like quartz, cause the circular polarisation of light, and also in the granular and massive states. It possesses a cochineal-red colour often inclined to brownish-red and lead-grey; its streak is scarlet, and it is sub-transparent or opaque, and possesses a conchoidal fracture and adamantine lustre. Theophrastus mentions this mineral as κιννάβαρις; the term, however, was afterwards used to designate dragons' blood. Pliny terms this latter substance *cinnabaris*, and the mineral cinnabar, being frequently confounded with red lead, is termed by him *minium*.

The artificial preparation of this compound was first described by the Latin Geber under the name of *usifur*. At the beginning of the seventeenth century, Turquet de Mayerne found that by rubbing mercury and sulphur together a black powder was obtained, and in 1689 Walter Harris showed that this compound could be obtained by intimately mixing dry sulphur and mercury. Prepared in this way, it was termed *Æthiops mineral*, and was employed as a medicine. In the year 1757, J. C. Jacobi proposed to employ for the same purpose the precipitate obtained by adding caustic soda to a solution of a mercury salt. This was known under the name of *pulvis hypnoticus*. The mode of preparing cinnabar by the wet way was first observed by G. Schulz, in 1687; he obtained it by shaking together for some time Boyle's volatile tincture of sulphur and metallic mercury. In 1773, Baumé showed that the black precipitate which this liquid produced in a solution of mercury was gradually converted into cinnabar. The difficulty of explaining the difference between the black and the red sulphides of mercury was increased by the fact that the one could be converted into the other. Stahl believed that the black compound contained more sulphur than the red one; others asumed that in the latter compound the sulphur was more intimately combined than in the former, or that both being compounds of oxide of mercury with sulphur, the cinnabar contained mercury in a higher state of oxidation. Berthollet, on the other hand, considered cinnabar as mercury sulphide, whilst he regarded the black modification as a compound of mercury with sulphuretted hydrogen. It was not until 1833 that the identity in composition of these substances was ascertained by Fuchs,[1] and the difference between them explained by the fact that

[1] *Schweiggers' Journ.*, 1833, 67, 1864.

the black compound was amorphous whilst the red was crystalline.

In order to prepare cinnabar in the dry way, according to the Dutch process, mercury is added to an excess of fused sulphur and the cold broken mass brought into earthenware pots which are heated in a sand-bath until the excess of sulphur is driven off. The crucible is then covered with an iron plate, and the temperature is raised until the cinnabar sublimes and is deposited upon the plate.

In the process of manufacturing vermilion in Idria, 8 parts of sulphur and 42 parts of mercury are placed in small barrels which are caused to rotate on their axes until the contents are converted into a brown powder; this substance is then distilled in iron retorts, furnished with a head and receiver; the purest cinnabar condenses in the head of the retort, whilst the portions deposited in the receiver consist of a mixture of this substance with sulphur and require redistillation. The sublimate is very finely levigated, treated with caustic soda, and then washed with water and dried.

Vermilion obtained in the wet way possesses a much finer colour than the sublimed vermilion, and it can be prepared in a variety of ways. According to Brunner's [1] process, 100 parts of mercury and 38 parts of flowers of sulphur are rubbed together for some hours and then the mass is mixed with 25 parts of potash dissolved in 150 parts of water at 45°. The mixture is then heated, the quantity of water being kept constant for about eight hours. After this time it begins to exhibit a red colour, and when the right tint has been attained the mass is quickly washed with water, as by the further action of potash the vermilion becomes brown. In another process described by Firmenich,[2] 5 kilos. of mercury mixed with 2 kilos. of sulphur and 4·5 litres of a solution of potassium pentasulphide are heated in a water-bath, the potassium pentasulphide solution being obtained by reducing 20 parts of potassium sulphate with carbon and boiling the product with 3·5 parts of water and 15 parts of sulphur. The mixture is then poured into strong stoppered bottles which are well shaken whilst the liquid is being heated. After the lapse of from three to four hours a brown powder is formed. The liquid is then allowed to cool to 50°, and is digested at this temperature for some days until the colour of the product reaches the right shade: then it is mixed

[1] *Pogg. Ann.*, 1828, **15**, 593. [2] *Dingl. Polyt. Journ.*, 1864, **172**, 370.

with caustic soda in order to withdraw the excess of sulphur, washed with water, and dried at 60°.

Sublimed cinnabar is often observed in distinct crystals having the form of the natural mineral. Generally, however, it forms a fibrous mass, having a cochineal-red colour, but when powdered it has a scarlet-red tint. Its specific gravity is 8·124 (Boullay); the specific gravity of its vapour is 5·34 (V. Meyer), from which it appears that in the gaseous condition the compound undergoes dissociation. Cinnabar is not attacked by hot nitric acid, but aqua regia dissolves it easily with liberation of sulphur. It is soluble in concentrated hydriodic acid in the cold and also in the dilute acid when warmed, sulphuretted hydrogen being evolved (Kekulé). Vermilion is used as an oil- and water-colour paint, for red lithographic and printers' ink, and for colouring sealing-wax, etc. It is sometimes adulterated with red lead or red oxide of iron. The presence of these impurities can be readily ascertained, inasmuch as pure vermilion sublimes without leaving any residue.

Black or amorphous mercuric sulphide, which occurs as a mineral in California,[1] is formed, as has already been stated, when flowers of sulphur and mercury are mixed together. The excess of sulphur can be removed by carbon disulphide, and the excess of mercury by dilute nitric acid. It is likewise formed when the component elements are gently heated together, and also by gently heating cinnabar in absence of air, although by the application of a stronger heat the latter compound again sublimes. When solutions of the polysulphides of the alkali metals act upon mercury, the black sulphide is likewise obtained, and the same compound may also be prepared by acting with an excess of sulphuretted hydrogen or sulphide of ammonium on a solution of a mercuric salt. Mercurous salts treated in this way yield a mixture of mercuric sulphide and finely divided mercury. On passing sulphuretted hydrogen into a solution of mercuric chloride, a white precipitate is first obtained, and this becomes yellow and ultimately black by the further action of the gas. This white compound has the composition $2HgS,HgCl_2$, and on sublimation decomposes into cinnabar and corrosive sublimate. Other salts of mercury form similar compounds.

Mercuric sulphide also combines with the sulphides of the alkali metals; thus, for instance, if a solution of mercuric

[1] Moore, *J. pr. Chem.*, 1870, [2], 2, 319.

chloride be treated with a solution of potassium sulphide containing some free alkali, a clear solution is obtained and, on evaporation, very slender, silky needles of the compound $HgS,K_2S,5H_2O$ are deposited. It is a very unstable compound, and on washing is resolved into its constituents. It was first obtained by Brunner, in the preparation of vermilion according to his method. The conversion of the black, amorphous sulphide into vermilion probably depends upon the formation of this body.

Mercuric Sulphate, $HgSO_4$.—This salt was known in the fourteenth century, and is obtained by heating mercury with oil of vitriol. In order to prepare a product free from mercurous salt, the mercury must be heated with 1·5 times its weight of sulphuric acid, and evaporated to dryness. In this way a white, opaque mass is obtained, which crystallises from an excess of sulphuric acid in small, stellate plates, having a silvery lustre. When gently warmed it becomes yellow and afterwards red-coloured, and decomposes, when strongly heated, into mercury, oxygen, sulphur dioxide, and mercurous sulphate. Water decomposes it even at 25° with formation of the insoluble basic salt, $3HgO,SO_3$, a heavy, lemon-coloured powder which on heating becomes of a red colour, and dissolves in 2,000 parts of cold, and 600 parts of boiling, water. The basic compound was described by Basil Valentine, and was used by the iatro-chemists under the name of *turpetum minerale*. This appears to be the only definite basic mercuric sulphate which exists at 25°.[1]

Mercuric sulphate forms several compounds with hydrogen chloride.[2]

318 *Mercury Nitride* or *Trimercuric Diamine*, N_2Hg_3.—For the preparation of this compound, a solution of mercuric iodide or bromide in liquid ammonia is added to an excess of potass-amide dissolved in the same solvent:

$$3HgI_2 + 6KNH_2 = Hg_3N_2 + 6KI + 4NH_3.$$

It is a chocolate-brown powder, which in the dry state is very explosive. Aqueous acids and solutions of ammonium salts in liquid ammonia readily dissolve it.[3]

Mercuric Nitrate, $Hg(NO_3)_2$.—This salt was classed among

[1] Cox, *Zeit. anorg. Chem.*, 1904, **40**, 165. See also Hoitsema, *Zeit. physikal. Chem.*, 1895, **17**, 651; Guinchant, *Bull. Soc. chim.*, 1896, [3], **15**, 555.

[2] Baskerville and Weil, *J. Amer. Chem. Soc.*, 1901, **23**, 894.

[3] Franklin, *Zeit. anorg. Chem.*, 1905, **46**, 1.

the vitriols by the alchemists, and its preparation is thus described in the works of Basil Valentine:

"Vitriolum mercurii is easily made with an *aqua fort* distilled from saltpetre, and alum *ana*; if it is dissolved in it, crystals like a vitriol shoot out; these are then ablued and purified with *spiritus vini*, which previously has been rectified with *sal tartari*; thus it is made into a sweet oil. This is a noble medicine *ad luem gallicam*, it cures all sores, consumptions, disuries, gouts, and drives out many other diseases from the human body."

In order to prepare this salt, mercury is boiled with nitric acid until a portion of the liquid no longer gives a precipitate with common salt. On evaporating the solution over sulphuric acid large crystals separate out having the formula $2Hg(NO_3)_2,H_2O$. The same salt, which is very deliquescent, is obtained as a crystalline magma, by adding strong nitric acid to the concentrated solution. The mother-liquor from the large crystals is a thick liquid which possesses the power, first noticed by Libavius, of colouring the skin a dark-red tint. On evaporating the solution, a basic salt, $2Hg(NO_3)OH,H_2O$, separates out in long, transparent prisms which possess a metallic, but not an acid taste.

When mercuric nitrate is treated with water at 25° it yields the basic salt, $Hg(NO_3)_2,2HgO$, as a heavy, white powder, which is decomposed by the further action of water, leaving mercuric oxide.[1]

Mercuric Nitrite, $Hg(NO_2)_2$, is obtained by the action of mercuric chloride on silver nitrite or by the decomposition of mercurous nitrate by water.[2]

Mercuric Hyponitrite, HgN_2O_2, is prepared by the action of sodium hyponitrite on mercuric nitrite, and is a light buff-coloured powder. It decomposes spontaneously into nitric oxide and mercurous hyponitrite, and is the only mercuric salt which decomposes into a mercurous salt.[3]

Mercuric Phosphide is obtained as a black powder, together with mercuric phosphate, by heating mercuric oxide and phosphorus together in water. If a current of gaseous hydrogen phosphide is passed over gently heated mercuric chloride, an orange-yellow sublimate of mercuric phosphide is obtained which

[1] Cox, *Zeit. anorg. Chem.*, 1904, **40**, 159.

[2] Rây, *Journ. Chem. Soc.*, 1897, **71**, 341.

[3] Divers, *Journ. Chem. Soc.*, 1899, **75**, 119. See also Rây, *ibid.*, 1907, **91**, 1404; Rây and Gañguli, *ibid.*, 1399.

decomposes into its elements on heating (H. Rose). The phosphide, Hg_3P_4, is obtained in hexagonal prisms when mercury is heated with phosphorus di-iodide. It is readily decomposed by heat.[1]

Mercuric Arsenide, Hg_3As_2, is the final product obtained when a mixture of arsine and hydrogen is passed into an alcoholic solution of mercuric chloride. It is a black powder which oxidises in the air, forming arsenious oxide and mercury.[2]

319 *Mercuric Acetylide*, $3C_2Hg,H_2O$, is best prepared by passing acetylene into a solution of mercuric oxide in ammonia and ammonium carbonate. It is a heavy, white powder, which explodes when rapidly heated. When heated with hydrochloric acid a mixture of acetylene and acetaldehyde is produced.[3]

When acetylene is passed into a solution of mercuric nitrate derivatives of acetaldehyde are formed, which are decomposed by acids with formation of acetaldehyde, no acetylene being liberated.[4]

Mercuric Carbonates.—Only basic mercuric carbonates are known. If a solution of mercuric nitrate is poured into an excess of potassium carbonate solution, a dark brown precipitate of $HgCO_3,2HgO$ is formed, and if a solution of potassium bicarbonate is employed, an amorphous, brown precipitate of $HgCO_3,3HgO$ is formed.

Mercuric Cyanide, $Hg(CN)_2$.—This compound was discovered by Scheele, who obtained it by boiling Prussian blue with mercuric oxide and water. It is formed also by dissolving mercuric oxide in dilute hydrocyanic acid, or by boiling one part of potassium ferrocyanide with two parts of mercuric sulphate and eight parts of water:

$$2K_4Fe(CN)_6+7HgSO_4=6Hg(CN)_2+4K_2SO_4+Fe_2(SO_4)_3+Hg.$$

It may be prepared by adding a solution of sodium cyanide to mercuric sulphate.[5]

Mercuric cyanide dissolves in eight parts of cold water and crystallises from the hot aqueous solution in white needles or transparent, tetragonal prisms which are insoluble in absolute

[1] Granger, *Journ. Chem. Soc.*, 1898, **74**, ii., 474.

[2] Partheil and Amort, *Arch. Pharm.*, 1899, **237**, 121.

[3] See Plimpton and Travers, *Journ. Chem. Soc.*, 1894, **65**, 264, where references to the earlier literature are to be found.

[4] Hofmann, *Ber.*, 1898, **31**, 2212, 2783. See also Erdmann and Kothner, *Zeit. anorg. Chem.*, 1898, **18**, 54.

[5] Rupp and Goy, *Apoth. Zeit.*, 1908, **23**, 374.

alcohol. The salt is only dissociated to a very minute extent in aqueous solution, which, therefore, does not yield all the reactions characteristic of mercuric ions; thus its solution gives no precipitate with caustic soda or potassium iodide. It is however, decomposed by sulphuretted hydrogen and by boiling with hydrochloric, hydrobromic, hydriodic, or dilute sulphuric acid, hydrocyanic acid distilling over. It forms crystalline double compounds with many other salts. In aqueous solution it yields with potassium iodide the salt, $Hg(CN)_2,HgI_2,2KCN$.[1] When heated it decomposes into cyanogen and metallic mercury. Its aqueous solution readily dissolves mercuric oxide, and on evaporating the alkaline solution thus obtained, small needles of a basic cyanide, $Hg(CN)_2,HgO$, are formed. This is known as *mercuric oxycyanide*, and is used as an antiseptic.[2]

Mercuric Cyanate, $Hg(OCN)_2$, and *Mercuric Thiocyanate*, $Hg(SCN)_2$, are white, crystalline precipitates. In order to prepare the latter salt a solution of ammonium thiocyanate is precipitated with excess of corrosive sublimate solution. This compound is used for the preparation of the so-called "Pharaoh's serpents." The dried precipitate is rubbed up with gum-water to a thick, plastic mass, and short cones are formed of this mixture, which are then dried. On igniting them at the end they burn with a blue, sulphur-like flame, the ash being very bulky and extending in a serpent-like form.

Ammoniacal Compounds of Mercury.

320 Many different series of ammoniacal derivatives of mercury have been described, but very little is known as to their constitution. Most of the derivatives are insoluble in the ordinary solvents and cannot be volatilised without decomposition, so that their molecular weights cannot be determined. Rammelsberg[3] formulated all these compounds as derived from dimercurammonium salts, in which two atoms of mercury replaced the four hydrogen atoms of the ammonium radical. Many serious objections to this view have been urged by other investigators,[4] and it seems probable that the mercuri-

[1] Rupp and Goy, *Arch. Pharm.*, 1909, **247**, 100.

[2] See Holdermann, *Arch. Pharm.*, 1905, **243**, 600; 1906, **244**, 133; Rupp, *ibid.*, 1906, **244**, 1.

[3] *J. pr. Chem.*, 1888, [2], **38**, 558. See also Barfoed, *J. pr. Chem.*, 1889, [2], **39**, 201; Pesci, *Gazz.*, 1891, **21**, 569; *Zeit. anorg. Chem.*, 1899, **21**, 301.

[4] Hofmann and Marburg, *Annalen*, 1899, **305**, 198; *Zeit. anorg. Chem.*, 1900, **23**, 126; Franklin, *J. Amer. Chem. Soc.*, 1907, **29**, 35.

ammonium compounds fall into three classes[1]: (i) additive compounds of mercuric salts and ammonia, typified by fusible precipitate, $HgCl_2,2NH_3$, (ii) ammonolysed compounds in which NH_2, NH, or N is substituted for part of the acidic radicle in mercuric salts, *e. g.*, infusible precipitate, $Cl{\cdot}Hg{\cdot}NH_2$, and (iii) compounds which are both ammonolysed and hydrolysed, such as the chloride of Millon's base, $NH_2{\cdot}Hg{\cdot}O{\cdot}HgCl$. No ammoniacal mercurous compounds appear to have been obtained. Thus the supposed mercurous ammonium derivatives are mixtures of mercuric derivatives and finely divided metallic mercury, which latter gives them a black colour.

Millon's Base.—When mercuric oxide is gently warmed with pure dilute ammonia, a pale yellow powder having the composition $H_5O_3NHg_2$ is obtained, which deflagrates without explosion on rubbing, or when thrown on to hot charcoal. This compound is known as Millon's base and is variously formulated as $(HOHg)_2NH_2{\cdot}OH$ (Hofmann and Marburg), or $NHg_2{\cdot}OH,2H_2O$ (Rammelsberg). When exposed over caustic potash to an atmosphere of ammonia it loses water, yielding the dark yellow compound $(OHg_2)NH_2{\cdot}OH$. This substance and Millon's base both yield salts when treated with acids. When, however, the compound $(OHg_2)NH{\cdot}OH$ is heated at 125° in a current of ammonia, a second molecule of water is lost, and a non-basic highly explosive dark-brown powder of the composition NHg_2OH is produced, which is also formed when ammonia is passed over dried yellow mercuric oxide at 120°, and is known as *dimercuriammonium hydroxide.*

Salts of Millon's Base are formed when ammonia is added to mercuric salts of oxy-acids, and when the base is digested with 6 per cent. aqueous solutions of the acids. These salts have as a rule the empirical formula $H_2ONHg_2X^I$, and, like the base, have been formulated in two different ways—as oxydimercuriammonium salts, $(OHg_2)NH_2{\cdot}X^I$, or as dimercuriammonium salts, NHg_2X^I,H_2O. Anhydrous salts of the formula NHg_2X^I have also been prepared by the action of liquid ammonia or potassamide on mercuric bromide and iodide, but it is probable that these substances are not true derivatives of Millon's base, but are amino-compounds of the constitution Hg:N·HgX (Franklin[2]). Compounds of the same composition

[1] Holmes, *Journ. Chem. Soc.*, 1918, **113**, 74.

[2] *Zeit. anorg. Chem.*, 1905, **46**, 1.

have been described by François [1] and by Pesci [2] as formed by the action of aqueous ammonia on mercuric iodide and bromide.

The Chloride of Millon's Base, $(OHg_2)NH_2 \cdot Cl$, or $NHgCl,H_2O$, is formed by the action of hydrochloric acid on Millon's base, and may be prepared by digesting infusible white precipitate with a large amount of water at 60—70°. It forms a yellowish powder which is stable in an atmosphere of ammonia at 125°, but decomposes at 180° with separation of mercury (Hofmann and Marburg).

The Iodide of Millon's Base, $(OHg_2)NH_2 \cdot I$, which is frequently described as oxydimercuriammonium iodide, is formed by the action of an excess of ammonia on mercuric iodide, and also when ammonia is passed at a temperature of 180° over the basic oxy-iodide of mercury, $HgI_2,3HgO$.

The same compound is easily obtained by adding ammonia to a solution of mercuric potassium iodide, containing an excess of potash, and hence this liquid, known as Nessler's solution (Vol. I., p. 330), is employed as a very delicate reagent for the detection of ammonia. It is a brown powder which often exhibits a reddish-purple colour, and, on heating in absence of air, fuses to a brown liquid, whilst when more strongly heated, it decomposes with emission of light, into water, mercuric iodide, ammonia, and nitrogen.

Infusible White Precipitate, which appears to have been first prepared by Lemery, is formed when a solution of mercuric chloride is precipitated by ammonia, and has the empirical formula $NHgH_2Cl$. It is formed also by the action of liquid ammonia and of potassamide on mercuric chloride (Franklin). It is a bulky, white powder having an earthy, metallic taste, and is insoluble in water, but on long-continued washing or on treatment with caustic potash it becomes yellow, owing to partial decomposition with formation of the yellowish-coloured chloride of Millon's base. It decomposes below a red heat without fusion, forming calomel, ammonia, and nitrogen:

$$6NH_2HgCl = 3Hg_2Cl_2 + N_2 + 4NH_3,$$

and in warming with ammonium chloride yields the fusible, white precipitate described below. If it is mixed with iodine and alcohol is poured on to it, mercuric iodide is first formed and

[1] *Compt. rend.*, 1900, **130**, 332, 1022.

[2] Compare, however, Hofmann and Marburg, *Annalen*, 1899, **305**, 191.

then a violent explosion occurs. This mixture also deflagrates in the dry state after some time.

The constitution of this substance has given rise to much discussion. Rammelsberg and Pesci regard it as NHg_2Cl,NH_4Cl, a double salt of dimercuriammonium chloride and ammonium chloride, whereas Hofmann and Marburg, and Franklin assign to it only half this molecular weight, formulating it as $NH_2{\cdot}HgCl$, or aminomercuric chloride. The latter view is supported by the existence of an analogous compound derived from ethylamine, $NH_2{\cdot}C_2H_5$, which has the formula $NH{\cdot}C_2H_5HgCl$, and resembles infusible white precipitate in properties, although ethylamine is incapable of yielding a compound corresponding with Rammelsberg's formula.

Fusible White Precipitate.—This compound was first prepared by Raymond Lully, by precipitating mercuric nitrate with sal-ammoniac and salt of tartar. He was acquainted with its property of fusing when heated. At a later time this body was confounded, not only with the foregoing compound, prepared first by Lemery, but also with calomel prepared by the wet process. Kunkel, although he gave both to this last preparation and to fusible white precipitate the name of *lac mercurii*, was aware of their difference. He says, "Whether these two have the same effect in medicine, I leave to the physicians and surgeons; *in examine chymico* they are very different." Wöhler, in 1838, pointed out the difference between the fusible and infusible precipitate.

Fusible white precipitate is obtained by the action of gaseous ammonia on mercuric chloride, by adding a solution of corrosive sublimate to a boiling aqueous mixture of sal-ammoniac and ammonia as long as the precipitate which is formed dissolves, or by boiling the infusible white precipitate, or the chloride of Millon's base, with a solution of sal-ammoniac. Small, regular dodecahedra or crystalline crusts are deposited on cooling. The compound fuses on heating, losing nitrogen and ammonia, whilst a mixture of calomel, corrosive sublimate, and sal-ammoniac sublimes.

It has the empirical formula $N_2H_6HgCl_2$, and has been formulated as the double salt, $NHg_2Cl,3NH_4Cl$, or as the additive compound, $Hg(NH_3)_2Cl_2$. As in the case of the infusible white precipitate, an analogous derivative of ethylamine is known, a fact which is in favour of the latter formula. By digesting infusible white precipitate with a solution of mercuric chloride

and ammonium chloride in water, by use of proper concentrations either $3HgCl,2NH_3$ or $HgCl_2,NH_2{\cdot}HgCl$ may be prepared.[1]

Mercuriphosphonium compounds analogous to the above mercuriammonium salts have also been prepared.

Therapeutic Uses of Mercury and its Compounds.

321 The poisonous effects of mercury were known to Dioscorides and Pliny, and it appears that even in those days mercurial preparations were employed as medicines. From that period up to the fifteenth century mercury was but sparingly used in medicine, and then for external purposes only. Even in the fifteenth century, the outward use of mercurial compounds was discountenanced by the then prevailing schools of medicine, and at the beginning of the sixteenth century the few physicians who had dared to employ mercurial ointment were vigorously assailed. The employment of mercurial preparations was, however, soon afterwards introduced by Paracelsus, and by degrees became common.

Metallic mercury rarely leads to toxic phenomena when taken internally. Large quantities (several pounds) used to be given to overcome intestinal obstruction, and when the mere weight of the liquid metal was sufficient to remove the obstruction mechanically, the mercury passed through the intestines rapidly and was excreted without any absorption. In small quantities, especially if it be in a state of fine division, mercury is rapidly absorbed, and exercises medicinal or toxic effects, according to the quantity employed. Metallic mercury can be absorbed through the unbroken skin, and may lead to local disturbances (dermatitis) and to general toxic symptoms, and mercury vapour is frequently the cause of severe forms of poisoning.

The salts of mercury are poisonous. In some respects, the poisonous action of mercury compounds resembles that of salts of other heavy metals, but a special action on the animal economy lends an important therapeutic value to these salts. In general, mercury is employed therapeutically both for local and general inflammations, the disease for which it is most valuable being syphilis.

Calomel, Hg_2Cl_2, corrosive sublimate, $HgCl_2$, and mercuric iodide, HgI_2, are most commonly used. In the intestines, small quantities of calomel may be completely absorbed and give

[1] Holmes, *Trans. Chem. Soc.*, 1918, **113**, 74.

rise to poisonous symptoms, while larger quantities, acting as a purgative, are less dangerous; as a rule, from 0·032 to 0·32 gram is the dose used in medicine. It is supposed that calomel is acted upon by sodium chloride present in the body, forming mercuric chloride and metallic mercury, while some authors believe that oxychlorides are also formed.

Corrosive sublimate, when in concentrated solution, acts as a powerful caustic. In small doses, it produces severe toxic symptoms, and only in very small quantities is it tolerated therapeutically. Even 0·1 gram, when rapidly absorbed, is a fatal dose. The iodide acts similarly.

When small quantities of mercury are absorbed daily for a prolonged period, a complex of symptoms, known as mercurialism, appears. These include salivation, ulceration of the mucous membranes of the mouth, tremors, nervous symptoms, headache, anæmia, and wasting.

Chronic mercurial poisoning is met with in those who habitually work with the metal, namely, miners in quicksilver mines, persons engaged in extracting gold by the amalgamation process, and those employed in making mirrors, thermometers, barometers, etc.

Detection and Estimation of Mercury.

322 Bunsen's flame-reaction may be conveniently employed in order to detect the presence of mercury in a solid body. For this purpose the substance is mixed with a small quantity of anhydrous sodium carbonate and nitre, and the mixture is heated in a tube held in the flame by means of a platinum wire wound round it, the mouth of the tube being placed directly under a small porcelain basin filled with cold water. The mercury is then volatilised, and condenses on the cool lower surface of the porcelain basin in the form of a grey film. This is wiped off with a small piece of filter paper, when the minute globules of liquid metal are rubbed together and a larger globule is obtained. If a large quantity of mercury be present, globules are at once formed on the cold basin.

A similar film can be more simply obtained by heating the compound on a piece of asbestos in the reducing zone of the flame beneath a porcelain basin. The metal may also be detected by heating the compound in a bulb tube with sodium carbonate and potassium cyanide, the mercury being deposited on the cool part of the tube.

When a liquid has to be tested for mercury, it is in the first place acidified with hydrochloric acid. If this produces a white precipitate, a mercurous salt may be present together with silver, lead, and thallium. The last two metals may be removed by boiling the precipitate with water. The residue is then treated with ammonia, in which the chloride of silver is soluble. If a black powder remains, mercury is present, and its presence can be confirmed by the flame reaction just described. The filtrate from the first precipitate, or the solution in which the hydrochloric acid gives no precipitate, is saturated with a current of sulphuretted hydrogen gas. If mercury is present, a white precipitate will first be formed, but this rapidly changes colour, becoming yellow, brownish-red, and finally black. In order to separate mercury from the other sulphides which may be present, the precipitate is first washed with hot water, then warmed with sulphide of ammonium, again washed with water, and the residue treated with hot dilute nitric acid. If a heavy black powder remains undissolved, this is treated with aqua regia, the solution concentrated, and stannous chloride added to this solution, when calomel is precipitated; if an excess of the precipitant is added, finely divided metallic mercury is deposited as a black powder, which on boiling with hydrochloric acid unites to form distinct globules. The following equations represent the decomposition :

$$(a)\ 2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4,$$
$$(b)\ Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4.$$

The spark spectrum of mercury contains a large number of lines, and has been carefully mapped by Huggins and Hartley and by Adeney.[1]

Mercury is best estimated quantitatively by precipitating the solution with sulphuretted hydrogen. The sulphide thus precipitated frequently contains free sulphur, and it is therefore warmed with hydrochloric acid, nitric acid being added drop by drop until the sulphur, which separates out, has become yellow. Then the solution is diluted with water, nearly neutralised with caustic soda, excess of potassium cyanide added, and the sulphide again thrown down with sulphuretted hydrogen; the precipitate thus obtained is quickly washed with cold water, dried at 100°, and weighed. The sulphur may also be removed by washing the precipitate with alcohol to remove water, and then with carbon disulphide. Mercury is also sometimes estimated

[1] See Watts, "Index of Spectra," p. 105 (Heywood, Manchester, 1889).

in the form of mercurous chloride, or as the free metal obtained by distillation with lime or iron, or by electrolysis of a solution of the cyanide in potassium cyanide, or better by the electrolysis of acid solutions with a mercury cathode.

Atomic Weight of Mercury.—The atomic weight of mercury was determined by Turner,[1] and by Erdmann and Marchand,[2] by the analysis of mercuric oxide, and also by the latter investigators by the analysis of the sulphide. Millon [3] and Svanberg [4] estimated the quantity of mercury formed by heating the chloride with lime in a current of hydrogen. Hardin [5] compared the weights of silver and mercury deposited by the same current, and also effected the electrolytic analysis of mercuric chloride, bromide, and cyanide, arriving finally at the value 199·93.

Easley obtained a higher figure (200·48) by reducing mercuric chloride by means of hydrogen peroxide and partly by electrodeposition. At the same time, from the ratio $HgCl_2 : 2AgCl$, he obtained the figure 200·62.[6] Later he obtained the value 200·63 by the analysis of the chloride,[7] and by the analysis of the bromide, 200·64.[8] Taylor and Hulett,[9] by reduction of mercuric oxide with metallic iron, obtained the relatively low value 200·37, but Baker and Watson,[10] using Easley and Brann's method of converting mercury into mercuric bromide, found Hg = 200·57. The value now adopted (1922) is Hg = 200·6.

Positive ray analysis (*q. v.*) has, however, shown that mercury probably consists of a mixture of at least six isotopic elements with atomic weights ranging from 197—204, and there is already some evidence that some separation of these isotopes can be effected by fractional distillation.[11]

[1] *Annalen*, 1835, **13**, 14.
[2] *J. pr. Chem*, 1844, **31**, 385.
[3] *Compt. rend*, 1845, **20**, 1291.
[4] *Jahresb.*, 1847-8, 445.
[5] *J. Amer. Chem. Soc*, 1896, **18**, 990.
[6] *Ibid.*, 1909, **31**, 1207.
[7] *Ibid.*, 1910, **32**, 1117
[8] Easley and Brann, *J. Amer. Chem. Soc*, 1912, **34**, 137.
[9] *J. Physical Chem*, 1913, **17**, 755.
[10] *Journ. Chem. Soc*, 1914, **105**, 2530.
[11] Bronsted and Hevesy, *Nature*, 1920, **106**, 144.

GROUP III.

Sub-Group (*a*)—Boron and the Rare Earth Metals.

Boron.
Scandium.
Yttrium.
Lanthanum and the Rare Earth Metals.

Sub-Group (*b*)—The Aluminium Group of Metals.

Aluminium.
Gallium.
Indium.
Thallium.

323 These elements all form oxides of the formula R_2O_3, and unite with the halogens to form compounds of the type RX_3 or R_2X_6.

Boron hydroxide behaves as an acid to most bases, and acts as a base only towards the strongest acids, but the basic character of the oxides becomes more marked in this group as the atomic weight increases. The oxides of the metals of sub-group (*a*) are, as in the second group, more basic than those of sub-group (*b*). Thus the latter form salts with strong alkalis, whereas the former do not.

The element boron, being the least electropositive element of the group and usually occurring in an anion, has already been described among the non-metals (Vol. I., p. 713). Since the chemical relations of the rare earth metals are so little known at present, all the metals of sub-group (*a*) are described among the rare earth metals.

THE ALUMINIUM GROUP.

324 These metals are permanent in the air at ordinary temperatures, but become oxidised when strongly heated in air or oxygen. The volatility of the metals increases with the atomic weight, and the same order is observed in the ease of reduction from the oxide. Thus indium and thallium both yield an incrustation of the oxide and a metallic bead when their compounds are reduced on charcoal, whereas aluminium compounds do not give this reaction.

All these metals have small atomic volumes, and occur just after the minima on Lothar Meyer's diagram (p. 62). They are all malleable and fusible, and form typical hydroxides which act as weak bases, the corresponding salts being often readily decomposed by boiling with water. These hydroxides also act as weak acids towards strong bases. Thus the hydroxide of gallium is soluble both in potash and ammonia, and those of aluminium and of indium in potash, whilst thallic hydroxide is insoluble in alkalis.

Aluminium, gallium, and indium form characteristic double sulphates of the formula $M_2SO_4,R_2(SO_4)_3,24H_2O$, known as the alums, in which M represents a monovalent metal. Similar compounds have not yet been obtained from thallium. Both aluminium and thallium yield organo-metallic derivatives.

Special interest attaches to the position of gallium in this group, because its properties and relations to aluminium and indium show that it is identical with the "eka-aluminium" of Mendelćev, the existence of which was predicted by that chemist four years before the actual discovery of the element by Lecoq de Boisbaudran (p. 70).

In addition to compounds of the type RX_3, lower chlorides of indium and gallium are also known, whilst thallium forms a whole series of salts, in which it acts as a monovalent metal. These salts are more stable than those which correspond in type to the aluminium salts and bear a remarkable chemical resemblance to the salts of the alkali metals, with which they are in many cases isomorphous. Physically, the metal thallium closely

resembles lead, which occupies the corresponding place in Group IV, and its compounds with the halogens (except fluorine) and sulphur are very similar in properties to the corresponding lead compounds. In consequence of this remarkable behaviour, Dumas, on the occasion of the discussion of Lamy's investigation in the French Academy, termed it the ornithorhynchus amongst the metals.

ALUMINIUM. Al = 27·0. At. No. 13.

325 The name of this metal is derived from *alumen*, alum. This, as well as the corresponding Greek word (στυπτηρία), was originally used to designate very different bodies, all of which possessed the common property of an astringent taste. There can, however, be little doubt that alum itself was included amongst these bodies, and this salt was well known to the Latin Geber and the later alchemists, being, however, classed amongst the vitriols, until Paracelsus showed that it differed from this last family of salts. In his second treatise, *De Generibus Salium*, he states: "Alum is in no wise connected with the metals, but is a salt, standing alone in the acid, and taking its *corpus* from the intermixture of the earths; vitriol does not do so, but solely from the intermixture of metallic *corpora*." The nature of the earth, which is combined in alum with sulphuric acid, remained long undetermined. It was usually supposed to be a calcareous earth, although it was noticed in the seventeenth century that clay, when treated with sulphuric acid, gave an alum: and hence Pott, in his *Lithognosy*, published in 1746, stated that the basis of alum was an argillaceous earth. It was not till 1754 that Marggraf showed that alumina differed totally in its properties from lime, and that clay contained this earth, combined with silica.

Davy, as well as other chemists, endeavoured to decompose alumina into its elements, as it was generally acknowledged to be an oxide. The results they obtained were, however, but unsatisfactory, and Wohler, in 1827, was the first to prepare pure aluminium.

Of all the elements, with the exceptions of oxygen and silicon, aluminium is the most widely distributed, and contained in the largest quantity in the solid crust of the earth. It occurs as the oxide, Al_2O_3, in the mineral corundum, of which the ruby and sapphire are varieties. It is found more commonly as diaspore, $Al_2O_4H_2$, and bauxite, a hydrated aluminium oxide in which

varying portions of aluminium are replaced by iron, whilst it occurs in far larger quantity in combination with silica, forming a great variety of double silicates, amongst which potash-felspar or orthoclase, $(K,Na)AlSi_3O_8$, may be mentioned as being most important, as this forms the chief constituent of granite, gneiss, syenite, porphyry, trachyte, etc. Soda-felspar or albite, and lime-felspar or labradorite, also occur in large quantities. Amongst other important double silicates we find the garnet group, the members of which are named from the different isomorphous metals which they contain; for instance, we have lime-alumina garnet or grossular, $Ca_3Al_2(SiO_4)_3$; iron-alumina garnet, or almandine, $(Fe,Mg)_3Al_2(SiO_4)_3$; lime-iron garnet, or andradite, $Ca_3Fe_2(SiO_4)_3$. The micas also comprise a large number of important minerals, as common mica or biotite, $K_2HAl_3(SiO_4)_3,(Mg,Fe)_6(SiO_4)_3$; and chlorite or ripidolite, $H_9(Fe,Mg)_5Al_3Si_3O_{20}$, the latter compounds forming the chief constituents of many slate rocks.

Aluminium occurs also in large quantities as cryolite, a double fluoride of aluminium and sodium, Na_3AlF_6, the name being derived from the ice-like appearance of the mineral, which is largely worked at Ivigtut in South Greenland [1] and has served as an industrial source of the metal.

The weathering of felspar gives rise to porcelain-clay, china-clay, or kaolin, $Al_2Si_2O_7,2H_2O$, whilst the different varieties of coloured clays are obtained from a similar disintegration of felspathic rocks containing iron.

Although alumina is largely contained in all fertile soil, it is found only in small quantity in most plants.[2] Certain cryptogams, however, especially the species of lycopodium, take it up largely. Thus the ash of *L. clavatum* contains up to 26·65, and that of *L. chamaecyparissus* even as much as 57·26 per cent. of alumina.[3] Aluminium is present also in the solar atmosphere.

326 *Preparation of Metallic Aluminium.*—The process which Wöhler used for the preparation of aluminium is one which may be employed for the preparation of all those elements which occur in nature combined with oxygen, and whose oxides are not reducible either in the presence of carbon or of hydrogen. It consisted [4] in fusing together potassium and chloride of

[1] Halland, *J. Ind. Eng. Chem.*, 1911, **3**, 63.

[2] Yoshida, *Journ. Chem. Soc*, 1887, **51**, 748; Berthelot and Andrée, *Compt. rend.*, 1895, **120**, 288; see also Smith, *Chem. News*, 1903, **88**, 135.

[3] Aderholdt, *Annalen*, 1852, **82**, 111.

[4] *Pogg. Ann.*, 1827, **11**, 146.

aluminium in a closed crucible. The metal was thus obtained in the form of a grey powder, which, under the burnisher, exhibited a metallic lustre, and when pressed in an agate mortar adhered together in the form of glittering particles.

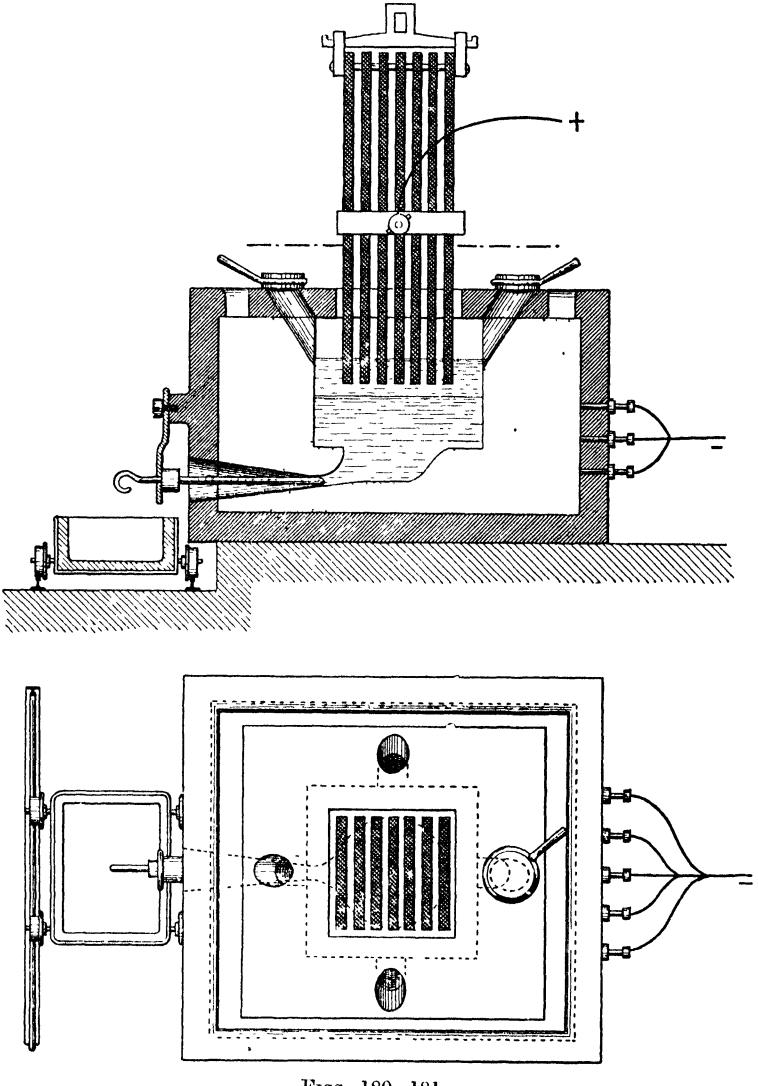
Wöhler afterwards improved his method, and, by passing the vapour of aluminium chloride over potassium, obtained the metal in fused globules.[1] In the year 1854 Bunsen[2] prepared aluminium by electrolysis of the chloride, and in the same year Deville commenced his first experiments on the preparation of aluminium on a large scale. The process he employed was that of Wohler, potassium being, however, replaced by sodium, and he found that instead of the pure chloride it was preferable to use the double chloride of aluminium and sodium. In the Paris Exhibition of 1855 the "silver made from clay" naturally attracted great attention. Deville then, in concert with other chemists, and with the pecuniary help of Napoleon III., extended his experiments; with their help the process was still further improved, and aluminium was first prepared on the large scale at works near Alais, under the direction of Merle. Pure aluminium hydroxide (p. 741) was made into balls with common salt and coal dust, and the mixture exposed at a white heat to a current of chlorine, by the action of which the volatile double chloride of sodium and aluminium, $NaCl,AlCl_3$, was produced. The latter was then heated with metallic sodium and a flux, and the aluminium run into moulds.

Electrolytic Production of Aluminium.—The above method for the preparation of the metal has now, however, been entirely superseded by an electrolytic process. Instead of electrolysing fused sodium aluminium chloride, a fused mixture of cryolite and common salt was substituted for the chloride by Bernard Bros., of Paris, who from 1887 manufactured the metal in this manner.

There are two processes at present employed, which differ only in detail:—the Hall process used in the United States, and the Héroult process employed by the British Aluminium Co. and in Europe. Figs. 180 and 181 represent the Héroult furnace. Pure aluminium oxide is dissolved in a bath of fused cryolite and electrolysed with carbon anodes. The walls of the box containing the electrolyte, which is of iron lined with carbon, act as the cathode. When the electrolysis has proceeded for a short time the molten aluminium acts as the cathode. In order

[1] *Annalen*, 1836, **17**, 44; 1841, **53**, 422. [2] *Pogg. Ann.*, 1854, **92**, 648.

to prevent loss of heat by radiation and to minimise the burning away of the electrodes, the top of the bath is covered with a layer



FIGS. 180, 181.

of charcoal. From time to time the aluminium is tapped off and the bath renewed by the addition of fresh quantities of alumina. The cryolite simply acts as a solvent for the alumina and by proper regulation of the current takes no part in the electrolysis.

Aluminium is deposited at the cathode and oxygen is liberated at the anode. The anodic oxygen unites with the carbon of the anode, forming carbon monoxide which burns to dioxide. For every pound of metal produced, from 0·5 to 0·7 lb. of anode is consumed. Several anodes are used in each bath and the anodes used by the British Aluminium Co. are about 10 inches square and made from petroleum coke. The current density is 700 amperes per square foot of cathode surface, the voltage being 8 to 10 volts.

When possible, as at Foyers, Niagara, Neuhausen, Christiansand, etc., water power, as being cheaper than steam power, is utilised for the production of the necessary electric current. Alloys can also be made directly, instead of the metal itself, by carrying out the electrolysis in the presence of the desired metal, which dissolves the aluminium as it is liberated. Manufactured electrolytically, aluminium contains uniformly over 99 per cent. of metal and is very soft and ductile, the chief impurities being iron and silicon, and occasionally traces of sodium and copper.[1] A sample of commercial aluminium manufactured at Foyers, which contained 99·75 per cent. of the metal, was found by spectroscopic examination to contain sodium, potassium, calcium, copper, silver, gallium, iron, manganese, lead, and traces of indium. Silver, copper, and gallium were also found in the bauxite of Glenravel from which the aluminium was extracted.[2] The annual output of aluminium slowly increased between 1859 and 1888 from one ton to three tons, but from about the latter date the production rose very rapidly, and now reaches about 150,000 tons per annum.

Pure aluminium was prepared by Mallet [3] from a compound of aluminium bromide with the chlorides of potassium and sodium, by heating with sodium in a crucible lined with a mixture of alumina and sodium aluminate. The product was quite free from silicon, iron, sodium, and potassium.

327 *Properties.*—Aluminium is a tin-white metal, which is capable of assuming a bright polish. The appearance of objects made of aluminium is often improved by giving to the surface of the metal a dead appearance. This is accomplished by acting on the surface with weak soda-lye, and afterwards washing with

[1] Moissan, *Compt. rend.*, 1895, **121**, 794, 851; 1897, **125**, 276; Defacqz, *ibid.*, 1897, **125**, 1174.

[2] Hartley and Ramage, *Journ. Chem. Soc.*, 1897, **71**, 547.

[3] *Phil. Trans.*, 1880, **171**, 1022.

dilute nitric acid. Aluminium is malleable and can be drawn into fine wire and hammered into very thin leaf. It can be best worked at a temperature of 100° to 150°. The commercial metal is very sonorous, emitting a tone when struck like that of flint glass. The cast metal has a density of 2·70 at 18°, and is as hard as silver, whilst the hammered metal has the hardness of soft iron, and a specific gravity of 2·67. The hardness is again diminished by further heating, and at 600° the metal can easily be broken and at a somewhat higher temperature can be crushed in a mortar.[1] It fuses at 658° ± 1° and boils at 1800°.[2] In order to remelt the metal, a fusing mixture of common salt and potassium chloride must be employed, as the presence of other fluxes, such as borax, glass, etc., renders the metal very impure.

On slowly cooling it assumes a crystalline structure, the forms indicating that it crystallises in octahedra. Its electrical conductivity is 61 per cent. of that of pure copper, whilst its thermal conductivity is 50 per cent. of that of copper, being second to this metal among the commoner metals. The mean specific heat of the metal between 0° and 100° is 0·218.[3] The tensile strength of aluminium in the sand cast form is about 12,000 lb. per square inch and in drawn bars 28,000 lb. per square inch, whilst that of a high carbon cast steel is 132,000. Pure aluminium does not oxidise at ordinary temperatures on exposure to air, but the impure metal soon becomes covered with a thin coating of oxide. When heated in oxygen it oxidises only on the surface without combustion. If a fine aluminium wire be wound round a piece of charcoal, the metal burns brightly with the charcoal in oxygen, and if a piece of thin aluminium foil or leaf be heated in a glass globe in an atmosphere of oxygen, it burns with a sudden flash of intensely white light. Clean aluminium powder, however, burns completely in air if strongly heated at one point, a small amount of nitride being formed along with the oxide.[4] Aluminium foil or powder decomposes water at 100°, being slowly converted into the hydroxide, which in the former case retains the form of the foil. It is not attacked at the ordinary temperature by water which has been boiled, but is acted on by

[1] Granger, *Bull. Soc. chim.*, 1902, [3], **27**, 789.

[2] Day, Sosman and Allen, *Amer. J. Sci.*, 1910, [4], **29**, 93; Greenwood, *Proc. Roy. Soc.*, 1909, [*A*], **82**, 396; 1910, [*A*], **83**, 483

[3] E. H Griffiths and E. Griffiths, *Phil. Trans.*, 1913, [*A*], **213**, 119.

[4] Matignon, *Compt. rend.*, 1900, **130**, 1391.

ordinary water.[1] It precipitates the metals lead, silver, and zinc from alkaline solutions, whilst neutral or acid solutions are not altered by it. It also precipitates metallic copper from a solution of copper sulphate.

Hydrochloric acid is the best solvent for aluminium. Dilute sulphuric acid, however, also dissolves it slowly with evolution of hydrogen, and concentrated sulphuric acid dissolves it on heating with evolution of sulphur dioxide. Dilute nitric acid acts slowly on the metals in the cold, ammonium salts being produced, but exerts a fairly vigorous action at the boiling point. The action diminishes as the concentration of the acid increases.[2] Organic acids attack it only slightly, but it dissolves in them with ease if the protecting layer of hydrogen which is produced is mechanically removed.[3] Aluminium is dissolved by aqueous alkalis, including ammonia, hydrogen being evolved. It is attacked also by sodium carbonate, both hydrogen and carbon dioxide being evolved and sodium aluminate produced. Sodium chloride also attacks the metal slowly, its action being greatly accelerated by the presence of a weak acid such as acetic acid, which dissolves the hydroxide formed (Ditte). The action of such a mixture is, moreover, greatly increased by exposure to the air. According to Wohler aluminium foil takes fire in a current of chlorine, but according to Böttger this is the case only when it is tied round with brass wire to which some Dutch metal is fastened. At high temperatures aluminium also combines with sulphur, selenium, tellurium, phosphorus, arsenic, and carbon,[4] and it forms characteristic alloys with many metals.

Aluminium also forms organo-metallic bodies such as aluminium methide, $Al(CH_3)_3$, and ethide, $Al(C_2H_5)_3$, both of which are liquids spontaneously inflammable in the air.

Aluminium possesses so many valuable properties, such, for instance, as its low specific gravity, fine lustre, unalterability in the air and in hydrogen sulphide, non-poisonous qualities, and ease of working, that a widespread application of the metal was

[1] Donatti, *Zeit. angew. Chem.*, 1895, 141; Seligman, *J. Inst. Met.*, 1920, **23**, 159.

[2] Lunge and Schmidt, *Zeit. angew. Chem.*, 1892, 7; Stillman, *J. Amer. Chem. Soc.*, 1897, **19**, 711; Woy, *Zeit. öffentl. Chem.*, 1903, **9**, 158; Watson Smith, *J. Soc. Chem. Ind*, 1904, **23**, 475. Compare van Deventer, *Chemisch Weekblad*, 1906, **4**, 69.

[3] Ditte, *Compt. rend.*, 1898, **127**, 919; 1899, **128**, 195, 793. See also Seligman and Williams, *J. Soc. Chem. Ind.*, 1916, **35**, 88; 1918, **37**, 159.

[4] See Matignon, *Compt. rend.*, 1900, **130**, 1391.

made as soon as the cheaper processes of manufacture lowered the price.

Aluminium is largely used for the production of carbon-free metals, especially manganese and chromium, and for the generation of intense heat to be used locally for the welding of iron and steel rails, etc. These processes have been developed by Goldschmidt,[1] whose patented " Thermite " consists of a mixture of granulated aluminium and the oxide of another metal, in equivalent proportions, the ignition of which causes the reduction of the metallic oxide present, owing to the strong affinity of aluminium for oxygen : *e.g.;*

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe.$$

The reaction can only be commenced at a high temperature, and for this reason an ignition powder is used, consisting of a mixture of aluminium with barium peroxide; this mixture can be ignited by means of a match, and yields sufficient heat to commence the thermite reaction. The temperature resulting from the above reaction may reach 3,000° C., and hence the process can be made use of in welding iron and steel materials, such as tram-rails, etc. According to one method the hot alumina resulting from the interaction of the aluminium and ferric oxide is poured round the two portions of metal to be welded, which are clamped tightly together when they have become sufficiently hot; in a second method the molten iron formed is itself allowed to flow around the portions of the metal to be welded, the exceedingly hot metal effecting a junction of the two surfaces and simultaneously by its own solidification mechanically strengthening the joint.

Aluminium is also added to steel during casting, as it tends to prevent the formation of blow-holes on solidification, acting in a similar manner to silicon.

Aluminium is now largely used in the automobile, cycle, and aircraft industries, for electric cables, for the manufacture of boiling pans for varnish and for heating oils and melting waxes, for condenser tubes and cooking utensils, and in the form of powder for paint.

Aluminium is also employed as a constituent of certain explosives, since it raises the temperature of explosion; thus *ammonal* consists of 72 per cent. ammonium nitrate, 3 per cent. carbon, and 25 per cent. aluminium.[2]

[1] See *J. Soc. Chem. Ind.*, 1898, **17**, 543.

[2] Bichel, *Zeit. angew. Chem.*, 1905, **18**, 1889.

328 *Alloys of Aluminium.*—Copper forms alloys with aluminium possessing the colour of gold and very many of these are in use.[1] That containing about 10 per cent. of aluminium is usually known as aluminium bronze and possesses the appearance of standard gold. For the preparation of this alloy pure copper must be employed, as that which contains iron yields an inferior product. The alloy is malleable, yields fine castings, takes a high polish, and has a tensile strength almost equal to that of cast steel. It is now used for the manufacture of physical apparatus as well as of ornamental goods.

Light alloys of aluminium and copper containing about 4 per cent. copper have been largely used during recent years. In the form of rolled bars and sheets they give a test approaching 17 tons per square inch. In some cases a portion of the copper has been replaced by manganese, 3 per cent. copper and 1 per cent. manganese or 2 per cent. of each of these elements being usual.

Aluminium-copper castings are also made containing between 11 and 13 per cent. copper which should give in the cast condition a tensile strength of 9 tons per square inch. Tin is also used in conjunction with copper for castings, the alloys generally containing 9 to 11 per cent. of copper with 0·5 to 1·5 per cent. tin or 6 to 8 per cent. copper with 0·5 to 2·0 per cent. tin.

The most important alloys used for castings are those with zinc and copper. According to the British Aircraft Material Specifications these alloys should contain between 12·5 and 14·5 per cent. zinc and between 2·5 and 3·0 per cent. copper, and should give in a cast state a tensile test of 11 tons per square inch with an elongation of 4 per cent.

Nickel is sometimes used instead of copper in light allloys.

Various alloys of aluminium containing magnesium are also used, the best known being *magnalium* and *duralumin*. These contain copper and seldom more than 2·0 per cent. magnesium.

Aluminium can be alloyed with silver, yielding a hard, easily polished alloy. That containing 4 per cent. of silver has been employed for the construction of beams for chemical balances, on account of its lightness and its unalterability in the air.

Gold and aluminium form a very interesting series of alloys. Gold containing 1 per cent. of aluminium has a green colour; with 10 per cent. it is white and brittle; and with 22 per cent.

[1] Dagger, *J. Soc. Chem. Ind*, 1894, **13**, 4.

deep purple, this latter alloy having a melting point about 20° higher than that of pure gold.[1]

Aluminium combines easily with sodium and potassium, and the alloy containing only 2 per cent of sodium decomposes water.

Aluminium also combines with mercury when it is moistened with caustic alkali, or when the two metals are fused together in an indifferent gas. The amalgam is very brittle, oxidises easily in the air, and decomposes water at the ordinary temperature. The amalgam is also formed when aluminium foil is immersed in a solution of mercuric chloride. It has been employed as a reducing agent[2] for the estimation of water and for the preparation of many organic compounds.

The following are some of the aluminium alloys used in the industries with their technical names:

Acid Bronze	Cu 90, Al 10
Aluminium Brass	Cu 68–70, Zn 27–31, Al 1–3
Argentan	Cu 70, Ni 23, Al 7
Duralumin	Al 93·2–95·5, Cu 3·5–5·5, Mn 0·5–0·8, Mg 0·5
Gold Bronze	Cu 95–97, Al 3–5
Grossman's Alloy	Al 87, Cu 8, Sn 5
Partinium	Al 88·7, Cu 6·8, Zn 4·5
Steel Bronze	Cu 90·5, Al 8·5, Si 1·0
Tiers Argent	Al 66·6, Ag 33·3

COMPOUNDS OF ALUMINIUM.

Aluminium and Oxygen.

329 Aluminium and oxygen form the stable oxide, Al_2O_3, which corresponds with the aluminium salts. There is also some possibility of the existence of one or more *lower oxides*, formed by the incomplete oxidation of aluminium in the air, or by the reduction of alumina by metallic aluminium.[3]

Aluminium Oxide or *Alumina*, Al_2O_3, is found in nature as

[1] Roberts-Austen, *Proc. Roy. Soc.*, 1892, **50**, 367. Compare Heycock and Neville, *Phil. Trans.*, 1900, *A.*, **194**, 201.

[2] Ormandy and Cohen, *Journ. Chem Soc.*, 1890, **57**, 811; Wislicenus, *J. pr. Chem*, 1896, **54**, 18.

[3] Pionchon, *Compt. rend.*, 1893, **117**, 328; Duboin, *ibid.*, 1901, **132**, 826; Kohn-Abrest, *Bull. Soc. chim.*, 1904, [3], **31**, 232; *Compt. rend.*, 1905, **141**, 323.

the mineral corundum, which crystallises in hexagonal prisms, and occurs in several varieties. The more or less colourless crystals, as well as those which are coloured brown by ferric oxide and which are either translucent or opaque, are called corundum: those which are coloured red by chromium compounds are termed ruby, whilst those which have a blue tint, due to an oxide of titanium, are known as sapphires. The yellow crystals are termed oriental topaz, and the purple oriental amethyst, whilst the green are called oriental emeralds. Coarse and granular corundum containing magnetite or hæmatite intimately mixed with it, and having a grey or blackish colour, is termed emery. Of this mineral there are many gradations, from the finely ground emery to those kinds in which the corundum is present in distinct crystals. Crystallised alumina is excelled in hardness only by the diamond and silicon carbide (carborundum), and hence it is largely used for polishing and grinding the surfaces of glass and metal.

When aluminium hydroxide or aluminium salts containing volatile oxy-acids are heated, alumina remains either as a white powder or in amorphous gum-like masses. If this is not too strongly ignited it dissolves in concentrated acids, which, however, do not attack the crystallised compound. When more strongly ignited, amorphous alumina becomes denser and harder. After ignition in the flame of the spirit lamp it has a specific gravity of 3·5, and when more strongly heated in a porcelain-kiln it attains a specific gravity of 3·9. It is then nearly as hard as corundum but still amorphous (H. Rose). Alumina melts at 2010° to 2050° to a thin liquid, which, on cooling, assumes a crystalline structure and possesses all the properties of corundum. A similar oxide may be obtained by the combustion of the finely divided metal. If aluminium hydroxide is moistened with potassium dichromate and the dried mass fused before the oxy-hydrogen blow pipe, artificial ruby is obtained (Gaudin), and the same material may be prepared by heating to whiteness a mixture of borax and amorphous alumina containing a small quantity of chromium sesquioxide (Ebelmen). Crystallised alumina is also obtained when aluminium fluoride is allowed to act upon boron trioxide at a very high temperature (Deville and Caron), when aluminium phosphate is fused with sodium sulphate (Debray), and when alumina is heated to dull redness in hydrochloric acid gas at a pressure of three atmospheres.[1]

[1] Hautefeuille and Peney, *Compt. rend.*, 1890, **110**, 1038.

Fremy, Feil, and Verneuil [1] obtained crystallised alumina on the large scale by heating equal parts of alumina and lead oxide to a bright red heat. The product consisted of two distinct layers: one of these was composed of lead silicate derived from the action of the lead oxide upon the silica of the crucible; the other was a vitreous mass, and contained cavities filled with colourless crystals of corundum. By the addition of from 2 to 3 per cent. of potassium dichromate to the materials crystals of ruby were obtained. Splendid crystals of rose-red coloured ruby were obtained by heating a mixture of equal parts of alumina and barium fluoride with from 2 to 3 per cent. of potassium dichromate to a very high temperature in a glass furnace. This is explained by the production of a volatile fluoride of aluminium which undergoes decomposition in contact with the gases of the furnace, with evolution of hydrofluoric acid and deposition of crystalline alumina, the crystals being found in the upper part of the crucible. Similar rose-red crystals are formed when chlorine is passed over a heated mixture of sodium aluminate and 1 per cent. of potassium dichromate.[2]

Synthetic rubies are now prepared by the crystallisation of alumina containing 2·5 per cent. of oxide of chromium, the process being carried out in an oxy-coal gas flame according to a procedure devised by Verneuil.[3] The same chemist has devised a similar process for producing sapphires, by crystallising alumina containing 0·5 per cent. of oxide of titanium and 1·5 per cent. of magnetic iron oxide in an oxy-hydrogen reducing flame.[4]

In order to dissolve crystallised alumina it must either be fused with caustic potash or with acid potassium sulphate. It is also dissolved when heated in sealed tubes with concentrated sulphuric acid.

Hydroxides of Aluminium.—Several of these occur in nature. The most important are hydrargillite or gibbsite, $Al(OH)_3$; diaspore, AlO(OH), both of which are crystalline; and bauxite, impure Al_2O_3, which is found as an amorphous mass of varying composition.

When ammonia is added to a soluble salt of aluminium in the

[1] *Compt. rend.*, 1877, **85**, 1029; 1887, **104**, 737, 738; 1888, **106**, 565; 1890, **111**, 667.

[2] Loyer, *Bull. Soc. chim.*, 1897, [3], **17**, 345.

[3] *Ann. Chim. Phys.*, 1904, [8], **3**, 20.

[4] Verneuil, *Compt. rend*, 1910, **150**, 185

cold, a gelatinous precipitate falls down, but when it is added at the boiling point an opaque white precipitate is deposited.

The composition of the amorphous hydroxide thus obtained is a matter of some doubt. According to Ramsay,[1] when dried in the air it has the composition $Al_2O_3,5H_2O$ and gradually loses water as the temperature is raised, until at 300° it has approximately the composition Al_2O_3,H_2O. Allen,[2] on the other hand, considers that the amorphous hydroxide is $Al(OH)_3$ or $Al_2O_3,3H_2O$; when it is heated at 100° or dried over sulphuric acid it forms $Al_2O_3,2H_2O$, which is hygroscopic and takes up water again from the air, regaining its original composition.

The freshly precipitated hydroxide is easily soluble in acids, but the naturally occurring crystallised hydroxides are attacked by acids only after moderate heating. The ordinary hydroxide, however, when preserved under water for several months becomes very difficultly soluble in alkalis and acids, with the exception of concentrated sulphuric acid, in which it dissolves readily. This form of hydroxide has the composition $Al_2O_3,3H_2O$ and is termed by Tommasi [3] the δ-modification.

The amorphous hydroxide is also readily soluble in caustic alkalis, with which it forms salts of the type M^IAlO_2, which are considerably hydrolysed in solution.[4] Unless the atomic ratio M^I to Al exceeds two, these solutions are unstable, and slowly deposit aluminium hydroxide in a form which is much less soluble, both in acids and alkalis, than the original hydroxide. This precipitated hydroxide is generally regarded as being identical with the crystalline mineral gibbsite,[5] but according to Russ [6] it is not crystalline and is best known as the β-modification. The amount of precipitate obtained depends on the temperature, the concentration and the molecular ratio of soda and alumina present. Thus at 21°, with a solution containing $Al_2O_3 : Na_2O =$ 1 : 1·24, the maximum yield is obtained from a solution of specific gravity 1·173 and amounts to 86 per cent. of the alumina present.

This reaction is utilised in the preparation of aluminium hydroxide from bauxite, which is carried out on a very large

[1] *Journ. Chem. Soc.*, 1877, ii, 395.

[2] *Chem. News*, 1900, **82**, 75.

[3] *Journ. Chem. Soc.*, 1905, **88**, ii., 712.

[4] Noyes and Whitney, *Zeit. physikal. Chem.*, 1894, **15**, 694; Herz, *Zeit. anorg. Chem.*, 1900, **25**, 155; Hantzsch, *ibid.*, 1902, **30**, 296; Slade, *ibid.*, 1912, **77**, 457; J. Hildebrand, *J. Amer. Chem. Soc.*, 1913, **35**, 864; Blum, *ibid.*, 1913, **35**, 1499; Slade and Polack, *Trans. Faraday Soc*, 1914, **10**, 150.

[5] Ditte, *Compt. rend.*, 1893, **116**, 183.

[6] Russ, *Zeit. anorg. Chem.*, 1904, **41**, 216.

scale to provide material for the manufacture both of metallic aluminium and of many of the salts. The alumina is made from native bauxite, which contains ferric oxide, silica, and small quantities of titanic oxide. In order to remove these impurities the bauxite is roasted to oxidise the iron completely to the ferric state. It is then digested under pressure of about 80 lb. with caustic soda. Sodium aluminate is thus formed from which the impurities are filtered off after dilution. The solution of sodium aluminate is then treated with some pure precipitated aluminium hydroxide, when the bulk of the aluminium is precipitated as hydrated oxide, which after washing and drying is obtained as a snow white powder. The alkali solution is concentrated and employed again.

The hydroxide is also manufactured from cryolite by the process already described under the alkali manufacture (p. 316).

Aluminium hydroxide as usually obtained is only very slightly soluble in aqueous ammonia, but a form soluble in ammonia can be prepared by the decomposition of certain aluminates with ammonium chloride and a large excess of ammonia. The hydroxide readily dissolves in methylamine and other organic bases.[1]

Aluminium hydroxide occurs also in two soluble modifications, both of which are colloidal. One of these, which when dried at 100° has the composition $Al_2O(OH)_4 = Al_2O_3 + 2H_2O$, was obtained by Walter Crum [2] by preparing a solution of normal aluminium acetate by the mutual decomposition of lead acetate and aluminium sulphate. This, on heating, decomposes with separation of the basic acetate, $Al_2(C_2H_3O_2)_4(OH)_2,H_2O$, which becomes soluble on treatment for one and a half hours with 200 times its weight of boiling water. If this solution is allowed to stand for ten days and nights at the temperature of boiling water in a closed flask, the acetic acid separates from the alumina. After a sufficient quantity of water has been added to reduce the percentage of alumina to 0·25, the liquid is heated in a flat basin to the boiling point, fresh water being constantly added to replace that lost by evaporation, until all the acetic acid has been driven off. The solution then is perfectly neutral and tasteless, but becomes gelatinous on evaporation.

The second soluble hydroxide of aluminium was obtained by Graham [3] by dialysis of the basic chloride obtained by dissolving

[1] Renz, *Ber.*, 1903, **36**, 2751.

[2] *Chem. Soc. Quart. Journ.*, 1854, **6**, 216.

[3] *Phil. Trans.*, 1861, **151**, 183. See also Schneider, *Annalen*, 1890, **257**, 359; Hantzsch and Desel., *Annalen*, 1902, **323**, 30.

the hydroxide in the normal chloride. The normal salt passes through the parchment paper into the water, and a neutral tasteless solution containing alumina remains in the dialyser. This is very unstable, and after some days passes into a jelly. Both these soluble hydroxides are coagulated on the addition of traces of a salt, an acid, or an alkali. Graham's compound acts as a mordant, uniting with colouring matters to form lakes, and in the coagulated state is readily soluble in acids. Crum's compound, on the other hand, termed by Graham " meta-aluminium hydroxide," does not combine with colouring matter and does not dissolve in excess of acid.

Precipitated aluminium hydroxide possesses in high degree the power of withdrawing from solution both inorganic salts and organic bodies. This property is employed in dyeing.

Aluminium peroxide,[1] $Al_2O_3,Al_2O_4,10H_2O$, is obtained by adding an excess of 30 per cent. hydrogen peroxide to aluminium hydroxide dissolved in 30 per cent. solution of potassium hydroxide. Probably the first product of the reaction is Al_2O_4, which is changed by hydrolysis.

Aluminates.—Like other weak bases, alumina acts toward the stronger bases as an acid-forming oxide; thus precipitated alumina dissolves in solutions of the caustic alkalis forming definite salts, which can also be prepared by the action of the alkalis on metallic aluminium.[2]

Potassium Aluminate, $KAlO_2,1\frac{1}{2}H_2O$, is obtained in hard glistening crystals when alumina and potash are fused together in a silver basin, the solid residue dissolved in water, and the solution evaporated in a vacuum.

Sodium Aluminate, $NaAlO_2$.—This substance is prepared on the large scale by fusing cryolite with lime, or bauxite with soda or sodium sulphate and carbon, as well as with common salt in a current of steam. When the melted mass is lixiviated with water and the solution evaporated to dryness, sodium aluminate is obtained. As already mentioned, its aqueous solution decomposes in presence of aluminium hydroxide. This substance is used as a mordant in dyeing and calico-printing, for the preparation of coloured lakes and of pure alumina, and for the sizing of paper, &c.

Magnesium Aluminate, $MgAl_2O_4$.—This substance occurs in

[1] Terni, *Atti R. Accad. Lincei*, 1912, [5], **21**, ii., 104.

[2] See Allen and Rogers, *Amer. Chem. J.*, 1900, **24**, 304; Hawley, *J. Amer. Chem Soc*, 1907, **29**, 300.

nature as spinel. It crystallises in regular octahedra, isomorphous with magnetite, and is either colourless or variously tinted, and is classed in various species according as either the whole or a part of the magnesium and aluminium is replaced by isomorphous metals. Thus spinel is $(Mg,Fe)(Al,Fe)_2O_4$; zinc-spinel or gahnite is $(Zn,Fe,Mg)(Al,Fe)_2O_4$, etc.

The naturally occurring aluminates were artificially prepared by Ebelmen, by fusing alumina and the corresponding oxide with boron trioxide. This latter substance, which served as a solvent, was almost entirely volatilised at a very high temperature. In this way colourless spinel was obtained, and this was coloured red by chromium, blue by cobalt, and black by iron; by a similar process the aluminates of barium, glucinum, iron, manganese, etc., can be prepared. Deville and Caron also obtained crystals of gahnite and chrysoberyl, $Be(AlO_2)_2$, by heating aluminium fluoride, together with fluoride of zinc or glucinum, in a carbon crucible which contained a platinum basin filled with boron trioxide.

Salts of Aluminium.

330 Aluminium forms only one series of salts, in which one atom of the metal replaces three atoms of hydrogen. Alumina acts as a very weak base and the salts, especially those derived from weak acids, such as acetic acid, are very readily decomposed by boiling their aqueous solutions, a basic salt or the hydroxide being formed.

Many compounds of aluminium are isomorphous with the corresponding compounds of iron, manganese, and chromium.

Aluminium and the Halogens.

331 *Aluminium Fluoride*, AlF_3, is best obtained by evaporating to dryness a solution of aluminium in hydrofluoric acid, and subliming the residue, contained in a carbon tube, in a current of hydrogen.[1] It forms transparent, very obtuse rhombohedra, which were formerly supposed to be cubes. It is permanent in the air, insoluble in water, and unaltered in the presence of acids and aqueous alkalis, but it is decomposed by long-continued fusion with sodium carbonate. Aluminium dissolves readily in excess of hydrofluoric acid, and from this solution the

[1] Brunner, *Pogg. Ann.*, 1856, **98**, 488; Deville, *Ann. Chim. Phys.*, 1857, [iii.], **49**, 79; 1861, [3], **61**, 333.

hydrate, $2AlF_3,7H_2O$, can be obtained in two forms, one soluble and the other insoluble in water.[1] The fluoride forms a series of double fluorides, of which the most important is:

Aluminium Sodium Fluoride, $AlF_3,3NaF$.—This occurs as the mineral cryolite at Ivigtut, in the Arksutfjord, on the south-west coast of Greenland, where it forms a bed 80 feet thick and 300 feet long. It was discovered in this locality by Andrada at the end of the eighteenth century. Its mineralogical name was given to it by him inasmuch as it had an ice-like appearance. The investigations of Albidgaard showed that it contained hydrofluoric acid, alumina, and an alkali metal, and Klaproth found the alkali to be soda. The exact composition of cryolite was determined by Vauquelin, Berzelius, and Deville, and in 1849—1850 Julius Thomsen showed that this mineral could be decomposed in the dry way by means of lime and lime salts as well as in the wet way, and upon this observation an important Danish industry was founded (p. 316). Cryolite usually occurs in masses of a snow-white, reddish, brownish, or bluish colour, which possess easy cleavage; it is found more rarely in triclinic crystals. When acted upon with concentrated sulphuric acid it evolves hydrofluoric acid, and the residue contains sodium sulphate, which may be dissolved by the action of cold water, the anhydrous aluminium sulphate, which is formed at the same time, dissolving only in boiling water.

Aluminium Chloride, $AlCl_3$, was first prepared by Oersted by heating a mixture of carbon and alumina in a current of dry chlorine. This method was afterwards adopted and improved by Wohler,[2] Liebig,[3] Bunsen,[4] and Deville.[5] It may also be readily prepared in a pure condition by heating aluminium in chlorine or in hydrochloric acid gas,[6] the reaction, in the latter case, proceeding when once started without requiring any external heating.[7] The oxide is readily converted into the chloride by heating it in a stream of sulphur chloride and chlorine.[8]

$$4Al_2O_3 + 3S_2Cl_2 + 9Cl_2 = 8AlCl_3 + 6SO_2.$$

[1] Baud, *Compt. rend.*, 1902, **135**, 1103; *Ann. Chim. Phys*, 1904, [8], **1**, 8.
[2] *Pogg. Ann.*, 1827, **11**, 146. [3] *Ibid.*, 1830, **18**, 43.
[4] *Ibid.*, 1854, **92**, 648. [5] *Compt. rend.*, 1849, **29**, 321.
[6] Nilson and Pettersson, *Zeit. physikal. Chem.*, 1887, **1**, 459; Stockhausen and Gattermann, *Ber.*, 1892, **25**, 3521; Gustavson, *J. pr. Chem.*, 1901, [2], **63**, 110.
[7] Escales, *Ber.*, 1897, **30**, 1314.
[8] Matignon and Bourion, *Compt rend*, 1904, **138**, 631, 760, Bourion, *Ann. Chim. Phys*, 1910, [8], **20**, 547.

Pure aluminium chloride is a white crystalline solid. It usually possesses, however, a yellowish or greenish colour, due to the presence of ferric chloride and other impurities. When heated it volatilises slowly without fusion, and condenses in hexagonal tablets, but if a large quantity is quickly heated the mass fuses and then boils. When heated in a sealed tube it melts at 194°; the boiling point of the liquid appears to be about 179°.[1] The density of the vapour, according to the experiments of Nilson and Pettersson (p. 33), corresponds to the formula $AlCl_3$, at temperatures above 750°.[2] The molecular weight of the chloride in solution in pyridine,[3] as determined by the boiling point method, also corresponds with the formula $AlCl_3$. Aluminium chloride is hygroscopic, absorbing water from the air and emitting fumes of hydrogen chloride. It is also easily soluble in alcohol and ether.

When hydrochloric acid gas is passed into a solution of aluminium chloride in concentrated hydrochloric acid, large hexagonal prisms having the composition $AlCl_2,6H_2O$ separate out;[4] these are obtained also by the evaporation of a solution of aluminium chloride in water or of aluminium hydroxide in hydrochloric acid, and on further heating are easily decomposed into water, hydrochloric acid, and residual alumina.

Aluminium chloride absorbs dry ammonia gas and yields a bulky white powder of the composition $AlCl_3,6NH_3$, which loses one molecule of ammonia at 180°, and when heated in a stream of hydrogen at 450° yields a sublimate of the compound $6AlCl_3,7NH_3$. At — 23° a compound, $AlCl_3,9NH_3$, is produced.[5] Aluminium chloride also combines with phosphorus pentachloride, phosphorus oxychloride, carbonyl chloride, sulphuretted hydrogen,[6] sulphur dioxide, sulphur tetrachloride,[7] the chlorides of silver, selenium, and tellurium, as well as with other metallic chlorides. It is largely employed in the synthesis of organic compounds.

Sodium Aluminium Chloride, $AlCl_3,NaCl$, is a colourless crystal-

[1] Seubert and Pollard, *Ber.*, 1891, **24**, 2575.

[2] *Zeit. physikal. Chem*, 1887, **1**, 459; 1889, **4**, 206.

[3] Werner, *Zeit. anorg. Chem*, 1897, **15**, 1. Compare Kohler, *Amer. Chem. J.*, 1900, **24**, 385.

[4] Dennis, *Zeit. anorg. Chem.*, 1895, **9**, 339.

[5] Baud, *Compt. rend.*, 1901, **132**, 134, 690; *Ann. Chim. Phys*, 1904, [8], **1**, 8. Compare Stillman and Yoder, *Amer. Chem. J.*, 1895, **17**, 748; and Persoz, *Ann. Chim. Phys*, 1830, [2], **44**, 319.

[6] Baud, *Compt. rend.*, 1902, **134**, 1429; 1905, **140**, 1688.

[7] Ruff, *Ber.*, 1901, **34**, 1749; 1902, **35**, 4453.

line mass which melts at 185° (Bunsen) and volatilises at a red heat. It readily absorbs water, but in the compact state it is less hygroscopic than aluminium chloride, and for this reason it was formerly used instead of the latter compound in the preparation of aluminium by the method of Deville.

Aluminium Bromide, $AlBr_3$.—When aluminium and bromine are brought together they combine with evolution of heat, forming the above compound. It is obtained by passing the vapour of bromine over the metal or a heated mixture of alumina and carbon. It forms pale yellow rhombohedral crystals [1] which melt at 93°, boil at 263·3° (747 mm.), and sublime in crystalline scales. The specific gravity of the solid is 2·54. In other respects it is analogous to the chloride, and forms the hydrate $AlBr_3,6H_2O$. The molecular weight as determined by the boiling point and freezing point methods with a solution of the bromide in bromine,[2] and by the boiling point method with a solution in carbon disulphide,[3] corresponds with the formula Al_2Br_6. The bromide forms a conducting solution in ethyl bromide, from which aluminium may be deposited by electrolysis.[4]

Aluminium Iodide, AlI_3, is formed when the metal and iodine are heated together in closed tubes, or brought together in presence of carbon disulphide. It is deposited in colourless crystals which melt at 125° (Weber) and boil at a temperature of 350°. Its specific gravity is 2·63. The vapour is combustible, giving rise to an explosive mixture when diluted with air. It is soluble in water, alcohol, and carbon disulphide, and forms a crystalline hydrate, $AlI_3,6H_2O$. Aluminium iodide has been employed for the purpose of converting organic chlorine compounds into iodides. Thus carbon tetrachloride yields the corresponding tetraiodide when heated with aluminium iodide (Gustavson):

$$4AlI_3 + 3CCl_4 = 4AlCl_3 + 3CI_4.$$

Aluminium and the Elements of the Sulphur Group.

332 *Aluminium Sulphide*, Al_2S_3.—Aluminium combines with sulphur at a red heat to produce this compound,[5] which is a yellow

[1] Patten, *J. Physical Chem.*, 1904, **8**, 548.

[2] Beckmann, *Zeit. anorg. Chem.*, 1906, **51**, 96.

[3] Kohler, *Amer. Chem. J.*, 1900, **24**, 385.

[4] Poltnikoff, *J. Russ. Phys. Chem. Soc.*, 1902. **34**, 466; Patten, *J. Physical Chem.*, 1904, **8**, 548.

[5] Knapp and Ebell, *Dingl. Polyt. Journ.*, 1878, **229**, 69, 173; Fonzes-Diacon, *Compt. rend.*, 1900, **130**, 134; W. Biltz and Caspari, *Zeit. anorg. Chem.*, 1911, **71**, 182.

mass. It is also formed when sulphur is added to a strongly heated mixture of alumina and charcoal,[1] when the vapour of carbon disulphide is passed over strongly heated alumina and, along with oxysulphide, when sulphuretted hydrogen is passed over heated alumina.[2] It melts at 1110°, and at 2100° in an inert atmosphere it loses sulphur and is converted into *aluminium subsulphide*, AlS (Biltz and Caspari).

It is decomposed with water with formation of sulphuretted hydrogen and aluminium hydroxide. The *selenide*[3] and *telluride*[4] are also formed by direct union of the elements.

Aluminium Sulphate, $Al_2(SO_4)_3$, is obtained by dissolving the hydroxide in dilute sulphuric acid. It crystallises with difficulty, forming pearly six-sided monoclinic tablets containing $18H_2O$. It possesses a sweet astringent taste, and dissolves in two parts of cold water, scarcely at all in alcohol (Berzelius), and readily in glycol. This hydrated salt is found as the mineral keramohalite in the neighbourhood of active volcanoes, and in alum shale. It melts on heating in its water of crystallisation, and then swells up, the anhydrous compound being left behind as a porous mass, dissolving only slowly again in water. At a red heat it is decomposed, leaving a residue of pure alumina. The concentrated solution of this salt is a useful reagent for potassium salts, as potassium alum, $Al_2K_2(SO_4)_4,24H_2O$, is precipitated as a crystalline powder, which is almost completely insoluble in an excess of aluminium sulphate.[5] A hydrate with $9H_2O$ is precipitated from aqueous solutions of the sulphate by alcohol, and a hydrate with $6H_2O$ is formed when $Al_2(SO_4)_3,18H_2O$ is heated with concentrated sulphuric acid.[6]

Aluminium sulphate is prepared on the large scale, and is known in commerce under the name of concentrated alum or sulphate of alumina. For this preparation china clay, as free as possible from iron, is employed. This is roasted in a reverberatory furnace, by which any iron which may be present is rendered insoluble, whilst the aluminium silicate becomes more soluble in sulphuric acid. It is then heated in leaden boilers with sulphuric acid of specific gravity 1·45, and the

[1] Bucherer, *Zeit. angew. Chem*, 1892, **5**, 483.

[2] Gautier, *Compt. rend.*, 1906, **143**, 7.

[3] Fonzes-Diacon, *Compt. rend.*, 1900, **130**, 1314; Chikashige and Aoki, *Mem. Coll. Sci. Kyoto*, 1917, **2**, 249.

[4] Whitehead, *J. Amer. Chem. Soc.*, 1895, **17**, 849; Chikashige and Nosé, *Mem. Coll. Sci. Kyoto*, 1917, **2**, 227.

[5] Wurtz, *Dict.*, i., 174.

[6] Schmatolla, *Zeit. angew. Chem.*, 1903, **16**, 202.

solution is allowed to deposit the silica and any undecomposed silicate. The clear liquid is then evaporated down until a small portion on cooling is found to solidify. After cooling, the soft mass is cut into square blocks and thus brought into the market. This material is employed by the dyer as a mordant, and also for the purpose of weighting paper and for the treatment of sewage.

An impure product, known under the name of *alum-cake*, also used largely by paper-makers, is obtained by heating a white china clay or bauxite with sulphuric acid. The whole mass then becomes solid. It consists of about 12–15 per cent. of soluble alumina as sulphate, together with silica and undecomposed aluminate.

For many purposes a sulphate perfectly free from iron is needed. This is prepared by dissolving the pure hydroxide in sulphuric acid, or by treating a solution of the crude sulphate with pyrolusite (Spence) or calcium ferrocyanide solution (Kynaston).

According to Berzelius a series of basic sulphates of aluminium exists, but these are probably mixtures. One of them occurs in clay deposits as the mineral aluminite or websterite. It forms an earthy mass, having the composition $Al_2(SO_4)(OH)_4,7H_2O$. The same salt is formed when aluminium sulphate is precipitated with a quantity of ammonia insufficient to throw down the whole of the alumina. When a concentrated solution of aluminium sulphate is boiled with the freshly precipitated hydroxide a thick solution is formed, and this, on standing for some months, deposits a crust of small needle-shaped crystals of a salt having the composition $Al_2(SO_4)_2(OH)_2,2Al_2(SO_4)(OH)_4,25H_2O$ (Rammelsberg).

A crystalline soluble basic sulphate, $Al_2O_3,2SO_3$, can be prepared by heating an excess of alumina with sulphuric acid under pressure, adding a little lime, evaporating the clear liquor, and allowing to crystallise.[1]

A crystalline *chlorosulphate*, $AlSO_4Cl,6H_2O$, is formed when concentrated hydrochloric acid is added to a solution of the sulphate. It is at once decomposed by water.[2]

The Alums.

333 Aluminium sulphate forms with the sulphates of the alkali metals double salts, which crystallise in regular octahedra,

[1] Spence, German Patent 167419 (17/4/1903).

[2] Recoura, *Compt. rend.*, 1902, **135**, 736.

and the potassium double salt, $Al_2(SO_4)_3,K_2SO_4,24H_2O$, has long been known under the name of *alum*. This name is, however, now used to designate a whole group of bodies. A number of substances with an astringent taste were known to the Greeks (στυπτηρία) and the Romans (alumen), and among these the naturally occurring aluminium sulphate and alum seem to have been included. We also find the name occurring in the writings of the Latin Geber, who speaks of an ice-alum, which is obtained from Roccha, and which he was able to purify by recrystallisation. The alchemists of the West described this salt as *alumen de rocca*, in order to distinguish it from the vitriols, and this name was afterwards erroneously translated by the French chemists, who termed pure alum *alun de roche*.

In the thirteenth century an alum factory, erected by Italians, existed near Smyrna. They obtained their alum by roasting alum-rock, lixiviating the product, and crystallising. In the fifteenth century the Genoese erected alum works on the island of Ischia, and at the same time the celebrated works at Tolfa, in the Papal States, were established. The so-called Roman alum, which was there prepared, was, up to recent times, considered to be the best, and the manufacture has been resuscitated, 10,000 tons of alum being made annually at Tolfa by a French company. The material from which the alum is manufactured in various places in Italy, as well as in Hungary, is the alum-rock, the chief constituent of which is the mineral alunite or alum-stone, which is itself a double compound of potassium sulphate and basic aluminium sulphate, possessing the formula $K_2SO_4,3Al_2(SO_4)(OH)_4$. The rock is a product of the action of steam and sulphur dioxide on trachyte, and consists chiefly of a mixture of quartz and alum-stone. This is mixed with fuel in heaps, or in a furnace similar to a lime-kiln, and the roasted mass exposed for some weeks to the air. It then falls to a soft material, which is lixiviated with hot water, and the clear liquid, on standing, is concentrated in copper pans, and allowed to crystallise in wooden vessels. The crystals have a slightly orange-red colour, a very characteristic property of Roman alum, due to the presence of very finely divided ferric oxide, which is mechanically mixed in the mass. On crystallising the alum from hot water this is left behind in the form of a reddish deposit.

Another method for preparing alum has long been known and is described by Agricola and Libavius. For this purpose shale is employed. This chiefly occurs in the Silurian and

Devonian formations, and contains finely divided iron pyrites, distributed through a mass of bituminous shale. The shale is heaped together and is either allowed to decompose slowly by exposure to the air, or it is roasted. In either case the pyrites is oxidised with formation of ferrous sulphate and free sulphuric acid, both of which act upon the clay, producing aluminium sulphate, which is then dissolved out with water. It was early known that the ley thus obtained did not crystallise until an alkali had been added to it. Both Agricola and Libavius state that it is customary to add decomposed urine to the ley, in order, as the latter author remarks, to separate out the vitriol which is contained in solution. The alum thus prepared must have been chiefly ammonia-alum. This conclusion is corroborated by Kunkel's remark, for we find that he states distinctly in his *Laboratorium Chymicum* that alum contains the volatile alkali. Instead of urine, potash was soon used, and Hoffmann, in 1722, explained why an alkali was added, and this explanation, namely, that the crude ley was unable to crystallise because it was too acid, and also because it contained a sulphurous impurity which had to be removed by the addition of alkali, was the one which was accepted as correct until the end of the eighteenth century. At that time, and even up to a later date, it was not generally admitted that an alkali formed an essential constituent of alum. Moreover, alum was often prepared without the addition of such an alkali, for in those days the existence of a potassium compound in a mineral such as alunite was not known. Bergman and Scheele, who were well aware that alum contained potash, considered it to be an impurity. Marggraf then showed that pure alumina and sulphuric acid formed an alum only when an alkali was added, and hence Lavoisier concluded that two bases were contained in alum, viz., the alumina and the fixed alkali. These views were not generally accepted until 1797, when Chaptel and Vauquelin showed that potash was an essential constituent of alum; the latter chemist, moreover, proved that this fixed alkali could be replaced by ammonia, and asserted that when aluminous minerals yielded an alum with sulphuric acid, it was proof that these minerals contained potash.

The crude ley from the lixiviation of the burnt shale consists essentially of the sulphates of aluminium and iron. The solution is then evaporated down in order that the iron salt may be deposited, and the solution ultimately obtained, which has a specific gravity of 1·4, contains aluminium sulphate, with a small quantity of ferric sulphate. In order to obtain alum from this

solution a potassium salt is added, and as the double salt formed is sparingly soluble, it separates out at once from the concentrated solution. It is most economical to employ a mixture of potassium sulphate and chloride, in different proportions, to be determined according to the composition of the ley, in order to avoid loss of aluminium as aluminium chloride or of potassium as ferrous potassium sulphate if ferrous sulphate be present. The crude potassium chloride from Stassfurt is now usually employed as the source of the potash. This substance is dissolved in a small quantity of hot water, and the solution added to the crude ley, and alum-meal is then obtained by well stirring the mixture until it is cold. The small crystals of which the meal consists are washed with a small quantity of cold water, the first wash-water being allowed to run into the boiling-down pans, and the last wash-water being employed for washing the crude alum. The purified meal is then dissolved in boiling water or by means of a current of steam, and the solution is brought into large crystallising vats built of movable staves bound together with iron hoops, where the alum is deposited in the large crystals of commerce.

Until recent years the chief quantity of alum made in England has been ammonium alum, prepared according to Spence's method. In this process the black bituminous shale lying above the coal-measures is employed as the source of alumina. This is made into heaps about 1·5 m. in height and slowly roasted. The mass, which when roasted has a light red colour and is brittle, is then brought into large covered pans, mixed with sulphuric acid diluted with washings obtained in the final stages of the process, and heated by means of steam coils placed in the pan, until the liquors contain only a small percentage of free acid. The impure solution of aluminium sulphate is then run into cooling tanks, on the way receiving a sufficient quantity of either ammonium or potassium sulphate to convert it into ammonium or potassium alum as required. It is then diluted with liquors from a later stage in the process and stirred until cold to obtain small crystals of alum meal, the liquor run off, and the mealy alum washed with liquors and a small quantity of water. This is then drained and brought into a funnel-shaped vessel, where steam is allowed to blow on it in such a manner that the whole of the steam is condensed and all the salt dissolved. In half an hour about four tons of alum meal can thus be dissolved. The solution is allowed to settle in lead-lined cisterns, and then brought into crystallising vats and allowed to remain in them for

a week. The staves are then knocked away, and a cylindrical block of alum remains, which is allowed to stand another week. A hole is afterwards drilled into the bottom of the block, the mother-liquor allowed to run out, and the mass broken up. Each vat yields three tons of large crystals, which frequently possess an amethystine tint resembling alum containing much iron, although they contain less than 0·001 per cent. of that metal. This colour is probably due to minute quantities of iron and chromium, and not to organic matter.

Since the introduction of cheap potassium chloride from Stassfurt, ammonium alum is no longer so largely made in England, the potassium compound being manufactured and employed instead.

Shale is no longer used in many works as a source of alum, bauxite being employed and submitted to a similar treatment.

331 *Potassium Alum*, $Al_2(SO_4)_3,K_2SO_4,24H_2O$, is found in nature in feathery or mealy crusts or masses, as an efflorescence on alum shale, and in volcanic districts, where it is formed by the action of sulphur dioxide and oxygen on trachyte and lava. In some places, as in the districts near Naples and in Sicily, alum is produced in sufficient quantity to render its manufacture possible, and a very pure alum is obtained from this source. Potash alum has a specific gravity of 1·751; it crystallises in transparent regular octahedra, which often exhibit the cube and dodecahedron faces; its solution possesses a sweet astringent taste, and has an acid reaction. One hundred parts of water dissolve (Locke): [1]

At	0°	10°	20°	30°	40°	
$K_2Al_2(SO_4)_4,24H_2O$	5·65	7·6	11·4	16·6	23·8	parts

At	50°	60°	70°	80°	
$K_2Al_2(SO_4)_4,24H_2O$	36·4	57·4	110·5	321·3	parts.

It is insoluble in alcohol. On exposure to the air the surface becomes opaque and white. This is not, however, due to a loss of water, but is caused by the absorption of ammonia and the formation of a basic sulphate. When a crystal of alum is placed over sulphuric acid or heated to 61°, it loses 18 molecules of water (Graham); at 92° it melts in its own water of crystallisation; it loses the whole of its water slowly at 100°, and quickly at a higher temperature, with formation of what is known as burnt alum. This forms a porous mass, which dissolves slowly

[1] See *Amer. Chem. J*, 1901, **26**, 174; *Phil. Trans.*, 1904, **203**, [*A*], 214.

but completely in water. When alumina is fused with hydrogen potassium sulphate, an anhydrous salt is obtained which crystallises in small six-sided crystals, and remains behind when the fused mass is treated with hot water.

Neutral and Basic Alums.—If an alkali is slowly added to an alum solution, a precipitate is thrown down which disappears on stirring, but after a further addition of the alkali it remains unaltered. The solution in which the precipitate just redissolves has a neutral reaction, and is termed in commerce neutral alum; it is employed in dyeing, as it readily gives up alumina to the colouring matter, and is free from iron, inasmuch as the alkali decomposes any iron sulphate which the liquid may contain. If this solution is allowed to evaporate at the ordinary temperature, a crystalline crust is deposited which contains the basic salt $Al_2(SO_4)_3,2Al(OH)_3$, together with potassium sulphate. If the solution is heated above 40°, common alum is formed, and a precipitate of $K_2SO_4,Al_2SO_4(OH)_4$ is thrown down, this latter substance being identical in composition with alunite from Tolfa. When a solution of basic alum is heated in sealed tubes to 230°, this compound is also obtained in crystals (Mitscherlich). Solutions which contain a small quantity of basic alum yield, on spontaneous evaporation, cubical crystals. These were first observed by Sieffert in 1772, and obtained by him by boiling alum with milk of lime. This so-called cubic alum has the same composition as common octahedral alum, and on heating the solution, to which a small quantity of alkali has been added, to a temperature of above 100°, ordinary octahedral alum separates out. Roman alum obtained from alunite often occurs in commerce in cubical crystals.

Rubidium and *cæsium* also form alums which are very sparingly soluble,[1] and hence are employed, as has already been described, for the separation of these metals from potassium.

Ammonium Alum, $Al_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$.—This salt is very similar to potassium alum. It has a specific gravity of 1·626, melts at 95°, loses water on heating, and, on ignition, leaves a residue of pure alumina. One hundred parts of water dissolve (Poggiale):

At	0°	10°	20°	30°	
$Al_2(NH_4)_2(SO_4)_4,24H_2O$	3·9	9·5	15·1	22·0	parts.

At	40°	50°	60°	
$Al_2(NH_4)_2(SO_4)_4,24H_2O$	30·9	44·1	66·7	parts.

[1] See Locke, *Amer. Chem. J.*, 1901, **26**, 166.

Commercial alum frequently contains both potassium and ammonium in varying proportions.

A hydroxylamine alum is also known.[1]

Sodium Alum, $Al_2(SO_4)_3,Na_2SO_4,24H_2O$.—It was formerly believed that aluminium sulphate did not form an alum with sodium sulphate, but this salt was prepared in the year 1816 by Zellner.[2] Sodium alum is much more readily soluble in water than the other alums. Its specific gravity is 1·6. It effloresces in the air, and loses the whole of its water at a temperature of from 40° to 50°, leaving an easily soluble residue. It is not manufactured on the large scale, as on account of its solubility it is difficult to prepare in the pure state.

Silver Alum, $Al_2(SO_4)_3,Ag_2SO_4,24H_2O$, is said to be obtained by heating a mixture of silver sulphate and aluminium sulphate, together with some water, in sealed tubes, until the silver sulphate is dissolved, when, on cooling, octahedral crystals are deposited, which are decomposed into their constituents by water.[3] Retgers denies the existence of this alum.

Besides the above-mentioned alums, a number of other alums are known in which the aluminium is replaced by isomorphous metals, such as iron, manganese, and chromium. A peculiar nomenclature has arisen in the description of these compounds. If none of the isomorphous metals replaces aluminium, as in the above-mentioned alums, each is an aluminium alum. The names, iron alum, chromium alum, and manganese alum, on the other hand, are used, as a rule, to designate the potassium double sulphates of these metals. If potassium is replaced by other metals, then the names of both metals must be mentioned, as, for instance, ammonium chromium alum, and so forth.

Selenic acid also forms a series of alums, having the general formula $M_2^{III}(SeO_4)_3,M_2^{I}SeO_4,24H_2O$.

Aluminium sulphate also forms double salts with potassium and ammonium sulphates containing $8H_2O$, which are obtained by fusing the corresponding alums and maintaining the liquid at about 86°. Slender crystals of the new hydrates then separate, but they are difficult to prepare, and have not been carefully examined.[4] Their formation is of interest, because compounds of the same type are formed by the sulphates of thallium and the metals of the rare earths, which do not form true alums.

[1] Meyeringh, *Ber.*, 1877, **10**, 1946.

[2] See also Wadmore, *Proc. Chem. Soc.*, 1905, **21**, 150; W. R. Smith, *J. Amer. Chem. Soc.*, 1909, **31**, 245; Dumont, German Patent 141670.

[3] Church and Northcote, *Chem. News*, 1864, **9**, 155.

[4] Marino, *Gazz.*, 1905, **35**, ii., 341.

Aluminium and Nitrogen and Phosphorus.

335 *Aluminium Nitride*, AlN, is formed in small yellow crystals when aluminium is strongly heated in nitrogen[1] or ammonia.[2] It is rapidly decomposed by water. It is manufactured by the Société Générale des Nitrures in Savoy, by strongly heating bauxite with carbon and passing nitrogen over the mixture :

$$2Al_2O_3+3C_2+2N_2=4AlN+6CO.$$

The nitride is then treated with water and ammonia produced :

$$2AlN+6H_2O=2Al(OH)_3+2NH_3.$$

The alumina can be used for the manufacture of aluminium, or employed over again.[3]

Aluminium Nitrate, $Al(NO_3)_3$, is obtained by dissolving the hydroxide in nitric acid, and evaporating the solution with occasional addition of nitric acid. On cooling, the salt $Al(NO_3)_3,9H_2O$ separates out either in very deliquescent monoclinic prisms or in flat orthorhombic crystals. In nitric acid of density 1·5 the stable phase is the hexahydrate, $Al(NO_3)_3,6H_2O$, which often separates as a metastable form from less concentrated acid.[4] The salt decomposes at 150°, leaving a residue of pure alumina (Deville), and this reaction may be employed for the separation of aluminium from calcium and magnesium, metals whose nitrates do not decompose at so low a temperature. The solution of the normal nitrate, obtained by exactly precipitating a solution of lead nitrate with aluminium sulphate, is used as a mordant in calico-printing with alizarin colours.

Phosphides of Aluminium.—When a mixture of aluminium powder and red phosphorus is fired, the two elements unite, forming the compound AlP, which is decomposed by water with formation of aluminium hydroxide and phosphine.[5] Various other compounds, Al_5P_3,Al_3P_7 and Al_3P, have been described.[6]

Phosphates of Aluminium.—Normal *aluminium orthophosphate*, $AlPO_4$, is obtained as a gelatinous precipitate by adding

[1] Mallet, *Journ. Chem. Soc*, 1876, ii., 349; Fichter, *Zeit. anorg. Chem*, 1907, **54**, 322; 1913, **82**, 192.

[2] Matignon, *Compt. rend.*, 1900, **130**, 1390; White and Kirschbraun, *J. Amer. Chem. Soc*, 1906, **28**, 1343.

[3] Serpek, German Patents 235213 and 236044; also 239909.

[4] Seligman and Williams, *Trans Chem Soc*, 1916, **109**, 612; Inamura, *J. Tokyo Chem Soc*, 1920, **41**, 1.

[5] Fonzes-Diacon, *Compt. rend.*, 1900, **130**, 1314; Matignon, *ibid.*, 1900, **130**, 1390.

[6] Franck, *Chem. Zeit.*, 1898, **22**, 236.

a neutral solution of an aluminium salt to a solution of sodium phosphate. It is soluble in mineral alkalis and acids, and in ammonia.[1] If an acid solution of the salt be precipitated with ammonia, a basic salt, $3AlPO_4,5Al(OH)_3$, is thrown down; this combined with nine molecules of water, forms the crystalline mineral wavellite. In addition to this, many other basic and double phosphates of aluminium occur in the mineral kingdom, of which the mineral turquoise or calaite, occurring in Persia and valued as a gem, is one of the most important. This is coloured a greenish or bluish colour by copper, and is the basic salt, $AlPO_4,Al(OH)_3,H_2O$. Most of the turquoise, not artificial, used in jewellery in former centuries as well as at the present time, and described in early works on mineralogy, is bone-turquoise or odontolite, a fossil bone or tooth coloured by phosphate of iron. An aluminium phosphate containing 38 per cent. of phosphoric oxide occurs in Algiers, at Fauzan and in the Island of Grand Connétable, and is employed as a source both of alumina and of phosphoric acid.[2]

Aluminium and Boron, Carbon, and Silicon.

336 The compounds of aluminium and boron have been described in Vol. I., p. 723.

Aluminium Carbide, Al_4C_3, was obtained by Moissan by heating aluminium in a carbon crucible in the electric furnace,[3] and appears to be formed from the carbon monoxide produced, although the carbon and aluminium can unite directly and rapidly *in vacuo* at 1400°.[4] It is also produced when alumina is heated with calcium carbide, and when aluminium is heated in carbon monoxide in presence of aluminium chloride.[5] It forms yellow crystals and is decomposed by water with formation of pure methane:

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4.$$

337 *Silicates of Aluminium.*—It has already been stated that the various silicates of aluminium occur in combination with other silicates to form the chief constituents of the solid crust

[1] See Caven and Hill, *J. Soc. Chem Ind*, 1897, **16**, 29.

[2] Grognot, *Rev. Gen. Chim*, 1906, **9**, 149.

[3] *Compt. rend*, 1895, **119**, 9.

[4] Pring, *Journ. Chem. Soc.*, 1905, **87**, 1530; 1908, **93**, 2107.

[5] Guntz and Masson, *Compt. rend.*, 1897, **124**, 187. See also Matignon, *Ann. Chim. Phys.*, 1908, [8], **13**, 276.

of the earth. The number of these compounds is extremely large, and only those can be mentioned in this work which possess a general interest.

Topaz, $Al_2SiO_4F_2$, occurs in granite, gneiss, and mica-schist in the form of rhombic prisms, which are transparent and usually colourless, or of a light- or dark-yellow colour. The finest topaz occurs in the Urals, Siberia, and Brazil. The common forms are not infrequently employed for the manufacture of polishing powder instead of emery.

Noble Garnet, $(Mg,Fe)_3Al_2Si_3O_{12}$.—This, like the other members of the group of garnets, crystallises in the regular system, the dodecahedron being the most prominent form. The crystals are transparent, and are coloured, according to the quantity of iron which they contain, from a pale yellow up to a dark red tint.

Potash Felspar or *Orthoclase*, $K_3,Al_3(Si_3O_8)_3$, is mined in great quantity for the manufacture of porcelain and similar materials, and it has also been utilised as a source of potash by roasting with lime and then extracting with water; beyond selection at the mines of the cleavage fragments of the crystalline mineral, no artificial work is put upon the native product. Large quantities are shipped to the pottery districts of the Midlands, and before being used it is very finely ground, either alone or along with other materials. When strongly heated, felspar fuses, and on cooling does not again crystallise, but solidifies to a colourless glass; hence it is used either to act as a frit or fusible material to bind together most firmly the infusible particles of clay forming the body of the porcelain or earthenware, and so produce a hard, translucent, lustrous mass, or else to act as a flux on the surface of the porcelain or earthenware so as to give it a smooth, glazed surface which it would not otherwise possess.

Hydrated Aluminium Silicate or *Kaolin*, $H_2Al_2Si_2O_8,H_2O$, is formed by the weathering of felspar, which loses the whole of its potash and two-thirds of its silica, and takes in their place a small proportion of water. This substance is a distinct mineral species and frequently occurs crystallised in four- or six-sided tablets belonging to the rhombic system; even where the mass appears to be an amorphous powder, the microscope and also the peculiar soapy feeling between the fingers show it to consist of very fine crystalline scales. It is frequently accompanied by crystals of quartz, and if the original felspar rock or its admixed minerals contained iron, the kaolin is coloured more or less yellow, red, or green by the presence of ferric or

ferrous oxides. Kaolin is found in China, near the Kauling Mountains, whence its name is derived; in Europe the finest china clay is found in Yrieux near Limoges, and it is from this that the celebrated Sèvres porcelain is made; good china clay is likewise found in Cornwall, Saxony, various localities in America, and elsewhere. The following table gives the composition of some varieties:

	SiO_2.	Al_2O_3.	H_2O.	$(K,Na)_2O$.	Fe_2O_3.	$(Ca,Mg)O$.
$H_2Al_2Si_2O_8 + H_2O$ . .	46·4	39·7	13·9	—	—	—
Kaolin from China . .	50·6	32·7	10·0	2·5	2·6	0·8
„ „ Yrieux . .	48·4	34·9	12·6	2·4	1 3	—
„ „ Cornwall .	46 4	38·6	9·1	1·8	—	3·5
Cornwall Clay . . .	45 8	39·4	14·3	—	—	—
Dorsetshire blue clay .	46·4	38 0	13·4	—	1·0	1·2

Ordinary clay consists of a mixture of kaolin with silica, ferric oxide, calcium carbonate, magnesium carbonate, and organic matter. Thus Stourbridge clay used for making crucibles, fire-bricks, gas retorts, etc., contains approximately 40 per cent. of free silica and 60 per cent. of kaolin. Kaolin kneaded to a paste with water forms a plastic mass easily cut, pressed to any shape, squirted by pressure through dies to form rods or tubes, cut into lengths to make bricks, etc.; when gradually dried such worked clay does not crumble and when the articles are subsequently heated to drive off the combined water they shrink about 10 per cent. in their length and bake into a hard, porous solid. At all ordinary furnace temperatures, kaolin cannot be fused, but the presence of very small quantities of foreign materials induces partial fusion so that the mixture becomes more or less soft and pasty in the furnace; oxide of iron particularly has this effect, as well as lime and the alkalis. Upon his skill in choosing and admixing certain fusible materials with kaolin and impure clays the success of the potter depends.[1]

338 *History of Earthenware, Pottery, and Porcelain.*—The potter's art is one of the oldest in existence. The Egyptians were well acquainted with the means of glazing ware made of burnt clay, as well as with the art of enamelling in colours. Amongst European nations the Etruscans were especially celebrated in early times for their proficiency in the manufacture of painted pottery ware, and in Pliny's time several towns in Greece and Italy were well known for the beauty and artistic taste of their vases, urns, and other pottery wares.

Porcelain was not known to the Romans, although the Chinese

[1] For a fuller account of Pottery and Porcelain, consult Burton's article in Vol. IV. of Thorpe's *Dictionary of Applied Chemistry* (1913).

have manufactured it for ages, and the Egyptian tombs contain remains of vessels of a material closely allied to porcelain. The art of glazing pottery with the oxides of lead and tin was generally practised in Europe during the Middle Ages, and we find a description of the process then adopted in the writings of the alchemists Peter Bonus and Albertus Magnus at the beginning of the thirteenth century. In the following century the potter's art made great strides. Agricola published many receipts concerning this manufacture; amongst others, he states not only that a mixture of litharge with tin oxide gives a good glaze, but that the former oxide may be employed alone for this purpose.

Amongst those who have been most active in promoting the progress of the ceramic art the name of Bernard Palissy stands pre-eminent. Devoting himself with self-sacrificing assiduity to the production of glazed and coloured faience, Palissy laid the foundation of modern art pottery. His numerous writings, published during the latter half of the sixteenth century, spread a knowledge of his experimental methods throughout Europe; but his works *L'Art de Terre et des Terres d'Argile* are confined to a description of the manufacture of earthenware; it was not until the year 1709 that the method of making porcelain was discovered by Böttticher, and in the following year the celebrated porcelain manufactory at Meissen, in Saxony, was established.

The mode of preparation of the Meissen porcelain being naturally kept secret, the King of Prussia instructed the celebrated chemist Pott to determine the nature of the materials used, and he, being unable to obtain any satisfactory information, was obliged to investigate the properties of those substances which might possibly be used in the manufacture, mixed in varied proportions; for this purpose Pott is said to have made no fewer than 30,000 experiments. To these we are mainly indebted for the establishment of the reactions which occur when various minerals are heated, and much valuable information applicable to the manufacture of porcelain was thus obtained. About the same time Réaumur endeavoured to ascertain the secret of porcelain-making, and found that it is produced by the union of two earths, one of which is fusible, whilst the other is infusible at the same temperature, so that by the firing of an intimate mixture a non-porous, translucent mass is formed.

His investigations were taken up in the year 1758 by Lauraguais, D'Arcet, and Legay, in France, and by the help of

Macquer they succeeded in re-discovering the art of porcelain-making, and in the year 1769 the celebrated porcelain manufactory of Sèvres was founded.

Even up to the beginning of the nineteenth century real porcelain was a material of great rarity and value. At the present day, however, it is cheap, and is employed for making the most ordinary articles of everyday use.

Hard Porcelain or *True Porcelain* is distinguished by its fine and hard, translucent structure, and is with difficulty attacked by chemical reagents. According to Emmerling's experiments, water and acids, even when boiled, have next to no action on porcelain, and it is attacked by alkalis less powerfully than glass, and hence in chemical and analytical operations the use of porcelain is much to be preferred to that of glass. Porcelain also stands rapid alteration of temperature without cracking, and this property is one of extreme value to chemists; whilst its beauty, and the fact that its surface is capable of taking colours which will stand firing, render it of great importance in the manufacture of objects of art.

In the manufacture of porcelain the infusible kaolin is mixed with a frit, flux, or fusible material, consisting of a silicate. This on fusion penetrates into the pores of the heated clay, producing a hard, apparently homogeneous, translucent mass lustrous on its fractured faces. The name porcelain is derived from a Portuguese word *porcellana*, a shell which is similar in general appearance to porcelain. The ordinary flux employed is felspar, but other materials may be admixed with it, depending upon the composition of the kaolin employed.

When a mixture has proved to be successful, each manufacturer adheres strictly to his special receipt, not only because an alteration in the proportions would render a different temperature necessary for burning, but especially because it would also entail a variation in the shrinking of the mass, and as the manufacturer has frequently to prepare his wares to pattern, it is necessary to keep to one rate of shrinkage. On the determination of the purity of the materials and of the fire-resisting power of clays Bischof and Richters [1] have published elaborate investigations, to which we must refer the reader.

The greatest care has to be taken in the thorough mixing of the materials, and in obtaining them in a very finely-divided state. For this purpose they are ground together with water

[1] C. Bischof, *Dingl. Polyt. Journ.*, **159-211**; Richters, *ibid.*, **191-197**.

to a thin cream which is passed through very fine sieves, and the excess of water is then got rid of by means of a special pattern of filter press. The lumps of moist material are then stocked ready to be worked up on the potter's wheel, or brought into the requisite shape by pressing into moulds, and the objects thus prepared are allowed to dry at the ordinary temperature before being fired in the upper portion of the porcelain kiln. The fired goods are then dipped into water containing the finely-divided glaze in suspension. The composition of porcelain glaze is seen in the following table:

Sèvres.	Meissen.		Berlin.	
Pure ground felspar.	Quartz	37	Quartz	43
	Kaolin from Seilitz	37	Kaolin from Moil . .	31
	Lime	17·5	Gypsum	14
	Broken porcelain .	8 5	Broken porcelain . .	12
		100 0		100

The articles are dried and exposed to a higher temperature in the porcelain kiln, which consists essentially of a high reverberatory furnace. The flame and hot gases surround the earthenware "seggars," or infusible crucibles, in which the porcelain ware is placed to protect it from the smoke and direct action of the flame. When the temperature has reached its maximum, the kiln with its contents is bricked up, and the whole allowed to cool very slowly. This annealing process is necessary, as the glaze forms a true glass, and if the heated mass were quickly cooled the porcelain would be brittle from the unequal tension of its different parts.

Painting on porcelain is a branch of the art of glass-staining and the same substances are employed for painting upon porcelain as are used in colouring glass. They are divided into two classes: (1) Those which are not destroyed at the temperature of the porcelain kiln, and can be painted on the ware below the glaze—these are termed refractory colours, and include cobalt-blue, chrome-green, the brown produced by oxide of iron or manganese, chromate of iron, etc., and uranium black; and (2) those colours which are injured when heated above a certain temperature—these are termed muffle-colours, because they are fixed on the glazed ware by a separate firing at a lower temperature in a muffle. The following substances are used as muffle-colours: iridium oxide, cupric oxide, cuprous oxide, chromate of lead, silver chloride, purple of Cassius, etc., and an admixed flux for these is employed, consisting of quartz or sand, borax

or boric acid, felspar, litharge or red lead, nitre and the carbonates of potassium and sodium, in suitable proportions.

Tender or *Fritted Porcelain.*—This form of porcelain was first prepared in 1695 by Morin in St. Cloud. The mass resembles that of true china, but the frit and glaze are much more fusible. This is the kind of porcelain specially manufactured in England. The materials employed in this manufacture are: (1) The mass or body, composed of Cornish stone, China clay, or decomposed pegmatite. (2) The frit or fusible material, consisting of bone ash or mineral phosphate with, sometimes, the addition of borax. (3) The glaze, consisting of bone ash, sand, borax, potashes, and lead oxide. The following are mixtures in use for English china:

	I.	II	III.
Bone ash . . .	47	41	47·3
Cornish stone . .	31	30	—
China clay . . .	22	29	33·8
Felspar	—	—	18·9
	100	100	100·0

The glaze used for English table ware consists of:

Cornish stone	34
Chalk	17
Ground flint	15
Borax	34
	100

These materials are fritted, ground, and mixed with 10 per cent. of Cornish stone and 20 per cent. of white lead.

Parian or *Carrara Biscuit-ware* is a white, unglazed porcelain, less fusible than ordinary tender porcelain and largely used for the preparation of statuettes.

Stoneware is distinguished from porcelain by its opacity, due to the fact that the mass is not nearly so finely ground and consequently not so intimately mixed with the frit as is the case with porcelain. The materials used are the plastic clays and pipe-clays found in large quantity in the coal-measures, and these are mixed with a frit which is either felspathic or may contain lead or borax, the proportion of frit used being larger than in the case of porcelain. The mass often contains

quartz granules of considerable size, and the materials used are not specially selected to be particularly free from iron oxides. Stoneware is therefore much cheaper than porcelain and is largely used for the construction of chemical manufacturing plant, such as condensing tubes and bottles for hydrochloric and nitric acids, evaporating pans, centrifugal machines, large store tanks, cooling worms, pumps, injectors, fans, taps, etc.

Semi-porcelain.—This is a fine kind of stoneware, prepared from a white, plastic clay, to which ground quartz or flint, or even felspathic stone, is added in the requisite quantity. After the first burning it is porous and adheres to the tongue. It is then glazed with a transparent glaze consisting of borax, quartz, soda, and oxide of lead.

Earthenware or *Common Pottery Ware.*—This material is like the foregoing, inasmuch as it is porous, but it is comparatively soft and easily broken or cut by steel tools and will not long withstand the action of strong chemicals. Earthenware is made from a coloured plastic clay the impurities of which act as the frit, and in order to diminish the shrinking it is frequently mixed with marl, *i. e.*, a clay containing a considerable proportion of admixed sand grains. It is glazed by throwing common salt into the kiln when the burning is nearly complete. This is volatilised and decomposed by the aqueous vapour and the products of combustion, with formation of hydrochloric acid and soda, which latter unites with the clay to form a sodium aluminium silicate. It may also be glazed with a lead glaze. Earthenware is largely used for agricultural drain-pipes, tiles, bricks, flower-pots, and in the glazed form for pans and basins for domestic use.[1]

Faience is an opaque, porous, generally soft body pottery, always coloured, with either a glaze rendered white and opaque by tin or sometimes by calcium phosphate (*faience émaillée*), or else a transparent lead glaze. In this latter case a slip of finer clay generally covers the coarse body. It was known and manufactured in the 9th century by the Arabians, and the knowledge of the manufacture passed with the Moors into Spain, and established itself in the Island of Majorca, whence the name *Majolica* is derived, being the old Tuscan name for this island. The same ware in Italy was named faience from the name of

[1] Consult the article 'Fritts and Glazes," in Vol. II. of Thorpe's *Dictionary of Applied Chemistry.*

the town of Faenze, where the industry was established in the 13th century, and flourished until the 15th. In France, the manufacture was commenced by Bernard Palissy in the 16th century.

Crucibles.—The various kinds of melting crucibles which are made of clay have a special interest to the chemist. These require to be made of material which will stand a very high temperature without softening or breaking up, and is capable of withstanding rapid changes of temperature. The well-known Hessian crucibles are made of a clay containing about 71 parts of silica, 25 of alumina, and 4 of oxide of iron, and this is mixed with one-third to one-half its weight of quartz sand, while plumbago crucibles are made of a finer and purer clay admixed with plumbago scales which serve to knit the clay together instead of a frit.

Ultramarine.

339 A double silicate of aluminium and sodium containing sulphur, known as *lazurite*, occurs in the rock known as *lapis lazuli*, and has long been valued for its splendid blue colour. Its constitution is, however, as yet unknown. Lapis lazuli usually occurs in the massive condition, and is found in Central Asia, Siberia, Persia, China, etc. It is largely used for making vases and for inlaying ornamental furniture, and the powdered lazurite, extracted from the powdered rock by washing with water, forms a valuable paint termed ultramarine. This substance is, however, now artificially prepared on a large scale.

Tassaert observed in 1814 the formation of a blue colour in one of his black-ash furnaces at the celebrated glass-works of Saint Gobain, and Vauquelin showed that this colour was identical with lapis lazuli. In 1824 a prize was offered in France for the discovery of a practical method of manufacturing this colour, and this problem was successfully solved in the year 1828 simultaneously by Guimet[1] and Christian Gmelin, the latter of whom published the process in the year 1828.[2]

Since this date the ultramarine industry has largely increased. The chief quantity of the substance is manufactured in Germany, and the total production now amounts to about 10,000 tons per annum. Different varieties of ultramarine occur in commerce; these, however, can be divided into two classes.

[1] *Ann. Chim. Phys.*, 1831, **46**, 431. [2] *Quart. Journ. Science*, 1828, **2**, 216.

Ultramarine poor in sulphur is obtained by heating a mixture of china clay (100 pts.) with charcoal (12 pts.), soda ash (100 pts.), and sulphur (60 pts.) in closed crucibles placed in a furnace. Instead of charcoal, tar or resin is sometimes employed. In this way a colourless compound is first produced, termed white ultramarine, which, however, soon becomes of a green colour. The green ultramarine thus obtained, which is also used as a colour, is then mixed with 7 per cent. of sulphur and heated in a retort. The sulphur takes fire and is allowed to burn in the air, when the product becomes of a fine blue colour. *Ultramarine rich in sulphur* is generally obtained by heating china clay (100 pts.) with soda ash (103 pts.), kieselguhr (16 pts.), sulphur (117 pts.), and resin or charcoal (4 pts.) in a muffle furnace, when a blue product is at once obtained which, according to the quantity of silica originally added, retains more or less of a red tinge. The different kinds of both green and blue ultramarine are then finely ground and washed with water, and thus the several marketable varieties are obtained. The following table gives the composition of some different ultramarines:

		Blue.	
	Green	Poor in Sulphur.	Rich in Sulphur.
SiO_2	38·52	37·90	40·77
Al_2O_3	28·94	29·30	23·74
Na_2O	23·68	22·60	18·54
S	8·30	7·86	13·58
Earthy residue	1·94	2·36	3·61
	101·38	100·02	100·24

The ultramarine which is poor in sulphur is decolorised by the action of a cold solution of alum, whilst the ultramarines rich in sulphur withstand the action of this salt, and the more completely the more sulphur they contain. Hence these latter varieties are employed in cases in which the colouring matter comes in contact with aluminium salts, as, for instance, the blueing of paper and in calico-printing. The different kinds of ultramarine are very largely employed in the arts for water-colours, as oil-paint, and for paper-staining.

Ultramarine blue crystallises in the cubic system. It is fairly stable at a red heat, but loses a little of its brilliancy and turns somewhat greenish. It is stable towards caustic alkalis, but is easily decomposed by dilute mineral acids with deposition of

sulphur and evolution of sulphur dioxide and hydrogen sulphide, the latter being in excess and reacting with the former to produce more sulphur.[1] Curiously enough, cold concentrated sulphuric acid or a mixture of acetic anhydride and glacial acetic acid has no action on ultramarine.[2] It loses sulphur when heated with mercuric oxide. It is transformed into a white solid when heated to 200—300° with water, and sodium sulphide passes into solution. It also loses part of its sulphur when heated to 450° in hydrogen, but still remains blue. At 250°, in a stream of steam, chlorine, or hydrogen chloride, it changes into a *violet* ultramarine, which in turn can be converted into a *red* ultramarine.[3]

When blue ultramarine is heated with a solution of silver nitrate, the sodium is replaced by silver, and a yellow powder of *silver ultramarine* is obtained which under the microscope is seen in the form of dark lemon-yellow, transparent particles.[4] It is easily decomposed by acids with separation of silica, one-third of the silver being precipitated as silver sulphide, but without evolution of sulphuretted hydrogen. If silver ultramarine be heated with a solution of potassium chloride, the silver is replaced by potassium, and in this way blue potassium ultramarine is obtained, a substance which has hitherto not been prepared directly (Heumann). A bright blue lithium ultramarine and numerous other substituted ultramarines have been prepared in similar manner or by heating silver ultramarine with molten metallic chlorides.[5] Only those containing the alkali metals are blue in colour. Organic derivatives of ultramarine, such as ethyl ultramarine, have also been obtained from the silver compound by the action of the alkyl iodides.[6] Ultramarines containing selenium and tellurium in place of sulphur have been prepared, but they are not blue.

The preparation of these substituted ultramarines has not, however, led to the recognition of the chemical nature of ultramarine, and the difficult problem of the constitution of this

[1] Guckelberger, *Annalen*, 1882, **213**, 182.

[2] Hofmann and Metzener, *Ber*, 1905, **38**, 2482; Wunder, *Zeit. anorg. Chem.*, 1912, **77**, 209.

[3] See Wunder, *loc. cit.*

[4] Unger, *Dingl. Polyt. Journ.*, 1874, **212**, 232; de Forcrand and Ballin, *Bull. Soc. chim.*, 1878, [ii], **30**, 112; Chabrié and Levallois, *Compt. rend.*, 1906, **143**, 222.

[5] de Forcrand, *Bull. Soc. chim.*, 1879, [ii], **31**, 161; Wunder, *Zeit. anorg. chem.*, 1912, **77**, 209.

[6] de Forcrand, *Compt. rend.*, 1879, **88**, 30; Chabrié and Levallois, *loc. cit.*

remarkable coloured compound has not yet been solved. It has been suggested that the colouring matter of both natural and artificial ultramarine is a double compound of a sodium aluminium silicate and sodium sulphide, which has been variously formulated as $2Na_2Al_2Si_2O_8,Na_2S_2$ (Heumann) and $Na_4(NaS_3Al)Al_4(SiO_4)_3$ (Brögger and Backstrom),[1] the latter formula being closely analogous to that of haüyne, $Na_2Ca(NaSO_4Al)Al_2(SiO_4)_3$, a mineral which is also characterised by a blue colour. The existence of a definite compound of this or similar formula in ultramarine has, however, not been proved.

Another view, which finds much favour at the present time, is that the basis of ultramarine is a colourless substance, which appears blue because it holds in solid solution or colloidal suspension a small amount of some simple substance, probably elementary sulphur.[2] This view receives support from the fact that in various reactions in which traces of colloidal sulphur might be expected to be formed, a blue colour is developed, *e.g.*, addition of alkali polysulphides to various boiling organic solvents, addition of traces of sulphur to molten sodium chloride, and heating potassium thiocyanate to 400.[3]

Detection and Estimation of Aluminium.

340 Aluminium compounds do not impart any colour to the non-luminous gas-flame. The spark spectrum of aluminium has been mapped by Thalén, Kirchhoff, and Lecoq de Boisbaudran, and its spectrum in the electric arc by Liveing and Dewar and by Kayser and Runge. The last-named investigators found that the visible portion of the spectrum did not contain a single line. The aluminium bands in the ultra-violet, however, are extremely characteristic. These are contained in the invisible and highly refrangible portions of the spectrum which are only seen when the rays are allowed to fall on a fluorescent substance.[4] Alumina also shows a characteristic spectrum in the arc.

[1] *Zeit. Kryst. Min.*, 1891, **18**, 209.

[2] Knapp, *J. pr. Chem.*, 1888, [2], **38**, 48; Rohland, *Zeit. angew. Chem.*, 1904, **17**, 609; Hoffmann, *Chem. Zeit*, 1910, **34**, 821; *Zeit. Chem. Ind. Kolloide*, 1912, **10**, 275; Abegg, *Handbuch der anorganischen Chemie* (1906), Vol. III, pt. i, p. 126; Doelter, *Handbuch der Mineralchemie* (1911), Vol. II, pt. vii.

[3] For further information on ultramarine, see Thorpe's *Dictionary of Applied Chemistry*, Abegg, *op. cit.*, and Zerr and Rübencamp, *Treatise on Colour Manufacture* (trans. by Meyer, Griffin and Co. Ltd., 1909).

[4] Stokes, "On the Long Spectrum of the Electric Arc," *Phil. Trans.*, 1862, **152**, 599.

Aluminium occurs almost always combined with oxygen. Most of these compounds are insoluble in water; many of them, however, are decomposed by hydrochloric acid, the alumina entering into solution. Those compounds which withstand the action of acids are decomposed by fusion with sodium carbonate and treatment of the fused mass with hydrochloric acid. Corundum, spinel, and some other minerals are not, however, decomposed in this way, but must be fused with hydrogen potassium sulphate.

Aluminium can readily be separated from all the common metals. It is not precipitated from its acid solutions by sulphuretted hydrogen, whereas it is completely thrown down as the hydroxide by ammonia and ammonium sulphide, and thus can be readily separated from the metals of the alkalis and alkaline earths. It is distinguished from most of the metals precipitable by ammonium sulphide, inasmuch as its hydroxide is soluble in caustic alkalis. This property it possesses in common with the hydroxides of zinc, chromium, and glucinum. The first of these metals is precipitated from the alkaline solution by sulphuretted hydrogen, and chromium hydroxide is only soluble in the cold, and is precipitated on boiling. If to the solution from which the zinc and chromium have thus been separated hydrochloric acid and then ammonia be added, the aluminium is precipitated. This precipitate may, however, still contain glucinum hydroxide, which must be dissolved by digesting it with ammonium carbonate or sodium bicarbonate (p. 639). When the oxide is strongly heated with a salt of cobalt a bright blue, infusible mass is obtained.

For quantitative estimation, aluminium is precipitated as hydroxide, and then converted into the oxide by strong ignition.

The Atomic Weight of aluminium was first determined by Berzelius in 1812, who found that 100 parts of the anhydrous sulphate yielded 29·934 parts of pure alumina, according to which the atomic weight is 27·1.[1] Tissier[2] found the number 27 by the conversion of the metal into the nitrate and then into the oxide, and Dumas[3] 27·3 by the analysis of the chloride. Mallet[4] employed three distinct methods: the ignition of ammonium alum, which gave the number 27·15; the analysis of the bromide, from which the atomic weight appeared to be 27·11; and finally the direct determination of the equivalent to hydrogen. This

[1] *Pogg. Ann.*, 1812, **8**, 187.
[2] *Compt. rend.*, 1858, **46**, 1105.
[3] *Ann. Chim. Phys.*, 1859, [3], **55**, 151.
[4] *Phil. Trans.*, 1880, **171**, 1003.

last set of experiments was carried out by dissolving pure aluminium in concentrated aqueous soda and collecting and measuring the dry hydrogen produced. He thus found that 3·352 grm. of aluminium yielded 4161·6 c.c. at the normal temperature and pressure (in 45° north latitude). According to this, the atomic weight is 27·10. In a second series of less trustworthy experiments the hydrogen was burned and the water weighed. Thomsen[1] determined the ratios Al : H and Al : O independently by dissolving metallic aluminium in concentrated caustic potash solution and finding the weight of hydrogen evolved and the weight of oxygen required to burn the hydrogen. He used a somewhat impure aluminium and after allowing for the effect of the impurity, obtained from the two ratios somewhat lower numbers than Mallet, namely, 26·98 and 26·99 respectively.

A preliminary study by Richards and Krepelka[2] of the purification and analysis of aluminium bromide points to the value 26·96 as being more nearly correct, and this value, rounded off to 27·0, is the one at present adopted.

GALLIUM. Ga = 70·1. At. No. 31.

341 This metal, the eka-aluminium of Mendeléev (p. 70) was discovered in 1875 by Lecoq de Boisbaudran by means of spectrum analysis. He found the new element in the zinc blende of Pierrefitte in the Pyrenees and patriotically gave to it the name which it now bears. It is found also in the blende from other localities. Thus a yellow, transparent blende from the Asturias and a black blende from Bensberg contain it, and that from Bensberg, although the richest, contains only 16 mgrm. of gallium per kilo.; it occurs also in a grey zinc ore found at Pulwood, New South Wales.[3] It also occurs in American blendes, and from the continual redistillation of zinc prepared from these blendes final residues have been obtained comparatively rich in gallium, and serving as raw material for a number of recent researches on the chemistry of this element.[4]

An examination of the spectrum yielded by a large number

[1] *Zeit. anorg. Chem*, 1896, **11**, 14; 1897, **15**, 447.
[2] *J. Amer. Chem. Soc.*, 1920, **42**, 2221.
[3] Kirkland, *Austr. Assoc. Adv. Sci.*, 1893, 266.
[4] W. F. Hillebrand and J. A. Scherrer, *J. Ind. Eng. Chem.*, 1916, **8**, 225; Browning and Uhler, *Amer. J. Sci.*, 1916, **41**, 351.

of minerals in the oxy-hydrogen flame has revealed the fact that gallium, like lithium and rubidium, is very widely distributed in nature, although present only in very minute quantities. It occurs, for example, in a large number of iron ores, from which it passes into the iron prepared from them, so that Middlesbrough cast iron contains as much as 1 part of gallium in 33,000 parts and is the richest source of this element known.[1] It also occurs constantly in bauxite and the aluminium salts prepared from it, as well as in kaolin, and in zinc blende, and is occasionally found in pyrites and manganese ores. It is present also in all meteoric irons, but not in all meteorites.[2]

In order to prepare gallium, the ore, according to its physical character, is dissolved either in aqua regia, hydrochloric acid, or sulphuric acid. From the chloride solution germanium, if present, may be separated by distilling the liquid until the boiling point reaches 135—140°.[3] The solution is then decomposed by means of metallic zinc. The precipitate thus thrown down, which contains most of the foreign metals present in the blende, is then treated with hydrochloric acid, and the liquid again precipitated with zinc in the cold. As soon as the evolution of hydrogen becomes feeble the solution is poured off from the precipitate and saturated with sulphuretted hydrogen, the precipitate filtered off, the excess of sulphuretted hydrogen expelled, and the liquid fractionally precipitated with sodium carbonate in the cold until the precipitate thrown down no longer exhibits the gallium line when examined with the spectroscope. It is then dissolved in sulphuric acid, gently heated until the excess of sulphuric acid is almost completely removed, the residue treated for some time with cold water, the solution diluted with water, and then heated to boiling, when basic gallium sulphate separates out, which must be filtered off whilst hot. This precipitate is dissolved in a small quantity of sulphuric acid; to this liquid a slightly acid solution of ammonium acetate is added, sulphuretted hydrogen passed through to saturation, the solution filtered, and the filtrate, diluted with water, heated to boiling, the precipitate which forms being washed with boiling water. This is then dissolved in a small quantity of sulphuric acid, a slight excess of alkali added, and the alkaline solution

[1] Hartley and Ramage, *Proc. Roy. Soc.*, 1897, **60**, 35, 393; *Journ. Chem. Soc.*, 1897, **71**, 533, 547.

[2] *Sci. Proc. Roy. Dublin Soc.*, 1898, N.S., **8**, 703.

[3] H. C. Fogg and C. James, *J. Amer. Chem. Soc.*, 1919, **41**, 947.

submitted to electrolysis. Metallic gallium is thus deposited at the negative pole.[1]

The last traces of zinc and indium are difficult to remove from gallium, but both may be practically eliminated by fractional electrolysis of a slightly acid solution of the sulphates.[2] Last traces of zinc may also be removed from metallic gallium by heating it *in vacuo* at 800°, or by fractional crystallisation of the metal with centrifugal drainage of the crystals. Sixty-two grams of gallium were exhibited in the Paris Exhibition of 1878, having been prepared from 2,400 kilos. of blende by Lecoq de Boisbaudran and Jungfleisch.[3]

Gallium is a hard, brittle metal of bluish-white colour, melting at 29·75°. The molten metal possesses the colour of silver and remains liquid for many weeks, even when exposed to 0°, until touched with a small fragment of solid gallium. At a red heat the metal is slightly volatile. The density of solid gallium at its melting point is 5·904, that of the liquid being 6·095. Thus gallium, like water, expands upon solidifying. The coefficient of cubical expansion is $5{\cdot}5 \times 10^{-5}$, the compressibility is $2{\cdot}0 \times 10^{-6}$ for the solid and approximately twice as great for the liquid metal and the latent heat of fusion is 19·04 calories per gram. The atomic volume at 20° is 11·85, and the specific and atomic heats are 0·080 and 5·6 respectively. The metal is diamagnetic. Gallium only superficially oxidises when heated to redness in air or oxygen. It is easily soluble in dilute hydrochloric acid and caustic potash with evolution of hydrogen. It is scarcely attacked by dilute nitric acid in the cold, but on heating it slowly dissolves with evolution of red vapours. The best acid solvent is aqua regia. If a neutral solution of gallium chloride is warmed with zinc, gallium hydroxide or a basic salt separates out, but not the metal. In the electrochemical series gallium appears to come between indium and zinc. Like aluminium, it possesses some degree of passivity in the metallic state.

GALLIUM COMPOUNDS.

342 *Gallium Oxide*, Ga_2O_3, is a white mass, which is reduced to the metal by hydrogen at a bright red heat. The hydroxide

[1] Lecoq de Boisbaudran, *Ann. Chim. Phys.*, 1877, [5], **10**, 129; *Compt. rend.*, 1876, **82**, 1098; 1876, **83**, 636; 1881, **93**, 815.

[2] Dennis and Bridgman, *J. Amer. Chem. Soc.*, 1918, **40**, 1531; Richards and Boyer, *ibid.*, 1919, **41**, 133; 1921, **43**, 274; cf. Uhler and Browning, *Amer. J. Sci.*, 1916, **42**, 389; Uhler, *ibid.*, 1917, **43**, 81.

[3] *Compt. rend.*, 1878, **86**, 475.

is a white precipitate insoluble in water, but readily soluble in potash, and somewhat less so in ammonia.

Gallium Trichloride, $GaCl_3$.—Like aluminium, but unlike indium, gallium yields the trichloride when heated in hydrogen chloride as well as in chlorine, long, needle-shaped crystals being deposited in the tube close to the flame. It melts at 75·5°, and boils at 215—220°. Owing to its low boiling point, distillation of this compound in a dry and inert atmosphere affords an excellent method for eliminating zinc and indium from gallium.[1] The vapour density of gallium chloride as determined by the air-displacement method is 6·1 between 440° and 606°, and corresponds to the formula $GaCl_3$. Like aluminium chloride, its density near the boiling point is somewhat higher than this, being 8·8 at 350°.[2] It is a very deliquescent substance and dissolves in a small quantity of water to form a clear liquid, which on the further addition of water becomes turbid from deposition of a basic salt.

Gallium Dichloride, $GaCl_2$, is obtained by the action of the metal on the trichloride and melts at 164°, forming a limpid, refractive liquid which boils at 535°. The specific gravity of its vapour is 4·8 at 1,000°, corresponding to the formula $GaCl_2$.

Gallium Sulphate is also very soluble but non-deliquescent. It combines with ammonium sulphate to form an alum, $Ga_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$, which crystallises in combinations of the cube and octahedron. If its solution is boiled a precipitate is produced consisting probably of basic sulphate. The corresponding potassium, rubidium, cæsium and thallous-gallium alums have been described by Soret.[3]

Gallium Selenate, $Ga_2(SeO_4)_3,22H_2O$, may be obtained by treating the hydroxide with a slight deficit of aqueous selenic acid, filtering, and allowing the solution to evaporate at the ordinary temperature. The salt contains $16H_2O$ when dried to constant weight in air, and resembles the sulphate in properties. The corresponding cæsium gallium selenium alum, $Cs_2SeO_4,Ga_2(SeO_4)_3,24H_2O$, has also been prepared.[4]

Gallium Nitrate is also a soluble, well-crystallised salt.

The best means of detecting gallium is the spark spectrum

[1] Richards, Craig and Sameshima, *J. Amer. Chem. Soc.*, 1919, **41**, 131.

[2] Nilson and Pettersson, *Journ. Chem. Soc.*, 1888, **53**, 824.

[3] Soret, *Arch. Sci. phys. nat.*, 1885, [3], **14**, 96; 1888, [3], **20**, 520. See also Browning and Uhler, *Amer. J. Sci.*, 1916, [4], **42**, 389.

[4] Dennis and Bridgman, *J. Amer. Chem. Soc.*, 1918, **40**, 1531.

of the chloride or other salt.[1] This consists of two violet lines (4172, 4033), of which the brightest, Gaα, lies a little more towards the blue than the line Inβ, and the second Gaβ rather more towards the violet than Kβ. In the non-luminous gas-flame the chloride gives only a very slight indication of the line Gaα. Gallium is precipitated as the hydroxide by ammonium hydroxide or carbonate and the carbonates of the alkali and alkaline-earth metals, the precipitate being distinctly soluble in excess of precipitant. Precipitation by ammonia is complete if excess of ammonia is removed by boiling. A better precipitant is sodium or ammonium hydrogen sulphite.[2] In acetic acid or ammoniacal solution gallium can be precipitated as the sulphide, but only in the presence of excess of another element forming an insoluble sulphide, *e.g.*, silver, zinc, or manganese. The sulphide is soluble in dilute mineral acids. Gallium may be separated from many metals by precipitation as ferrocyanide in a solution containing as much as one-third its volume of concentrated hydrochloric acid.[3]

The Atomic Weight of gallium was determined by Lecoq de Boisbaudran[4] by igniting the ammonium alum, and also by dissolving the metal in nitric acid and igniting the residue, the oxide obtained in both cases being weighed. The first determination gave the atomic weight 69·6, and the second 69·2. More recently, some preliminary analyses of gallium trichloride by Richards, Craig, and Sameshima[5] have indicated the value 70·1, which is the number at present (1922) adopted.

INDIUM. In = 114·8. At. No. 49.

343 This metal was discovered in Freiberg zinc blende in the summer of the year 1863 by Reich and Richter by means of spectrum analysis.[6] Indium also occurs as sulphide in other zinc blendes, although present only in very small quantity. It has also been detected spectroscopically in a manganese ore of Spanish origin and in a number of samples of siderite, which

[1] Dennis and Bridgman, *loc. cit.*

[2] Porter and Browning, *J. Amer. Chem. Soc.*, 1919, **41**, 1491.

[3] Lecoq de Boisbaudran, *Ann. Chim. Phys.*, 1884, [6], **2**, 176, 429; Dennis and Bridgman, *loc. cit.*, Browning and Uhler, *loc. cit.*; Porter and Browning, *J. Amer. Chem. Soc.*, 1921, **43**, 111.

[4] *Bull. Soc. chim.*, 1878, **29**, 9.

[5] Richards, Craig and Sameshima, *loc. cit.*

[6] *J. pr. Chem.*, 1863, **89**, 444; **90**, 172; 1864, **92**, 480.

were obtained from various localities and all contained manganese.[1] In order to prepare indium it is best to employ metallic zinc, such as that from Freiberg, which, however, does not contain more than 0·1 per cent. The metal is treated with such a quantity of hydrochloric acid that a small portion remains undissolved, and when the solution is allowed to stand for two or three days the whole of the indium is found to be precipitated on the residual zinc. The metallic powder is then washed off from the zinc, and a few drops of dilute sulphuric acid are added to dissolve any basic zinc chloride which may be formed; the spongy metal is well washed with hot water, treated with nitric acid, and the acid solution, without filtration, boiled down with an excess of sulphuric acid until all the nitric acid is driven off. The solution is then filtered, the residue well washed, and a large excess of ammonia added to the filtrate. The zinc, cadmium, and copper remain in solution whilst the whole of the indium, together with iron, lead, and a small quantity of zinc, cadmium, and copper, remains behind. After being well washed, the residue is dissolved in a small quantity of hydrochloric acid, an excess of hydrogen sodium sulphite added, and the solution boiled until it no longer smells of sulphur dioxide. A precipitate is thus obtained of basic indium sulphite, which for further purification may be dissolved in sulphurous acid; on boiling this solution the pure salt separates out,[2] and this when strongly heated decomposes, leaving a residue of indium trioxide. The oxide can then be reduced to metal by ignition in a current of hydrogen or by fusion with sodium. The latter method appears to be the best suited for the preparation of large quantities. For this purpose the finely-divided oxide is placed in layers in a crucible with thin slices of sodium, the mixture pressed down and then covered with a thick layer of anhydrous sodium chloride. The porcelain crucible is next placed in a Hessian crucible provided with a cover, and heated first gently and, as soon as the reaction is over, to a moderate red heat. The brittle alloy thus obtained is boiled several times with water, washed with alcohol and ether, and again fused under a layer of potassium cyanide. The regulus is still not quite free from sodium, and to remove these traces it is thrown, in small pieces, into fused sodium carbonate, and the metal thus obtained in the pure state.[3]

[1] Hartley and Ramage, *Journ. Chem. Soc*, 1897, **71**, 533.
[2] Bayer, *Annalen*, 1871, **158**, 372.
[3] Winkler, *J. pr. Chem.*, 1867, **102**, 273.

The pure metal may also be separated electrolytically from solutions of the chloride or nitrate containing pyridine, hydroxylamine, or formic acid,[1] or from a solution of the sulphate.[2]

Indium is a white metal, easily malleable and softer than lead. It is obtained crystallised in regular octahedra [3] by the electrolysis of the sulphate, a branched metallic "tree" being formed. Its density at 20° is 7·277,[4] and its melting point 155° (Thiel); its specific and atomic heats (0° to 100°) are 0·057 and 6·54 respectively.[5] It retains its metallic lustre in the air and even in boiling water. Heated on charcoal before the blowpipe, it colours the flame blue and gives an incrustation of the oxide. It dissolves slowly in hydrochloric and dilute sulphuric acids, but readily in nitric acid.

INDIUM COMPOUNDS.

344 *Indium Sesquioxide*, In_2O_3, obtained by burning the metal in air or oxygen, or by igniting the hydroxide, carbonate, nitrate, or sulphate, is a pale yellow powder, which on heating becomes brown, but regains its original colour on cooling. After ignition it dissolves only slowly in mineral acids. The oxide is readily reduced to the metal by heating in hydrogen or ammonia, or by heating with sodium, magnesium, or carbon. At temperatures above 850°, the oxide loses oxygen and becomes converted into the oxide, In_3O_4, which is isomorphous with the corresponding oxide of iron.[6] The loss of weight associated with this change was at one time erroneously attributed to the volatility of the sesquioxide. Tri-indium tetroxide does not fuse even at the temperature of the oxy-hydrogen flame.

Indium Hydroxide, $In(OH)_3$, is formed when ammonia or dimethylamine is added to a soluble indium salt. The hydroxide is thrown down as a gelatinous precipitate, which on boiling becomes heavy and dense, and when heated is easily converted into the oxide. It dissolves in caustic potash,[7] from which solution it is precipitated on boiling or standing, but is not

[1] Dennis and Geer, *J. Amer. Chem. Soc.*, 1904, **26**, 437; *Ber.*, 1904, **37**, 961.

[2] Thiel, *Zeit. anorg. Chem.*, 1904, **40**, 280.

[3] Sachs, *Zeit. Kryst. Min.*, 1903, **38**, 495.

[4] Richards and Wilson, *Zeit. physikal. Chem*, 1910, **72**, 129.

[5] Bunsen, *Phil. Mag.*, 1871, [4], **41**, 161.

[6] Thiel and Koelsch, *Zeit. anorg. Chem.*, 1910, **66**, 288; cf. Renz, *Ber.*, 1903, **36**, 1847; 1904, **37**, 2110; Meyer, *Zeit. anorg. Chem.*, 1905, **47**, 281; Thiel, *ibid.*, 1906, **48**, 291.

[7] See Renz, *Ber*, 1901, **34**, 2763; 1903, **36**, 2751; 1904, **37**, 2110.

soluble in ammonia, and readily forms colloidal solutions in the absence of electrolytes.

Indium Trichloride, $InCl_3$.—The metal burns at a dull red heat in a current of chlorine, evolving a greenish-yellow light with formation of the chloride. The same compound is easily formed by heating the oxide, mixed with charcoal, in chlorine. It sublimes at about 600° in the form of soft colourless plates, is extremely deliquescent, and dissolves in water with a hissing noise and evolution of heat. On evaporating the solution, an insoluble basic salt is obtained. The vapour density of indium trichloride was found by V. and C. Meyer [1] at a bright red heat to be 7·87, corresponding to the formula $InCl_3$. An *oxychloride*, InOCl, is formed as a white powder by the action of chlorine and oxygen on the dichloride (Thiel).

Indium Dichloride, $InCl_2$, is obtained as a white, radiating, crystalline mass by heating the metal in a current of hydrogen chloride. The vapour density of the dichloride has been shown by Nilson and Pettersson [2] to be 6·43 at 1300°, corresponding to the above formula. This compound is decomposed by water with formation of the trichloride and separation of metallic indium :

$$3InCl_2 = 2InCl_3 + In.$$

Indium Monochloride, InCl, was prepared by the above-named chemists by distilling the vapour of the dichloride over the requisite amount of metallic indium; combination takes place, and the monochloride is obtained in the form of a mass resembling hæmatite, which melts to form a blood-red liquid and can readily be vaporised. Its vapour density was found to be 5·5—5·3 at 1100—1400°, corresponding to the simple formula. The monochloride undergoes a similar decomposition to the dichloride when brought into contact with water,

$$3InCl = InCl_3 + 2In.$$

Indium combines directly with bromine and iodine. The three *bromides* closely resemble the chlorides. Three *iodides* are also known (Thiel and Koelsch); the *tri-iodide* is a yellow, crystalline mass, which on heating melts to form a reddish-brown liquid. A sparingly soluble *fluoride*, InF_3, crystallising with $9H_2O$ or $3H_2O$, is formed when the oxide is dissolved in hydrofluoric acid.[3]

[1] *Ber.*, 1879, **12**, 611. [2] *Journ. Chem. Soc.*, 1888, **53**, 814.

[3] Thiel, *Zeit. anorg. Chem.*, 1904, **40**, 331; Chabrié and Bouchonnet, *Compt. rend.*, 1905, **140**, 90.

Indium Nitrate, $2In(NO_3)_3,9H_2O$, forms deliquescent needles soluble in both water and absolute alcohol. These on heating are easily converted into a basic salt (Winkler).

Indium Sulphide, In_2S_3.—Pure indium and sulphur combine together at a temperature near redness, with evolution of heat, to form a bright-red, infusible mass, which is also produced when the oxide is heated in a current of sulphuretted hydrogen. This gas, passed into a solution of an indium salt which is not too acid or too concentrated, precipitates yellow indium sulphide, which on heating with ammonium sulphide is converted into the white hydrosulphide and is soluble in concentrated acids. A lower sulphide, In_2S, has been obtained mixed with a little of the normal sulphide, by heating the latter in hydrogen, and is a yellowish-brown, fusible mass, readily soluble in warm dilute acids; the reddish-brown *disulphide*, InS, is obtained by heating the metal in a stream of hydrogen sulphide (Thiel and Koelsch).

Basic Indium Sulphite, $In_2(SO_3)_3,In_2O_3,8H_2O$, is a crystalline powder, the preparation of which has been already described.

Indium Sulphate, $In_2(SO_4)_3$, is obtained by the careful evaporation of a solution of the trioxide in an excess of sulphuric acid, in the form of a white powder very soluble in water. On strongly heating it is converted into an insoluble basic salt. On evaporating the acid solution over sulphuric acid, deliquescent crystals of the acid salt, $H_2In_2(SO_4)_4,8H_2O$, are deposited.

Indium Ammonium Alum, $In_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$, is deposited in well-defined, regular octahedra, which dissolve at 16° in half their weight, and at 30° in about a quarter of their weight of water, and melt at 36°.[1] If a solution is allowed to crystallise at or above this temperature crystals of the hydrate, $In_2(SO_4)_3,(NH_4)_2SO_4,8H_2O$, separate out.

The sulphates of potassium and sodium form analogous salts containing 8 molecules of water, but do not yield true alums, whilst cæsium and rubidium yield alums of the normal composition.[2]

Indium Selenate, $In_2(SeO_4)_3,10H_2O$, is a white, deliquescent salt resembling the sulphate. *Cæsium indium selenate*, $In_2(SeO_4)_3,Cs_2SeO_4,24H_2O$, has also been prepared.[3]

[1] Rössler, *J. pr. Chem.*, 1873, [2], **7**, 14.

[2] Soret, *Arch. Sci. phys. nat.*, 1885, [3], **13**, 5; 1888, [3], **20**, 520; Chabrié and Rengade, *Compt. rend.*, 1900, **131**, 1300; 1901, **132**, 472.

[3] Mathers and Schluederberg, *J. Amer. Chem. Soc.*, 1908, **30**, 211.

Detection and Estimation of Indium.

345 Indium compounds when moistened with hydrochloric acid tinge the non-luminous gas-flame a dark blue colour. The spectrum consists of an intense indigo-blue line, Inα 4511, and a less intense violet line, Inβ 4102. It is from this property that the metal derives its name.

When heated on charcoal with sodium carbonate indium compounds yield white beads of the metal and a yellow incrustation of oxide. Traces of indium can be detected by the spark spectrum [1] and microchemically by the formation of a double chloride of indium and rubidium which crystallises in colourless rhombic octahedra.[2] Caustic soda and potash precipitate the hydroxide, which partly dissolves in an excess, but is completely deposited again on boiling; it is insoluble in ammonia. This reaction is employed for the separation of indium from the other metals, as are also the formation of the insoluble basic sulphite (p. 779), the precipitation of a sulphide of indium which is insoluble in dilute acids, and the production of a precipitate with pyridine.[3]

The Atomic Weight of indium was determined by Reich and Richter, as well as by Winkler [4] and Bunsen,[5] by converting the metal into the oxide. The subsequent experiments of Thiel,[6] who used comparatively large amounts of carefully purified material, have shown that the early results were considerably too low, and that conversion of the metal into oxide is attended by considerable difficulties. The analysis of the chloride gave Thiel the number 114·97, whilst that of the bromide gave 114·75. The analyses by Mathers [7] of these same salts prepared from indium purified by fractional electrolysis, gave the numbers 114·83 and 114·80, whilst lower and less reliable numbers were obtained by the conversion of the metal into the sulpha e, and the analysis of the dichloride. At present (1922) the adopted number is 114·8.

[1] Dennis and Bridgman, *J. Amer. Chem. Soc.*, 1918, **40**, 1531.

[2] Kley, *Chem. Zeit.*, 1901, **25**, 563; see also Huysse, *Zeit. anal. Chem*, 1900, **39**, 9.

[3] Dennis and Geer, *Ber.*, 1904, **37**, 961.

[4] *Jahresb.*, 1867, 260.

[5] *Pogg. Ann.*, 1870, **141**, 1.

[6] *Zeit. anorg. Chem*, 1904, **40**, 280.

[7] *J. Amer. Chem. Soc.*, 1907, **29**, 485; *Ber.*, 1907, **40**, 1220.

THALLIUM. Tl = 204·0. At. No. 81.

346 Thallium was discovered in the year 1861 by Crookes [1] in a seleniferous deposit obtained from a sulphuric acid manufactory at Tilkerode in the Harz. Selenium was being prepared from this deposit, and a considerable residue was left when the material was distilled. This was supposed at first to contain tellurium, but examination with the spectrosope showed that a new element was present whose spectrum consisted of one bright green line, whence the name of the element, from θάλλος, a green twig. In 1862 Lamy,[2] who discovered the element independently of Crookes, published the results of his investigations. It was first believed that this element was a non-metal belonging to the sulphur group, but it was afterwards found to be a metal and was obtained in the metallic condition.

Thallium occurs in small quantities in many varieties of iron and copper pyrites, and in a few micas containing lithium. The mineral crookesite, discovered by Nordenskjöld [3] in a copper mine at Skrikerum, in Sweden, contains:

Tl	Se	Cu	Ag	
17·25	33·28	45·76	3·71	= 100·00.

Thallium is also found in the minerals lorandite, $TlAsS_2$ and vrbaite, $TlAs_2SbS_5$, which accompany realgar in Macedonia,[4] and occurs in traces in some iron ores, manganese ores, and zinc blendes.[5]

The mineral water of Nauheim, near Frankfort, and that of many other mineral springs, contains traces of thallium.

For the purpose of preparing thallium it is best to employ the flue dust from sulphuric acid works, in which pyrites containing thallium is burnt. The dust, which contains selenium, arsenious oxide, and small quantities of many other metals in the form of oxides or sulphates, is repeatedly boiled with very dilute sulphuric acid, the solution concentrated, and the thallium precipitated, in the form of needles or glittering plates, by adding

[1] "On the Existence of a new Element, probably of the Sulphur Group," *Chem. News*, 1861, **3**, 193, 303.

[2] *Société Impériale des Sciences de Lille*, May 2 and 16, 1862; *Compt. rend.*, 1862, **54**, 1255; **55**, 836.

[3] *Annalen*, 1868, **145**, 127.

[4] Krenner, *Zeit. Kryst. Min.*, 1897, **27**, 98; Goldschmidt, *ibid.* 1898, **30**, 272; Jézek, *ibid.*, 1912 **51**, 364; Krĕhlík, *ibid.*, 1912, **51**, 379.

[5] Hartley and Ramage, *Journ. Chem. Soc.*, 1897, **71**, 533.

metallic zinc. Thallium may be obtained in a purer condition by boiling up the flue dust with water, and adding hydrochloric acid or common salt to the concentrated clear solution. The precipitate is washed and gradually dissolved in half its weight of hot sulphuric acid, and then heated until all the hydrochloric acid and the greater part of the free sulphuric acid has been driven off. The residue is next dissolved in water, the solution treated with sulphuretted hydrogen for the purpose of precipitating mercury, silver, arsenic, antimony, and bismuth, and ammonia then added to the filtrate to throw down any iron or alumina which may still be present. The filtrate, when concentrated, yields crystals of pure thallium sulphate, from which the metal may be obtained by deposition on zinc or by electrolysis.[1] According to Bunsen,[2] the solution of zinc sulphate obtained at the Juliushütte, at Goslar, contains 0·05 per cent. of thallium chloride, and if metallic zinc is allowed to remain in contact with the solution, copper, thallium, and cadmium are thrown down in the metallic state. The precipitated metals are then carefully washed with water and digested with dilute sulphuric acid to dissolve the last two meals. If potassium iodide is then added to this solution, thallium iodide separates out, and this on treatment with potassium cyanide yields pure metallic thallium.

Pure thallium has a bluish-white tint and a lead-like, metallic lustre. It has the sp. gr. 11·85, and is crystalline, and so soft that it may be marked with the nail and leaves a streak on paper. It is malleable, but possesses little tenacity, and can only with difficulty be filed or sawn, as the articles stop up the interstices of the tool. It exists in two modifications, the transition temperature being 226°,[3] it melts at 303°,[4] volatilises at a very high temperature, and may be distilled in a current of hydrogen. Its specific and atomic heats (20° to 100°) are 0·0326 and 6·65.[5] Its vapour density[6] at very high temperatures corresponds with the simple molecular formula Tl. When heated before the blowpipe it oxidises, a pale reddish vapour

[1] Crookes, *Phil. Trans.*, 1873, **163**, 277; *Chem. News*, 1874, **29**, 14. See also Förster, *Zeit. anorg. Chem.*, 1897, **15**, 71.

[2] *Phil. Mag.*, 1865, [4], **29**, 168.

[3] M. Werner, *Zeit. anorg. Chem.*, 1913, **83**, 275.

[4] Petrenko, *Zeit. anorg Chem.*, 1906, **50**, 133.

[5] Schmitz, *Proc. Roy. Soc.*, 1903, **72**, 177.

[6] von Wartenberg, *Zeit. anorg. Chem.*, 1907, **56**, 320; cf. Meyer and Biltz, *Ber.*, 1889, **22**, 725; Biltz, *Math. natw. Mitt. Berlin*, 1895, 37.

being evolved which possesses a peculiar smell. It decomposes water at a red heat and dissolves readily in nitric and sulphuric acids, both dilute and concentrated, whilst it is less readily soluble in hydrochloric acid. It is slowly acted upon by alcohol in presence of air, forming an alcoholate, which is liquid at ordinary temperatures. Thallium readily forms alloys with other metals, and amalgamates with mercury. The metal is usually kept under glycerine or petroleum oil, owing to its oxidisability.

THALLIUM COMPOUNDS.

347 Thallium forms two distinct series of compounds, one of the type RX_3, corresponding with the position of the metal as a member of the aluminium group, the other of the type RX, closely analogous in many respects to the corresponding compounds of the alkali metals, but frequently bearing a strong physical resemblance to the corresponding compounds of lead.

THALLOUS COMPOUNDS.

348 Many of these compounds resemble the compounds of lead in their physical properties. Thus the halogen compounds (with the exception of the fluoride) are very sparingly soluble in water, and the sulphide is an insoluble black powder. On the other hand, the hydroxide, the sulphate, and the carbonate are all soluble in water, and closely resemble the corresponding potassium salts; the sulphate, perchlorate, and phosphate are, moreover, isomorphous with the corresponding salts of that metal.

Thallium Monoxide, Tl_2O.—When the metal is exposed to the air its surface assumes a dull grey colour, due to the formation of this compound. It may be obtained in the pure state by heating the hydroxide in absence of air to a temperature of 100°. It is a black powder melting at about 300°, and dissolves readily in water with the formation of the hydroxide.

Thallous Hydroxide, TlOH, is formed by the action of water upon the metal in presence of air. In order to prepare it in larger quantity a solution of the sulphate is precipitated with the necessary quantity of baryta water. It crystallises in long yellow needles having the formula $TlOH,H_2O$. It is readily soluble in water, and the solution is colourless, possesses a strong alkaline reaction, and readily absorbs carbon dioxide.[1] The brown colour it gives with turmeric disappears after some time

[1] See Bahr, *Zeit. anorg. Chem.*, 1911, **71**, 79.

as the hydroxide destroys the colouring matter. Hence if turmeric paper is written upon with metallic thallium the writing at first appears brown but gradually disappears.[1]

Rabe [2] has prepared an oxide having the formula TlO, by acting on a solution of thallous sulphate with H_2O_2 and potassium hydroxide. It has a bluish-black colour.

Thallous Fluoride, TlF, is formed by dissolving the carbonate in hydrofluoric acid. It crystallises in glittering octahedra and cube-octahedra. It dissolves in 1·25 parts of water at 15°, and less readily in boiling water. It melts on heating, and may readily be sublimed in a current of hydrogen fluoride.

Thallium Hydrogen Fluoride, $TlHF_2$, formed by allowing a solution of the fluoride in hydrofluoric acid to evaporate in a vacuum over sulphuric acid, crystallises in similar forms to thallous fluoride, and dissolves in its own weight of water.

Thallium Monochloride or *Thallous Chloride*, TlCl, is formed when the metal burns in chlorine, and separates out when hydrochloric acid is added to a tolerably concentrated solution of a soluble thallium salt, forming a white, curdy precipitate which assumes a violet tint on exposure to light (Hebberling). It crystallises from hot saturated solutions in the form of cubes, and melts at 426° to a yellowish liquid which on cooling solidifies to a white, shining, crystalline, somewhat flexible mass, having a specific gravity of 7·02 (Lamy) and boiling at 719—731°. Its vapour density has been found to be 8·5,[3] corresponding to the simple molecular formula. The solubility in water, in grams per litre of solution, is as follows : [4]

At	0°	20°	40°	60°	80°	100°
TlCl	1·7	3·4	6·0	10·2	16·0	24·1

It is less soluble in dilute hydrochloric acid, and hence the salt is precipitated from aqueous solution on addition of this acid.[5] It is scarcely soluble in ammonia, and is insoluble in alcohol.

Thallous Bromide, TlBr, is a very pale yellow precipitate less soluble than the chloride, to which it possesses strong analogies. Dry bromine does not react with the metal so readily as chlorine, but in presence of water the metal is readily attacked. It melts at 450° and boils at 800—814°.

[1] Erdmann, *J. pr. Chem.*, 1863, **89**, 381.

[2] *Zeit. anorg. Chem.*, 1908, **58**, 23. [3] Roscoe, *Proc Roy. Soc.*, 1878, **27**, 426.

[4] Earl of Berkeley, *Phil. Trans.*, 1904, [*A*], **203**, 208; Hill and Simmons, *J Amer. Chem. Soc.*, 1909, **31**, 821.

[5] See Bray and Winninghoff, *J. Amer. Chem. Soc.*, 1911, **33**, 1663.

Thallous Iodide, TlI, is formed when thallium and iodine are heated together. It may also be obtained by precipitating a solution of a thallium salt with potassium iodide, when it is thrown down as a beautiful yellow, crystalline powder, which passes at 168° into a red modification, the reverse change occurring on cooling. Both forms can exist in the metastable condition through a large range of temperature.[1] The red form melts at 431°. When precipitated from a hot solution containing potassium acetate, it is deposited in the form of microscopic orange-yellow cubes or cubo-octahedra (Werther). It is sparingly soluble in cold water, 1 part requiring 16,000 parts for its solution at 20°, whereas it dissolves in 830 parts of boiling water.[2] It separates from a filtered hot solution in water and from saline solutions in the red form, which then passes very slowly into the stable yellow modification. It is less soluble in a solution of potassium iodide, in alcohol, and in dilute acetic acid than in water itself. It is not decomposed by dilute sulphuric acid, hydrochloric acid, or caustic potash. Nitric acid, however, decomposes it with evolution of iodine.

Thallous Chlorate, $TlClO_3$.—This salt is formed by mixing equivalent quantities of thallium sulphate and barium chlorate, filtering, and concentrating the solution; the salt then separates out in microscopic prisms sparingly soluble in cold water.

Thallous Perchlorate, $TlClO_4$, is formed by dissolving thallium in aqueous perchloric acid, or by precipitating barium perchlorate with thallous sulphate. It crystallises in transparent, rhombic tablets, isomorphous with potassium perchlorate, and having a specific gravity of 4·844 at 15·5°. One part of this salt dissolves at 15° in 10 parts, and at 100° in 0·06 part of water; it is only slightly soluble in alcohol (Roscoe).

Thallium Monosulphide or *Thallous Sulphide*, Tl_2S, is a black precipitated formed when sulphuretted hydrogen is passed into an alkaline or acetic acid solution of a thallous salt. If the solution contains a trace of free sulphuric acid the sulphide separates out in the cold in microscopic tetrahedra (Hebberling). If the sulphide or a mixture of the metal with sulphur is melted in absence of air, a black, glittering mass is obtained on cooling, having a specific gravity of about 8 and melting at 448°.[3] It is insoluble in water, alkalis, ammonium sulphide, and potassium

[1] Gernez, *Compt. rend.*, 1904, **138**, 1695; 1904, **139**, 278; 1909, **148**, 1015.
[2] Bottger, *Zeit. phys'kal. Chem.*, 1903, **46**, 602.
[3] Pélabon, *Ann. Chim. Phys.*, 1907, [8], **17**, 526.

cyanide. When the sulphide is heated to 150—200° with colourless ammonium sulphide it crystallises in long needles of metallic appearance, or in thin, six-sided plates.[1] It dissolves with difficulty in acetic acid, but readily in mineral acids. The precipitated sulphide oxidises on exposure with formation of sulphate, and when heated in a current of hydrogen is reduced to thallium. Black, lustrous prisms of a compound, Tl_2S_5, which is probably *thallous pentasulphide*, are obtained by the action of a solution of ammonium polysulphide on thallous chloride.[2]

Normal Thallous Sulphate. Tl_2SO_4.—This salt crystallises in rhombic prisms isomorphous with potassium sulphate and has a specific gravity of 6·765. It melts at 632°. One hundred parts of water dissolve as follows :[3]

At	0°	20°	40°	60°	80°	99 7°
Tl_2SO_4	2·7	4·9	7·6	10·9	14·6	18·5

It is much more soluble in dilute sulphuric acid than in water.[4]

Thallous sulphate readily combines with other sulphates to form double salts such as $Tl_2SO_4,MgSO_4,6H_2O$, isomorphous with the analogous potassium compounds.[5] It can also replace the alkali sulphates in the alums. Thus *e.g.*, thallium alum, $Tl_2SO_4,Al_2(SO_4)_3,24H_2O$, crystallises in bright octahedra. Thallium iron alum and thallium chromium alum have also been prepared.

Hydrogen Thallous Sulphate, $HTlSO_4,3H_2O$, crystallises in short, thick prisms, which melt on heating, and then suddenly decompose into the normal sulphate with evolution of vapours of sulphuric acid. The anhydrous compound melts at 115—120°. A compound of the formula $Tl_2SO_4,TlHSO_2$ has also been described (Stortenbeker).

Thallous Nitrate, $TlNO_3$.—Nitric acid attacks thallium more easily than any other acid. Thallium nitrate crystallises in opaque, white rhombic prisms, having a specific gravity of 5·55; these pass at 72·8° into a rhombohedral form and at 142·5° into a regular modification.[6] The crystals melt at 206·1°, and the fused mass solidifies on cooling to a glass-like solid. It de-

[1] Staněk, *Zeit. anorg. Chem*, 1898, **17**, 117.
[2] Hofmann and Hochtlen, *Ber.*, 1903, **36**, 3090.
[3] Earl of Berkeley, *Phil. Trans.*, 1904, [*A*], **203**, 211.
[4] Stortenbeker, *Rec. trav. chim.*, 1902, **21**, 87; 1905, **24**, 53; 1907, **26**, 248.
[5] See Tutton, *Proc. Roy. Soc.*, 1910, [*A*], **83**, 211.
[6] van Eyk, *Proc. K. Akad. Wet. Amsterdam*, 1900, **2**, 1480; **3**, 98; *Zeit. physikal. Chem.*, 1905, **51**, 721.

composes rapidly at 450°, leaving a residue of thallic oxide.[1] One hundred parts of water dissolve, according to Berkeley:

At	0°	20°	40°	60°	80°	100°
$TlNO_3$	3·9	9·55	20·9	46·2	111·0	414·0

It is insoluble in alcohol.

Phosphates of Thallium.—These salts are isomorphous with the analogous potassium compounds.

Normal Thallous Orthophosphate, Tl_3PO_4, is obtained in the form of needle-shaped crystals by precipitating the corresponding potassium salt with a thallium salt. It is also formed by the precipitation of ordinary sodium phosphate, but this precipitation is not complete (Lamy). One part dissolves at 15° in 201, and at 100° in 149 parts of water (Crookes). It is easily soluble in ammoniacal salts.

Monohydrogen Thallous Orthophosphate, HTl_2PO_4,H_2O, is formed by neutralising a boiling solution of phosphoric acid with thallium carbonate. When evaporated to a syrup, the concentrated solution deposits rhombic crystals. These lose their water at 200°, and when they are heated to dull redness a glassy mass of pyrophosphate remains behind.

Dihydrogen Thallous Orthophosphate, H_2TlPO_4.—This salt is obtained when phosphoric acid is added to a solution of the foregoing salt until the liquid exhibits a distinctly acid reaction. It crystallises in monoclinic, pearly tablets, dissolves readily in water, and on ignition is converted into the glassy metaphosphate.

Normal Thallous Carbonate, Tl_4CO_3.—Thallium hydroxide readily absorbs carbon dioxide. Thus if the moistened metal is allowed to lie exposed to the air, it becomes covered with needle-shaped crystals of the carbonate. This salt crystallises from solution in water in glittering monoclinic prisms, which have a caustic, metallic taste and an alkaline reaction. One hundred parts of water dissolve, according to Lamy:

At	18°	62°	100·8°
Tl_2CO_3	5·23	12·85	22·40.

It is insoluble in alcohol. It fuses on heating and decomposes at a higher temperature with evolution of carbon dioxide.

Thallous Cynaide, TlCN.—This salt is obtained by mixing strong solutions of potassium cyanide and thallous nitrate

[1] Thomas, *Compt. rend.*, 1904, 138, 1697.

(Crookes). It separates in glittering plates not very soluble in water. When heated, it decrepitates and melts easily, volatilising when strongly heated on platinum foil without reduction and without acting on the platinum. It is readily soluble in potassium cyanide and forms crystalline double cyanides.

Silicate of Thallium.—A solution of the hydroxide when boiled with amorphous silica dissolves this substance, and when the solution is evaporated a crystalline mass, having the composition $Tl_6Si_{10}O_{23} = 3Tl_2O,10SiO_2$, and also containing water, separates out. When thallium oxide is fused with silica a yellow, strongly refracting glass is obtained, which is occasionally employed in place of lead silicate for optical glass.

Thallous Borate.—Various borates of thallium have been described by Buchtala.[1]

THALLIC COMPOUNDS.

349 Thallic oxide, like alumina, acts as a weak base. The salts with colourless acids are colourless, and are as a rule hydrolysed to a considerable extent in aqueous solution, so that many of them decompose when their solutions are largely diluted, or heated, the hydrated oxide being deposited. They are reduced by metallic thallium to thallous salts and show a greater tendency than these to form complex salts.[2]

Thallium Trioxide, Tl_2O_3.—When molten thallium is plunged into oxygen it takes fire with formation of this oxide. At a red heat this is, however, converted into the monoxide. It is also obtained by passing a current from a few Bunsen elements through acidulated water, the positive pole consisting of metallic thallium, which then becomes covered with a black deposit of this oxide [3] (Wöhler):

$$Tl_2 + 3H_2O = Tl_2O_3 + 3H_2.$$

It is also deposited on a platinum anode as a coherent film when an acid solution of thallous sulphate containing a little acetone is electrolysed,[4] and this separation may be utilised for the gravimetric estimation of thallium.

Thallic oxide is also obtained when hydrogen peroxide is

[1] *J. pr. Chem.*, 1913, [2], **88**, 771.
[2] See Spencer and Abegg, *Zeit. anorg. Chem.*, 1905, **44**, 379.
[3] *Annalen*, 1868, **146**, 243, 375.
[4] Heiberg, *Zeit. anorg. Chem.*, 1903, **35**, 347.

added to an alkaline solution of a thallous salt and the resulting precipitate washed with alcohol and ether and dried in vacuo. When cold solutions are employed the oxide is brown, has the sp. gr. 9·65, and is readily soluble in acids, whereas the oxide obtained from hot solutions is black, has the sp. gr. 10·19, and is only slowly attacked by acids.[1] The crystalline oxide obtained by heating the nitrate, however, has the sp. gr. 9·97.[2] The oxide melts at 725°, and loses oxygen slowly at 800° and rapidly at 1000°.

Thallic Hydroxide, $Tl(OH)_3$.—If a hot solution of thallous chloride in sodium carbonate is mixed with one of sodium hypochlorite, a brown precipitate is obtained which probably consists of amorphous thallic hydroxide, but on drying has the composition TlO(OH). The latter compound is also formed by the action of an alkali on thallic chloride. Thallic hydroxide is a reddish-brown powder. When treated with hydrochloric acid it evolves chlorine with formation of a thallous salt, whereas oxygen is given off when it is heated with concentrated sulphuric acid; on heating to 110—120° it is transformed completely into thallic oxide and at a red heat into the monoxide.

Thallic Chloride, $TlCl_3$, is formed when the monochloride is treated with chlorine under water. If the solution is evaporated at 60—70° and then cooled, deliquescent, colourless crystals of the hydrate $TlCl_3,4H_2O$ are obtained which pass slowly *in vacuo* at the ordinary temperature, more rapidly at 55°, into the monohydrate. The anhydrous chloride can be obtained, according to Thomas, by direct dehydration of the tetrahydrate over caustic soda in vacuo, or according to Meyer by the decomposition in vacuo of the compound $TlCl_3,(C_2H_5)_2O$ obtained by the action of ether on the tetrahydrate. It forms a hard mass consisting of six-sided crystals, and melts at 24°.[3]

When thallium is strongly heated in chlorine, a yellowish-brown mass of the composition $TlCl_3,3TlCl$ is formed, and this can also be obtained by the partial reduction of thallic chloride and by saturating a solution of this chloride with thallous chloride. It is sparingly soluble in cold, but readily in hot water, separating from this solution in dark-yellow, six-sided tablets, strongly

[1] Rabe, *Zeit. anorg. Chem.*, 1906, **48**, 427; 1906, **50**, 158; 1907, **55**, 130.

[2] Thomas, *Compt. rend.*, 1904, **138**, 1697; cf. Lepierre and Lachaud, *ibid.*, 1891, **113**, 196.

[3] Meyer, *Zeit. anorg. Chem.*, 1900, **24**, 321; Thomas, *Compt. rend.*, 1902, **135**, 1051; *Ann. Chim Phys.*, 1907, [8], **11**, 204; cf. McClenahan, *Amer. J. Sci.*, 1904, [4], **18**, 104.

resembling lead iodide in appearance. Many compounds intermediate in composition between this and the trichloride have been described, but according to Meyer,[1] these are probably solid solutions of thallous chloride in thallic chloride, a continuous series being possible up to the limit of composition represented by $TlCl_3,3TlCl$.

When the metal is treated with nitrosyl chloride, the compound $TlCl,TlCl_3,2NOCl$ is formed. If an alcoholic solution of the trichloride is heated with alcoholic ammonia, a white, crystalline precipitate of $(NH_3)_3TlCl_3$ separates out; this is decomposed on contact with water with formation of the violet-coloured trioxide:

$$2(NH_3)_3TlCl_3 + 3H_2O = Tl_2O_3 + 6NH_4Cl.$$

The chloride also forms double salts with the chlorides of ammonium and potassium.[2]

Thallic Bromide has not been obtained in the anhydrous state, but the monohydrate, $TlBr_3,H_2O$, is known. Like the chloride, it unites with the corresponding thallous salt, but forms two definite compounds, $TlBr_3,TlBr$ and $TlBr_3,3TlBr$, as well as a series of solid solutions.

A large number of chlorobromides have been described, which are obtained by the action of bromine on the chloride and of chlorine on the bromide, as well as by reactions between the chlorides and bromides themselves.[3]

Thallic Sulphide, Tl_2S_3, is formed when the metal is fused with an excess of sulphur. It is a black, amorphous mass which at a summer temperature is soft and plastic like pitch. Below 12° it is hard and brittle, exhibiting a glassy fracture.

If one part of thallium sulphate is fused with 6 parts of sulphur and 6 parts of potassium carbonate, and the mass treated with water, a red, crystalline powder remains behind having the composition $KTlS_2$. This substance is not attacked by caustic potash, but decomposes in presence of acids (Schneider).

Thallic Sulphate, $Tl_2(SO_4)_3$, crystallises on evaporation of a

[1] See also Cushman, *Amer. Chem. J*, 1900, **24**, 222; Thomas, *Compt. rend.*, 1906, **142**, 838; *Ann. Chim. Phys*, 1907, [8], **11**, 204.

[2] See Pratt, *Amer. J. Sci.*, 1895, [3], **49**, 398, 402; Meyer, *loc. cit.*; Wallace, *Zeit. Kryst. Min.*, 1911, **49**, 417.

[3] Meyer, *Zeit. anorg. Chem*, 1900, **24**, 321; Cushman, *Amer. Chem. J.*, 1900, **24**, 222; Thomas, *Compt. rend.*, 1900, **131**, 892, 1208; 1901, **132**, 80, 1487; 1901, **133**, 735; 1902, **134**, 545; 1902, **135**, 1051; *Ann. Chim. Phys*, 1907, [8], **11**, 204.

solution of the trioxide in warm dilute sulphuric acid in the form of thin, colourless tablets containing $7H_2O$, which are decomposed by water with separation of the hydrated trioxide.

It very readily forms the basic salt, $Tl(OH)(SO_4),2H_2O$, even in presence of sulphuric acid (Marshall), and yields the acid salt, $Tl_2(SO_4)_3,H_2SO_4,8H_2O$, when an excess of acid is present. This acid salt is decomposed at 220°, leaving the anhydrous sulphate (Meyer and Goldschmidt).

No true alums have as yet been prepared containing thallic sulphate in place of aluminium sulphate, but salts of the type $M_2SO_4,Tl_2(SO_4)_3,8H_2O$ have been prepared containing the sulphates of ammonium, potassium, and rubidium. Crystals of ammonium alum have, however, been obtained containing variable amounts of thallic sulphate, and it seems probable, therefore, that thallic sulphate, like the sulphates of aluminium, gallium, and indium, is capable of forming true alums.[1]

A number of complex thallo-thallic sulphates have been described. The simplest of these has the composition $Tl_2SO_4,Tl_2(SO_4)_3$, and is formed when equivalent amounts of thallous and thallic sulphate are dissolved in water and the solution is allowed to crystallise.[2]

Thallic Nitrate, $Tl(NO_2)_3,3H_2O$, is deposited from a solution of the oxide in nitric acid in colourless, deliquescent crystals which decompose on heating with water.

The complex salt, $2TlNO_3,Tl(NO_3)_3$, crystallises in prisms, melts at 150°, and is decomposed by moist air.[3]

Detection and Estimation of Thallium.

350 The salts of thallium are poisonous, and the soluble salts possess a disagreeable metallic taste. Their presence may be readily detected by the beautiful green colour which they impart to a non-luminous gas-flame. The spectrum of this flame consists of one bright green line having a wave-length of 5351, not coincident with any line in the solar spectrum. Thallium may be readily separated from all the other metals by treating an acid solution with sulphuretted hydrogen, filtering off the separated sulphides, and precipitating the filtrate with sulphide

[1] Piccini and Fortini, *Zeit. anorg. Chem.*, 1902, **31**, 451; Fortini, *Gazzetta*, 1905, **35**, ii., 450.

[2] Lepsius, *Chem. Centr.*, 1891, i., 694. See also Marshall, *Proc. Roy. Soc. Edin.*, 1902, **24**, 305; Meyer and Goldschmidt, *Ber.*, 1903, **36**, 238.

[3] Wells and Beardsley, *Amer. Chem. J.*, 1901, **26**, 275.

of ammonium, which throws down thallium sulphide as a black precipitate. This precipitate may contain also the sulphides and hydroxides of the metals of the iron group; to separate these, it is washed, dissolved in nitric acid, and the boiling solution neutralised with sodium carbonate; on cooling, chloroplatinic acid is added, when the pale yellow double chloride of thallium and platinum, $2TlCl,PtCl_4$, is precipitated. This compound dissolves in 15,600 parts of cold water, and hence may be employed for the quantitative estimation of thallium. Thallium may also be precipitated by potassium iodide as thallous iodide, which in presence of an alkali iodide is altogether insoluble in water.

Several other methods for the estimation of thallium have been proposed, based on the oxidation of thallous to thallic salts, by means of bromine, iodine, or auric bromide.[1] As already mentioned (p.788), thallium may also be estimated by the electrolytic deposition of thallic oxide. It can also be estimated as metal by using a mercury cathode and a rotating anode.[2] The salts derived from volatile acids may be converted into sulphate by careful heating with sulphuric acid, and the thallium weighed in this form. Finally, thallic salts may be precipitated in neutral solution by ammonia, the liquid boiled, and the resulting thallic oxide dried at 60—70° and weighed.

The Atomic Weight of thallium has been determined by Crookes[3] by converting the metal into the nitrate. Ten experiments gave numbers lying between 202·62 and 202·65 (H = 1). The corresponding number 204·1 (O = 16) has been confirmed by Lepierre, who analysed thallic oxide and thallous sulphate, and determined the amount of thallic oxide which could be obtained from a thallous salt.[4] The number accepted now (1922) is 204·0.

[1] Marshall, *J. Soc. Chem. Ind*, 1900, **19**, 994; Thomas, *Compt. rend*, 1900, **130**, 1316; 1902, **134**, 655.

[2] Morden, *J. Amer. Chem. Soc.*, 1909, **31**, 1045.

[3] *Phil. Trans.*, 1873, **163**, 277. [4] *Compt. rend.*, 1893, **116**, 580.

METALS OF THE RARE EARTHS.

Scandium, Sc
Yttrium, Yt

Lanthanum, La	Europium, Eu	Dysprosium, Dy
Cerium, Ce	Gadolinium, Gd	Holmium, Ho
Praseodymium, Pr	Terbium, Tb	Erbium, Er
Neodymium, Nd		Thulium, Tm
Samarium, Sa		Neo-ytterbium, Yb
		Lutecium, Lu
		Celtium, Ct

351 The term rare earth metal is generally applied to the extensive series of elements, the atomic weights of which lie between those of barium and tantalum. In addition, the two metals scandium and yttrium belonging to the boron group of metals are often classed with them. The most striking characteristic of the group is the extraordinary chemical similarity between the members: this similarity, coupled with the fact that the rare earths are always associated together in nature, makes their separation and preparation in the pure state a matter of very great difficulty.[1] The relation of these elements to the periodic system of classification has given rise to much discussion (p. 69), and opinions are still divided as to whether they form an anomalous group occupying a single position in the periodic system, or

[1] An elaborate monograph on the Rare Earths by R. J. Meyer, with a very full discussion of their atomic weights by Brauner, is contained in Abegg's *Handbuch der anorganischen Chemie*, vol. iii., part I. (Hirzel, Leipzig, 1906). See also *The Metals of the Rare Earths*, by J. F. Spencer (Longmans, Green and Co., 1919). A short article contributed by Brauner to Mendeléeff's *Principles of Chemistry*, vol. ii., pp. 105–124 (Longmans, London, 1905), Bohm's *Darstellung der Seltnen Erden*, 2 vols. (Veit & Co., Leipzig, 1905), and R. J. Meyer and O. Hauser's *Die Analyse der seltenen Erden und der Erdsäuren* (F. Enke, Stuttgart, 1912), also contain much valuable information on the subject.

whether they are to be assigned to the vacant spaces in series 8, 9, 10 (pp. 52–53).[1]

The earths formerly described as philippia and mosandria have been proved to be mixtures of other earths,[2] and it is probable that the compounds of decipium (Delafontaine)[3] and victorium (Crookes)[4] are also mixtures.

352 In the year 1794 Professor Gadolin, of Abo, in Finland, discovered a new earth in the mineral, termed after him gadolinite, which had been found at Ytterby in the year 1788. This discovery was confirmed in the year 1797 by Eckeberg, who found that the compound separated by Gadolin contained, together with glucina, a new earth, to which he gave the name of yttria. In 1803 Klaproth discovered a second peculiar earth in another Swedish mineral found at Riddarhyttan, which mineral had formerly been supposed to contain tungsten, and to this, because it became dark yellow on heating, he gave the name of ochroite. The same substance was examined simultaneously by Berzelius and Hisinger, who considered it as the oxide of a new metal which they termed cerium, after the planet Ceres, which had been recently discovered, whilst the mineral was called cerite.

In 1819 Berzelius observed that crude yttria also contained ceria; and Mosander, in 1839, showed, in a most careful investigation, that ceria contained the oxide of another metal, to which he gave the name of lanthanum (λανθάνω, I lie hidden).

In 1841 he discovered that the latter was not pure, but contained a third new element, to which he gave the name didymium (from δίδυμοι, twins). The same chemist in 1843 concluded from another series of investigations that yttrium was invariably accompanied by two other metals, to which he gave the names of terbium and erbium from the terminal letters of the stem of the word Ytterby. According to the investigations of Bunsen and Bahr,[5] only one of the last two metals appeared to exist, and for this they retained the name erbium, but the subsequent

[1] See Werner, *Ber.*, 1905, **38**, 914; Armstrong, *Proc Roy. Soc.*, 1902, **70**, 86; Brauner, *J. Russ. Chem. Phys. Soc.*, 1902, **34**, 142; *Zeit. Elektrochem.*, 1906, 17; Biltz, *Ber.*, 1902, **35**, 562; Brauner, *Zeit. Elektrochem.*, 1908, 525, also this volume, *Atomic Numbers*, p. 72.

[2] See Roscoe, *Ber.*, 1882, **15**, 1274.

[3] *Compt. rend.*, 1881, **93**, 63.

[4] *Proc. Roy. Soc.*, 1899, **65**, 237; Urbain, *Compt. rend.*, 1905, **141**, 954.

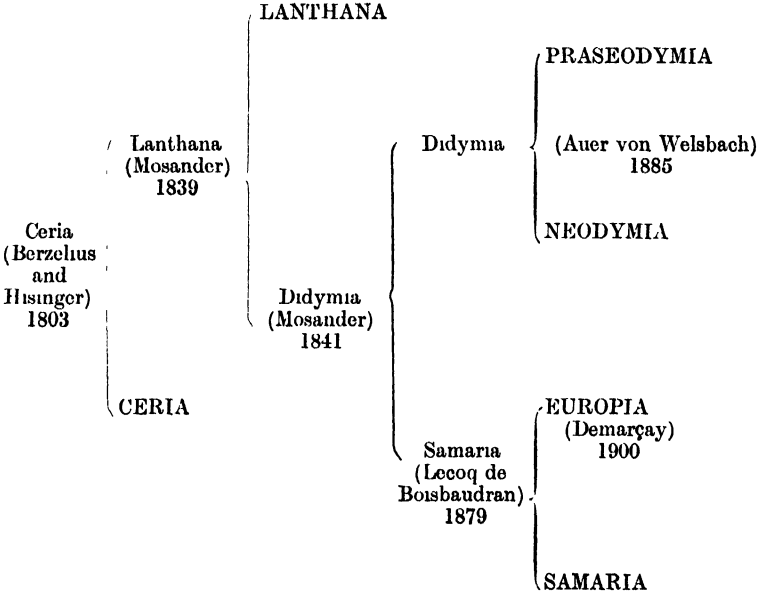
[5] *Annalen*, 1866, **137**, 1.

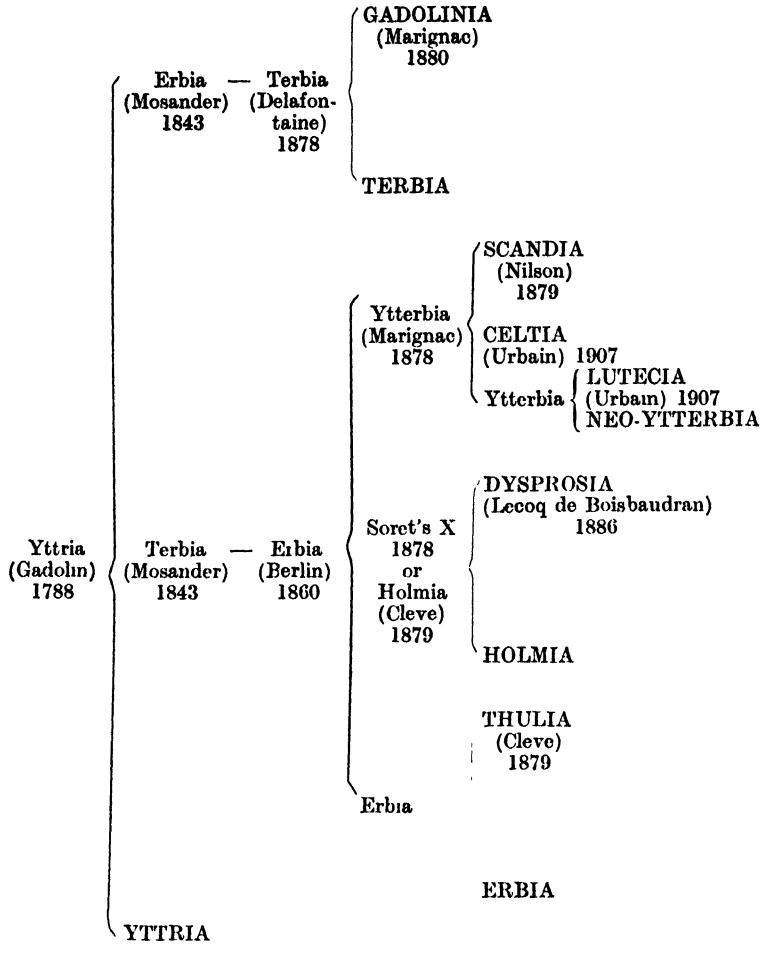
researches of Delafontaine and Marignac showed that both elements were present.

Further investigations have proved that the substances which all these chemists examined were in most cases highly complex mixtures, the complete separation of which has not yet been effected. This is illustrated by the two following tables which show the earths which have so far been obtained from yttria and ceria. The name of the investigator who effected each separation is added together with the date. Further details will be found under the headings of the separate metals.

Europia has also been found as a constituent of Delafontaine's terbia, and of both of the earths obtained from it by Marignac.

353 The rare earths occur in several rare minerals found in various localities in Scandinavia, Siberia, Greenland, North America, Ceylon, India, and Brazil. They are usually present in the form of silicates, less frequently as columbates, tantalates, phosphates, fluorides, and uranates, and are often accompanied by the oxides of glucinum and zirconium. The most important of these minerals are *gadolinite*, a basic orthosilicate of glucinum, iron, and the yttrium metals; *cerite*, a hydrated silicate of calcium and the cerium metals; *keilhauite*, a titanosilicate of yttrium, aluminium, iron, and calcium; *samarskite*, a columbate and





tantalate of iron, calcium, uranyl, and the metals of both the cerium and yttrium groups; *fergusonite*, a columbate of both the yttrium and cerium metals; *euxenite*, a columbate and titanate of yttrium, cerium, erbium, and uranyl; *monazite*, an orthophosphate of the cerite earths containing thorium; *xenotime*, an orthophosphate of the yttrium metals: and *thorianite*, a mineral found in Ceylon, containing 70 per cent. of thoria together with the oxides of uranium, cerium, lanthanum, didymium, yttrium, and zirconium.[1] The subjoined analyses[2] give some idea of the general composition of three of these minerals.

[1] Dunstan and Blake, *Proc. Roy. Soc.*, 1905, **76**, 253.

[2] Quoted from Dana's *Mineralogy* (1892).

Cerite. (Lindstrom, 1873).		Gadolinite from Ytterby. (Pettersson, 1890)		Samarskite from N. Carolina (Allen, 1877)	
SiO_2	22·79	SiO_2	23·88	Ta_2O_5	18·20
Ce_2O_3	24·06	ThO_2	0·41	Cb_2O_5	37·50
Di_2O_3, La_2O_3	35·37	Yt_2O_3	45·30	SnO_2, WO_2	0·08
FeO	3·92	Ce_2O_3	3·84	UO_3	12·54
Al_2O_3	1·26	Di_2O_3, La_2O_3	2·57	Ce_2O_3, Di_2O_3, La_2O_3	4·17
CaO	4·35	Fe_2O_3	0·60	Yt_2O_3	14·48
H_2O	3·44	FeO	12·89	FeO	10·75
Gangue	4·33	GlO	9·91	MnO	0·78
	99·52	CaO, MgO	0·54	CaO	0·55
		Na_2O	0·15	H_2O	1·12
		H_2O	0·57		100·17
			100·66		

The crude earths are obtained from the minerals by methods which differ somewhat according to the nature of the material to be treated. Cerite is evaporated with strong sulphuric acid, the excess of acid removed by heating, and the residue dissolved in ice-cold water. The clear solution is saturated with sulphuretted hydrogen, again filtered, and then made acid with hydrochloric acid and precipitated with oxalic acid, by means of which the insoluble oxalates of the earths, consisting mainly of ceria, lanthana, and didymia, are obtained and are finally converted into the oxides by ignition. Gadolinite, on the other hand, is decomposed by hydrochloric acid, and the oxalates are then precipitated from the solution of the chlorides. In other cases (fergusonite) the mineral is fused with potassium bisulphate, the fused mass is extracted with water, and the earths are precipitated as hydroxides or oxalates.

The most important source of the rare earths, at the present time, is the residue left after thorium has been separated from monazite sand in the preparation of compounds of this element for the incandescent mantle industry.

The nature of the crude oxide thus obtained varies very greatly according to the source from which it is derived. The different earths, with but few exceptions, resemble one another very closely, so that, in order to separate them, advantage

has to be taken of very slight differences in chemical behaviour, and the processes of separation are repeated a very large number, often amounting to many hundreds, of times. It is therefore advisable to commence the preparation of any particular earth with a mineral which contains a large proportion of this element and which is as free from admixture as possible, since in this way the length and tediousness of the processes of separation are lessened.

In some cases it is advisable first of all to remove the cerium, especially when this element is present in large proportion. This may be effected by a number of different methods, all of which depend on the fact that when the oxalates are calcined cerium forms an oxide, CeO_2, and that the derivatives of this differ very considerably from those of the oxides of the type R_2O_3 formed by the other earths. Of these methods one of the most effective is to convert the oxides into nitrates and pour a solution of these into a large amount of boiling water, under which circumstances a basic ceric nitrate separates, containing only a small amount of praseodymium and neodymium, from which it can be freed by several repetitions of the process. A second method is to add a solution of some salt of the earths to potassium permanganate solution containing magnesia in suspension. Ceric hydroxide is precipitated, and the filtrate is free from cerium (R. J. Meyer and Schweitzer).

A rough division of the mixed earths into two groups is obtained by saturating the neutral solution of the crude oxide in nitric acid with potassium sulphate. Double salts are formed of the general formula $R_2(SO_4)_3,3K_2SO_4$, those of the yttrium group (Yt, Yb, Lu, Er, Ho, Tm, Tb, Sc) being soluble, whilst those of the cerium group (Nd, Pr, La, Ce, Sa, Gd) are less soluble in a saturated solution of potassium sulphate. The sulphates thus obtained may be converted into oxalates, which are only sparingly soluble in dilute acids, or into oxides, and the separation repeated as often as is desired. For the further separation of the oxides which have been submitted to the foregoing treatment a number of different methods have been proposed, which may be grouped under the following four heads.[1]

(1) *Ignition of the Nitrates* (Bahr and Bunsen).—When the neutral nitrates of the earths of either of these groups are gently heated, it is found that the salts of the different earths are decomposed at different temperatures. In the case of the

[1] Compare Losse, *Zeit. anorg. Chem.*, 1892, **3**, 56.

yttrium group of oxides, to which the method is best applied, the nitrates decompose in the following order, Sc, Yb, Er, Ho, Tm, Tb, Yt, yttrium nitrate requiring the highest temperature. The heating is therefore continued only until a slight amount of decomposition has taken place; the cooled mass is then extracted with boiling water, and the basic salt which separates on cooling is removed by filtration. The filtrate is then evaporated and the process repeated.

(2) *Fractional Precipitation with Ammonia or some other Base.*—The neutral nitrate obtained from the crude earth is dissolved in water and ammonia added in such quantity as to precipitate a portion only of the earths which are present, the solution being so dilute that the precipitation takes place slowly. In this way the least basic earths are first precipitated, whilst the most basic are found in the filtrate. Among the cerium group of earths, lanthana appears to be the most basic, and is followed by ceria, praseodymia, neodymia, samaria, and gadolinia. The precipitated hydroxide is filtered off, redissolved in nitric acid, and again submitted to fractional precipitation, whilst the filtrate is treated in a similar manner to the original solution. This separation [1] is most efficiently effected in very dilute solution in the presence of a large excess of ammonium chloride. Other bases, such as caustic potash, magnesia, or the weak organic base aniline, may be employed in a similar manner.

(3) *Fractional Crystallisation of Salts.*—This method has been applied to a very large number of different salts, and has proved of the greatest value for the separation of many of the rare earths. The most important results have been attained by the crystallisation of the double ammonium nitrates (praseodymium and neodymium), the double magnesium nitrates (europium), and the double potassium sulphates (samarium, scandium), but the formates,[2] carbonates, oxalates, ethyl sulphates,[3] and aceto-acetates have all been employed. The crystallisation of the double magnesium nitrates of the earths of the terbium group with the addition of bismuth nitrate has led to the isolation of pure salts of gadolinium and terbium (Urbain and Lacombe).

James [4] effects a separation of the yttrium earths by crystallisa-

[1] Prandtl and Rauchenberger, *Ber.*, 1920, **53B**, 843.

[2] Urbain, *Compt. rend.*, 1906, **142**, 785.

[3] Bettendorf, *Annalen*, 1907, **352**, 88.

[4] James, *Chem. News*, 1907, **75**, 181; 1908, **97**, 61, 205; *J. Amer. Chem. Soc.*, 1912, **34**, 757.

tion of the bromates, the order of separation of the rare earth bromates from aqueous solution being samaria, europia, gadolinia, terbia, yttria, dysprosia, holmia, erbia, thulia, and ytterbia. In this way pure thulia and yttria can be obtained.

(4) *Fractional Precipitation of Salts.*—Lehner and Benner[1] effect a separation of the yttrium earths by fractional precipitation of a hot solution of the nitrates with sodium succinate. The earths precipitated first are holmia, terbia, and europia, whilst the major portion of the yttria is left in the solution. When a hot alcoholic solution of sodium stearate is added cautiously to a hot solution of the nitrates of the yttria earths a rapid separation can be effected (Stoddart and Hill).[2] The gadolinia and ceria earths can also be separated by this method.

354 The progress of the separation effected by any of these means may be followed by several methods, one of the most trustworthy of which is the determination of the mean chemical equivalent of the oxide obtained. This is accomplished by precipitating the earth in the form of oxalate, igniting, and weighing the oxide; this is then exposed to steam and afterwards evaporated with dilute sulphuric acid and heated gently over a small flame, or, better, at the temperature of sulphur vapour, until the weight is constant. The amount of sulphate formed from a known weight of oxide is thus ascertained, from which the equivalent of the earth can be calculated. This method is of great value when the earths which are being separated differ considerably in their equivalents, but is, of course, less useful when, as is often the case, the mixture consists of earths which have nearly the same equivalent.

Most other methods employed for detecting the progress of purification or separation are applications of spectrum analysis. In addition to the spark spectra, or those shown in the electric arc, the salts of many of the earths in solution exhibit characteristic absorption spectra. A number of the earths, moreover, show "phosphorescence spectra" when the ignited earth or its basic sulphate is exposed to an electric discharge in a highly exhausted glass bulb (Crookes), or exhibit a characteristic spectrum when an induction spark is made to pass from a positive pole of platinum on to the centre of the surface of a solution of one of the salts of the earth, which is connected with the negative pole (reversion spectra of Lecoq de Boisbaudran).

[1] *J. Amer. Chem. Soc.*, 1908, **30**, 572; 1911, **33**, 50.
[2] *Ibid.*, 1911, **33**, 1076.

Probably the most rapid method of controlling a fractionation of the rare earths is that depending on the measurement of the magnetic susceptibility of the mixtures. It has been found that this quantity varies considerably from element to element, more in fact than does any other property. Consequently a measurement of this quantity, which can be made in a few minutes by a magnetic balance, gives at once accurate information on the progress of the separation of any mixture.

The evidence afforded by the study of the spectra yielded by the earths in any of these ways is very difficult to interpret, because we are at present unacquainted with the exact influence of many variable conditions, especially the presence of other substances, upon the phenomena in question, and this influence is of very great importance, especially as regards absorption spectra and phosphorescence spectra. Kruss and Nilson,[1] arguing from the variation in the absorption spectra of the nitrates of the rare earths, and Crookes,[2] from a study of phosphorescence spectra, independently drew the conclusion that a very large number (24–30) of different elements were present in the rare earths. The chemical evidence, so far as it has been obtained, has not confirmed these views. The further study of absorption spectra, moreover, has shown that variations in the intensity and position of the bands may be produced by many factors and do not therefore necessarily indicate changes of composition. As regards phosphorescence spectra it has been shown that pure earths do not yield a discontinuous phosphorescence spectrum, but that such a spectrum is produced in the presence of small amounts of other substances and varies both with the amount and nature of this second substance.[3]

Moseley's work on *X*-ray spectra and atomic numbers (p. 72) has thrown much light on the number and homogeneity of the rare earth metals. It would appear from his results that the possible rare earth elements are 16 in number, of atomic numbers 57–72 and of atomic weights lying between those of barium and tantalum. Of these, 15 correspond with those already recognised on other grounds, and the elementary nature of which is thus confirmed. The missing element still to be discovered should come between neodymium and samarium, with an atomic number 61.

355 The metals of this group were at first supposed to be

[1] *Ber.*, 1887, **20**, 2170. [2] See *Journ. Chem. Soc.*, 1889, **55**, 260.
[3] Baur and Marc, *Ber.*, 1901, **34**, 2460.

divalent, the general formula of the earths being written RO. In 1870 Mendeléev found that whilst the equivalent of cerium was 46·3, its specific heat was about 0·05, whilst Hillebrand obtained the more accurate number 0·04479. According to this the atomic weight of cerium must be 139, and not 92·6 as previously supposed, since $139 \times 0{\cdot}04479 = 6{\cdot}3$, the lower basic oxide being therefore Ce_2O_3, and the higher oxide CeO_2.

It was suggested at the same time that the basic oxides of didymium and lanthanum, which had nearly the same equivalent as cerium, might be Di_2O_3 and LaO_2, didymium (138) being placed in the third group of the periodic system, and lanthanum, with an atomic weight of about 180, in the fourth group along with cerium. In this way these metals found a place in the periodic system, whilst no place existed for them in that system if their atomic weights were taken as about 92. The atomic weight of yttrium, the compounds of which were then but little known, was at the same time altered for similar reasons from about 59 to 88, the oxide being formulated Yt_2O_3 instead of YtO, and the metal placed in the third group of the periodic system.

The subsequent determination of the specific heats of lanthanum (0·04485) and the old didymium (0·04563) by Hillebrand showed that both these metals had an atomic weight of about 140, and a more accurate determination of their equivalents led to the atomic values La = 137·5, Di = 144. Oxide of lanthanum was, therefore, formulated La_2O_3 and the metal placed in the third group. The salts of didymium have since that date been shown to consist of the salts of at least two distinct elements, the oxides of which have been given the formulæ Pr_2O_3 and Nd_2O_3 respectively.

The tervalent character of the rare earths is confirmed by molecular weight determinations of the anhydrous chlorides in non-ionising solvents, by the electro-conductivity of aqueous solutions of the chlorides, and by the isomorphism of the crystalline hydrates of the sulphates of the rare earths with corresponding sulphates of other elements of undoubted tervalent character.

At present the general formula R_2O_3 is applied to the basic oxides of all the rare earth metals, and the formulæ of their salts are written in accordance with this.

SCANDIUM. Sc = 44·1. At. No. 21.

356 The oxide of this metal, which has not itself been isolated, was discovered in euxenite in 1879 by Nilson,[1] who obtained 2 grams of the pure oxide from 10 kilos. of the mineral. The element scandium is of very wide occurrence,[2] but only in very small quantities. The minerals wiikite and an orthite from Finland are the richest,[3] and both contain less than one per cent. of the oxide. The minerals wolframite [4] and cassiterite are also good sources for scandium compounds, they contain about 0·25 per cent. of the oxide. It is less basic than any of the other rare earths.

Scandium occupies the place in the periodic system which was assigned by Mendelécv in 1869 to the unknown element ekaboron (p. 70). Speaking of this undiscovered element, he said in the course of a full discussion of the subject [5] : Its atomic weight will be about 44, and its oxide, Ek_2O_3, will be a stronger base than alumina and will have a specific gravity of about 3·5, whilst the specific gravity of the chloride will be about 2. The oxide will be insoluble in alkalis and the salts colourless, yielding gelatinous precipitates with potash, potassium carbonate, sodium phosphate, etc.

Scandia is obtained from the mixed oxides of the rare earths either by precipitating as fluoride and further purification by the usual methods, or by precipitating as silicofluoride. The most persistent impurity is thoria and this is removed [6] by treatment with sodium thiosulphate, when the scandium is precipitated and the major part of the thorium left in solution. The last traces of thoria are removed [7] by adding excess of potassium iodate to a nitric acid solution of the nitrate, when the thoria is precipitated as iodate.

The extraction of scandium compounds from the wolframite [8]

[1] *Ber.*, 1879, **12**, 554; 1880, **13**, 1439.

[2] Ebethard, *Sitzungsber. K. Akad. Wiss. Berlin*, 1908, 851; 1910, 404; Crookes, *Proc. Roy. Soc.*, 1908, **80**, [*A*], 516; Vernadsky, *Bull. Acad. Sci. St. Petersburg*, 1908, 1273.

[3] Meyer, *Sitzungsber. K. Akad. Wiss. Berlin*, 1911, 379.

[4] Meyer, D.R.-P., 1908, 202253; Lukens, *J. Amer. Chem. Soc.*, 1913, **35**, 1470.

[5] *Annalen Supplementband*, 1872, **8**, 197.

[6] Meyer, *Zeit. anorg. Chem.*, 1908, **60**, 134; Meyer and Winter, *ibid.*, 1910, **67**, 398.

[7] Meyer, *Chem. News*, 1912, **106**, 13.

[8] Sterba-Bohm, *Zeit. Elektrochem.*, 1914, **20**, 289; Meyer, D.R.-P. 1908, 202253, 208355.

and cassiterite residues after the removal of tin is effected in the following manner. The residues are fused with soda and the cooled fusion extracted with water. The solution thus obtained contains all the tungsten as sodium tungstate. The residue is washed and dissolved in hydrochloric acid and the rare earths are precipitated by either oxalic acid or hydrofluoric acid, a large excess being used to keep the iron and manganese in solution. The precipitate of rare earths contain 90–95 per cent. of scandium, which is purified, by solution in hydrochloric acid and precipitation by boiling with sodium silicofluoride. The last traces of thoria are removed as described above.

Metallic scandium has not yet been isolated.

Scandium hydroxide, $Sc(OH)_3$, is a gelatinous, white precipitate which on ignition yields the *oxide*, Sc_2O_3. The latter is a white powder resembling magnesia, of specific gravity 3·864, and a specific heat 0·1530. It dissolves slowly in cold but rapidly in hot acids to form scandium salts. The salts are colourless and exhibit no absorption bands. The chloride[1] and bromide, $ScCl_3$ and $ScBr_3$, crystallise with $12H_2O$; the fluoride is anhydrous. *Scandium fluoride*, SiF_3, is formed by the addition of hydrofluoric acid or a soluble fluoride to a scandium salt. It is also formed by the addition of sodium silicofluoride to a boiling solution of a scandium salt.

$$Sc_2(SO_4)_3 + 3Na_2SiF_6 = Sc_2(SiF_6)_3 + 3Na_2SO_4$$
$$Sc_2(SiF_6)_3 + 6H_2O = 2ScF_3 + 12HF + 3SiO_2$$

Freshly precipitated scandium fluoride dissolves[2] in solutions of alkali fluorides and the solutions thus produced when concentrated deposit crystals of the double salts $(NH_4)_3SiF_6$, K_3SiF_6, and Na_3SiF_6. A similar double compound, Ag_3SiF_6, has also been obtained by crystallising a solution of scandium fluoride in silver fluoride solution. The existence of these salts points to the probable existence of a *fluo-scandic acid*, H_3SiF_6. The *sulphate*, $Sc_2(SO_4)_3$, crystallises with $6H_2O$ and is readily soluble in water, differing in these respects from the other sulphates of the group. The double sulphate of scandium and potassium, $Sc_2(SO_4)_3,3K_2SO_4$, is insoluble in a solution of potassium sulphate. The *nitrate*,[3] $Sc(NO_3)_3,4H_2O$, forms prismatic crystals and becomes anhydrous when heated on the water-bath. When heated in a vacuum at

[1] Crookes, *Phil. Trans.*, 1908, **209**, [*A*], 15; *ibid.*, 1910, **210**, [*A*], 359.
[2] Sterba-Bohm, *Bull. Soc. chim.*, 1920, [4], **27**, 185.
[3] Crookes, *loc. cit.*

100° a basic nitrate, $Sc(OH)(NO_3)_2$, is formed. *Scandium carbonate*, $Sc_2(CO_3)_3,12H_2O$, is formed as a bulky precipitate when ammonium carbonate is added to a solution of a scandium salt; it is readily soluble in hot solutions of alkali carbonates, and on evaporation these solutions deposit sparingly soluble double carbonates. The compounds $Sc_2(CO_3)_3,4Na_2CO_3,6H_2O$ and $2Sc_2(CO_3)_3(NH_4)_2(CO_3),6H_2O$ have been prepared, but no compound with potassium carbonate has yet been obtained. The borate, iodate, aurichloride, platinocyanide, and numerous salts of organic acids have been prepared.[1] The spark spectrum of the chloride is characteristic (Thalén). The arc spectrum has been mapped by Lockyer and Baxandall [2] and Crookes [3] and compared with the solar spectrum, in which many of the scandium lines are to be found.

A number of atomic weight determinations have been made recently by Honigschmidt [4] and Meyer and Schweig.[5] Both investigators agree that the atomic weight cannot be determined by the sulphate method, and the former gives 45·10 whilst the latter gives 45·3 as the atomic weight of scandium.

YTTRIUM. Yt = 88·7. At. No. 39.

357 Yttria is the most basic of all the yttrium group of earths, and its separation from the others is based on this fact. According to Crookes, it is a complicated mixture,[6] but this conclusion has not been confirmed.

Yttrium was obtained by Cleve as a dark-grey powder possessing a metallic lustre under the burnisher. He prepared it by the electrolysis of the double chloride of yttrium and sodium, and also by fusing this with sodium. Yttrium decomposes water slowly in the cold, but more quickly on boiling.[7] It melts at 1490°. Yttrium "mixed metal," [8] containing 37·5 per cent. of yttrium, has been obtained by the electrolysis of a mixture of the fused chlorides of the yttrium metals. This mixture burns in the air at a dull red heat, and is slowly oxidised in moist air at the ordinary temperature.

[1] Crookes, *loc. cit.*
[2] *Proc. Roy. Soc.*, 1905, **74**, 538.
[3] *Ibid.*, 1919, [*A*], **95**, 438.
[4] Honigschmidt, *Zeit. Elektrochem.*, 1919, **25**, 91.
[5] Meyer and Schweig, *Zeit. anorg. Chem.*, 1919, **108**, 303.
[6] *Journ. Chem. Soc.*, 1889, **55**, 260.
[7] Cleve, *Compt. rend.*, 1882, **95**, 1125.
[8] Hicks, *J. Amer. Chem. Soc.*, 1918, **40**, 1619.

Yttrium Oxide, Yt_2O_3, is obtained as a white powder of sp. gr. 5·046 by igniting the oxalate, nitrate, or hydroxide. On ignition, it emits a bright white light. It combines directly with carbon dioxide and is a strong base capable of liberating ammonia from ammonium salts. It has a specific gravity 5·326 and a specific heat 0·1173, and may be obtained crystalline by fusion with calcium chloride. It does not combine directly with water, but when an yttrium salt is precipitated with an alkali the *hydroxide* is thrown down as a gelatinous precipitate which readily absorbs carbon dioxide from the air. If the precipitation is effected in the presence of hydrogen peroxide, a hydrated peroxide, Yt_4O_9,xH_2O is obtained. Yttrium oxide dissolves slowly but completely in hydrochloric, nitric, and sulphuric acids.

Yttrium Fluoride occurs together with the fluorides of cerium and calcium in the mineral yttrocerite found near Fahlun in Sweden, at Amity, Orange County, New York, in Massachusetts, and at Mount Mica in Maine. It is massive, crystalline-granular, and earthy, having a glistening vitreous to pearly lustre, and a colour varying from violet-blue to grey and white. Sometimes it has a reddish-brown colour. It may be prepared anhydrous by the action of fluorine on the carbide, and hydrated, as $2YtF_3,H_2O$ by the action of hydrofluoric acid or a soluble fluoride on a solution of an yttrium salt.

Yttrium Chloride, $YtCl_3$, formed by heating the oxide mixed with carbon in chlorine, or more easily [1] by passing a mixture of dry chlorine, hydrogen chloride, and sulphur chloride over the heated residue obtained by evaporation of a solution of the oxide in hydrochloric acid, is a colourless, transparent substance, which melts at 680° and solidifies to form shining, white leaflets which volatilise at high temperatures. When the oxide is dissolved in hydrochloric acid the hydrate $YtCl_3,6H_2O$ is obtained on evaporation in deliquescent prisms which are soluble in alcohol but insoluble in ether. These decompose when heated alone with evolution of hydrogen chloride, but when ignited in presence of sal-ammoniac or in a current of hydrogen chloride [2] the anhydrous chloride is obtained. The anhydrous chloride is very soluble in alcohol and pyridine, with which it forms additive compounds.[2] The hydrated chloride forms a compound, $YtCl_3,11H_2O,2C_6H_{12}N_4$, when treated with hexamethylene tetramine.[3] Crystals of hydrated yttrium chloride, when strongly

[1] Matignon, *Compt. rend.*, 1905, **140**, 1181.

[2] *Ann. Chim. Phys.*, 1906 [8], **8**, 433.

[3] Barbieri and Calzolari, *Atti R. Accad. Lincei*, 1911, [5], **20**, i, 164.

heated, lose water and hydrochloric acid, forming basic salts, but when heated on a water-bath 5 molecules of water are lost and the last molecule can be driven off at 160° in the presence of hydrochloric acid gas. Yttrium chloride forms double compounds with some metallic chlorides, the compounds $2YtCl_3,3PtCl_2,24H_2O$; $4YtCl_3,5PtCl_4,52H_2O$; $YtCl_3,2AuCl_3,16H_2O$, and $YtCl_3,3HgCl_2,9H_2O$ have been obtained in the crystalline condition.

The bromide and iodide are very similar to the chloride.

Yttrium Sulphide, Yt_2S_3, is obtained as a yellow or grey powder by heating the oxide in the vapour of carbon disulphide (Popp), and by heating the chloride in sulphuretted hydrogen. It is not soluble in water, but is decomposed by acids (Wöhler).

Yttrium Sulphate, $Yt_2(SO_4)_3,8H_2O$, forms transparent crystals which lose their water at 115°. One hundred parts of cold water dissolve 9·3 parts of the salt, but when the solution is warmed to 100° 4·5 parts separate out in the crystalline state. It forms a microcrystalline powder with stannic sulphate [1] having the formula $YtSn(SO_4)_6$. On heating yttrium sulphate at 700° a basic sulphate, Yt_2O_3,SO_3, is formed, which crystallises in white needles.[2]

Yttrium Nitrate, $Yt(NO_3)_3,6H_2O$, is easily soluble in water, alcohol, or ether, forming large, deliquescent needles. At 25° 100 grams of water dissolve 141·6 grams of the nitrate. A basic nitrate [3] of the formula $3Yt_2O_3,4N_2O_5,20H_2O$ is formed by shaking the oxide with nitric acid at 25°. This compound is stable in the presence of an aqueous solution of $Yt(NO_3)_3$ containing 33 grams per 100 c.c. The normal nitrate forms a compound with hexamethylene tetramine,[4] having the formula $Yt(NO_3)_3,10H_2O,2C_6H_{12}N_4$.

Yttrium Orthophosphate, $YtPO_4,2H_2O$, is slightly soluble in water; the *metaphosphate*, $Yt(PO_3)_3$, is an insoluble crystalline powder; and the *pyrophosphate*, $2YtHP_2O_7,7H_2O$, is soluble in water.

Yttrium Carbide, YtC_2, is prepared by heating the oxide with carbon in the electric furnace. It forms yellow, microscopic crystals of sp. gr. 4·13, and yields with water a mixture of gases containing 72 per cent. of acetylene, along with methane, ethylene, and hydrogen.

[1] Weiland and Kuhl, *Zeit. anorg. Chem.*, 1907, **54**, 244.
[2] Brill, *Zeit. anorg. Chem.*, 1905, **47**, 464.
[3] James and Pratt, *J. Amer. Chem. Soc.*, 1910, **32**, 873.
[4] Barbieri and Calzolari, *Atti R. Accad. Lincei*, 1911, [5], **20**, i., 164.

Yttrium Carbonate, $Yt_2(CO_3)_3,3H_2O$, is a heavy, white powder insoluble in water, formed by the addition of an alkali carbonate to a solution of an yttrium salt, or by passing carbon dioxide into a suspension of yttrium hydroxide. It dissolves in excess of alkali carbonates and forms double carbonates, of which the compounds $Yt_2(CO_3)_3,Na_2CO_3,4H_2O$ and $Yt(CO_3)_3,(NH_4)_2CO_3,2H_2O$ have been isolated.

Yttrium Bromate,[1] $Yt_2(BrO_3)_6,18H_2O$, is a white, crystalline substance forming hexagonal prisms. It is formed by the action of barium bromate on yttrium sulphate, and dissolves to the extent of 168 parts in 100 parts of water at 25°.

Detection and Estimation of Yttrium.

358 This metal is most readily recognised by the spark spectrum of the chloride. This contains a large number of bright lines, of which two groups lying near the sodium line towards the red are especially characteristic. The salts show no absorption spectrum. The reactions of the yttrium salts are very similar to those of zirconium.

The Atomic Weight of yttrium was determined by Bahr and Bunsen by the analysis of the sulphate to be 92. According to Cleve and Hoeglund,[2] on the other hand, it is 89·2. This difference is probably due to the presence of other earths. From a still later determination[3] Cleve obtained the number 88·4, whilst the somewhat lower number, 88·3, was obtained by Jones.[4]

Kremers and Hopkins,[5] by means of the silver chloride method, using very highly purified salts, have obtained the value 89·33. The number at present (1922) adopted is 88·7.

LANTHANUM. La = 139·0. At. No. 57.

359 Lanthanum salts are best obtained pure by the fractional crystallisation of the double magnesium nitrates of the cerite earths.[6] A very rapid and successful method[7] of obtaining pure lanthanum compounds from mixtures of the cerium earths, from which the cerium has been removed, consists in dissolving the

[1] James and Langelier, *J. Amer. Chem. Soc*, 1909, **31**, 913.
[2] *Bull. Soc. chim.*, 1872, [2], **18**, 193.
[3] *Ibid.*, 1883, [2], **39**, 120. [4] *Amer. Chem. J.*, 1895, **17**, 154.
[5] Kremers and Hopkins, *J. Amer. Chem. Soc.*, 1919, **41**, 718.
[6] Drossbach, *Ber.*, 1902, **35**, 282C; Muthmann and Weiss, *Annalen*, 1904, **331**, 1.
[7] Prandtl and Rauchenberger, *Ber.*, 1920, **53B**, 843.

mixed oxides in fairly concentrated hydrochloric acid, making the solution nearly neutral, adding a quantity of ammonium chloride equal in weight to that of the oxides, and diluting with water until the solution is 2–3*N* with respect to ammonium chloride. The solution is heated to 50° in a large porcelain dish and a mixture of 4*N*-ammonia and 4*N*-ammonium chloride solutions added slowly with vigorous stirring until about 5 per cent. of the oxides have been precipitated, this is removed and the filtrate treated in the same way. The alternate precipitation and filtration is repeated until the filtrate no longer exhibits absorption lines. This filtrate then contains fairly pure lanthanum compounds only. Lanthana is the most basic of all the rare earths.

Lanthanum was obtained by Mosander as a grey powder by heating the chloride with potassium. Hillebrand and Norton[1] prepared it by the electrolysis of the fused chloride, and obtained it in the form of fused globules, some of which weighed as much as six grams, and it has since been prepared in large quantities by the same method by Muthmann and Kraft.[2] Thus prepared it has a specific gravity of 6·154 and an iron-grey colour; it takes a high polish but soon tarnishes, even on exposure to dry air, attaining a steel-blue colour. The metal can be hammered out to tolerably thin foil, and can be drawn into wire. The specific heat of the metal is 0·04485 and it melts at 810°. It is paramagnetic and has a heat of combustion of 1602 cal. per gram; it is slightly softer than zinc. When heated in the air it forms oxide and nitride, and when heated in hydrogen or nitrogen it forms the hydride and nitride respectively. The finely-divided metal burns brightly when thrown into the flame. It also takes fire when thrown into chlorine gas, burns less brightly in bromine vapour, and combines with iodine without evolution of light. Cold water oxidises it slowly with formation of the hydroxide. Cold concentrated sulphuric acid does not attack it, but in dilute sulphuric acid and in hydrochloric acid it dissolves with violent evolution of hydrogen, and it is oxidised by both concentrated and dilute nitric acid. Lanthanum forms alloys with iron and aluminium, in the case of the latter metal a compound, Al_4La, being formed in lustrous crystals which are quite stable in air. Alloys of lanthanum, up to a composition 30 per cent. lanthanum, are pyrophoric and give showers of sparks when struck.

[1] *Pogg. Ann.*, 1875, **156**, 466. [2] *Annalen*, 1902, **325**, 261.

Lanthanum Oxide, La_2O_3.—This is obtained in the form of a white powder which has a specific gravity of 6·48, by heating the hydroxide, oxalate, carbonate, or nitrate. It combines with water with evolution of heat, like lime, with formation of a voluminous snow-white powder of *lanthanum hydroxide*, $La(OH)_3$; this is obtained also by precipitating a lanthanum salt with an alkali in the form of a gelatinous precipitate which easily absorbs carbon dioxide from the air. The hydroxide has an alkaline reaction and decomposes ammonium salts on heating. It is therefore a somewhat stronger base than ammonium hydroxide.[1]

The oxide is readily reduced when it is heated with magnesium powder. If the reaction is carried out in an atmosphere of hydrogen, a *hydride of lanthanum*, LaH_3, is formed [2] which has been prepared pure by heating the pure metal in hydrogen at about 240° (Muthmann and Kraft). It is an unstable, black powder which does not take fire in the air.

A *peroxide*, which appears to be a hydrated form of the oxide La_2O_5, is precipitated when hydrogen peroxide and an alkali are added to a solution of a lanthanum salt.

Lanthanum Chloride, $LaCl_3$.—This substance is obtained in the anhydrous state by heating its ammonium double salt, or by passing a mixture [3] of chlorine, hydrogen chloride and sulphur chloride over the heated hydrated chloride. It is a crystalline mass very soluble in water and alcohol, has a density [3] of 3·95, at 18°, and melts at 907°. In aqueous solution lanthanum chloride is hydrolysed to a very slight [4] extent. When the oxide is dissolved in hydrochloric acid, and the solution evaporated to a syrup, large triclinic prisms having the compositions $2LaCl_3,15H_2O$ and $LaCl_3,7H_2O$ are deposited, and these when heated lose hydrogen chloride. Lanthanum chloride forms crystalline double salts with the chlorides of mercury, bismuth, antimony, platinum, gold, and pyridine. Double compounds are also obtained with alcohol, hexamethylene tetramine, and glycocoll.

Lanthanum Sulphide, La_2S_3, is obtained by heating the oxide in the vapour of carbon disulphide, in the form of a yellow mass

[1] Vesterberg, *Zeit. anorg. Chem*, 1916, **94**, 371; *Arkiv for Kemi, Min. och. Geol.*, 1917, **6**, No. 11.

[2] Winkler, *Ber.*, 1890, **23**, 787; 1891, **24**, 890.

[3] Matignon, *Compt. rend.*, 1905, **140**, 1339; 1181.

[4] Ley, *Zeit. physikal. Chem.*, 1899, **30**, 193.

which is decomposed by water. A disulphide,[1] LaS_2, has been prepared by heating $La_2(SO_4)_3$ in sulphuretted hydrogen at 600°. It decomposes at 650° into the trisulphide, La_2S_3.

Lanthanum Sulphate, $La_2(SO_4)_3,9H_2O$, crystallises at the ordinary temperature in six-sided pointed prisms which are more soluble in cold than in hot water, whilst at 0° a hydrate with $16H_2O$ separates out (Brauner and Pavlíček). One part of the anhydrous salt dissolves at 3° in less than 6 parts, whilst at 100° it dissolves in about 115 parts of water. The double potassium salt is insoluble in a solution of potassium sulphate. With stannic sulphate [2] it forms a compound, $LaHSn(SO_4)_4$, which crystallises in six-sided plates. On heating the anhydrous sulphate at 700° a basic sulphate is obtained [3] of the formula La_2O_3,SO_3, which forms white needles. The hydrated sulphate crystallises [4] with the sulphates of the alkalis and forms the compounds :

$$La_2(SO_4)_3,K_2SO_4,2H_2O;\ La_2(SO_4)_3,5K_2SO_4;$$
$$La_2(SO_4)_3,Na_2SO_4,2H_2O;$$
$$La_2(SO_4)_3,(NH_4)_2SO_4,2H_2O \text{ and } La_2(SO_4)_3,5(NH_4)_2SO_4.$$

It forms [5] double sulphates also with pyridine and quinoline sulphates. An acid sulphate, $LaH_3(SO_4)_3$, is formed in white, silky needles when a solution of the normal sulphate in concentrated sulphuric acid is kept for some time.

Lanthanum Bromate,[6] $La(BrO_3)_3,18H_2O$, is a white, crystalline compound, melting at 37·5° in its water of crystallisation. It is formed by the action of barium bromate on the sulphate, and dissolves to the extent of 416 parts in 100 parts of water at 25°.

Lanthanum Nitride, LaN, is a black powder which is formed by the direct union of its elements and is hydrolysed by water, with the formation of ammonia and lanthanum hydroxide.

Lanthanum Nitrate, $La(NO_3)_3,6H_2O$, is easily soluble in water and alcohol, from which it crystallises in oblique prisms or tablets. It forms double nitrates [7] with all the alkali metal nitrates and with ammonium nitrate of the formulæ :

[1] Biltz, *Zeit. anorg. Chem.*, 1911, **71**, 427.
[2] Weinland and Kuhl, *Zeit. anorg. Chem.*, 1907, **54**, 244.
[3] Brill, *Zeit. anorg. Chem.*, 1905, **47**, 464.
[4] Barre, *Compt. rend.*, 1910, **151**, 871.
[5] Kolb, Melzer, Merckle, and Teufel, *Zeit. anorg. Chem.*, 1908, **60**, 123.
[6] James and Langelier, *J. Amer. Chem. Soc.*, 1909, **31**, 913.
[7] Jantsch and Widgorow, *Zeit. anorg. Chem.*, 1911, **69**, 221; Wyrouboff, *Bull. Soc. franç. Min.*, 1907, **30**, 299.

$3La(NO_3)_3,4NaNO_3,3H_2O$;
$La(NO_3)_3,2NaNO_3,H_2O$; $La(NO_3)_3,2KNO_3,H_2O$;
$3La(NO_3)_3,4KNO_3,4{\cdot}5H_2O$;
$3La(NO_3)_3,4RbNO_3,8H_2O$; $La(NO_3)_3,2RbNO_3,4H_2O$;
$3La(NO_3)_3,4Cs(NO_3),5H_2O$;
$La(NO_3)_3,2CsNO_3,H_2O$ and $La(NO_3)_3,2NH_4NO_3,4H_2O$.

Double nitrates are formed also with thallium nitrate, pyridine nitrate, and quinoline nitrate.[1] A series of double nitrates[2] is formed with the nitrates of magnesium, nickel, cobalt, zinc, and manganese.

Lanthanum Carbide, LaC_2, is formed when a mixture of the oxide with sugar charcoal is heated in the electric furnace. It is a crystalline substance, and is readily attacked by acids. Water decomposes it with evolution of a mixture of acetylene, methane, a very small amount of ethylene, and traces of liquid and solid hydrocarbons.[3]

Lanthanum Carbonate, $La_2(CO_3)_3,8H_2O$.—This occurs as lanthanite, a mineral which contains varying quantities of cerium, and crystallises in greyish-white, pink, or yellowish rhombic prisms. It occurs at Bastnäs in Sweden; also in Silurian limestone with the zinc ores of the Saucon Valley, Lehigh County, Pa., and in other localities in the United States. When a lanthanum salt is precipitated with a soluble carbonate this same salt is obtained in the form of glittering scales. It forms sparingly soluble double carbonates with the carbonates of the alkalis.

Lanthanum forms complex tungstates[4] with silver oxide, barium oxide, and ammonia.

Detection and Estimation of Lanthanum.

360 Lanthanum chloride yields a spectrum consisting of many very bright and characteristic lines, by means of which even traces of the metal can be readily detected. The salts of lanthanum possess an astringent, sweet taste. They do not show an absorption spectrum, and, when quite pure, do not give a phosphorescence spectrum.

Lanthanum is determined quantitatively by precipitating it

[1] Kolb, Melzer, Merckle, and Teufel, *Zeit. anorg Chem.*, 1908, **60**, 123.
[2] Jantsch, *Zeit. anorg. Chem.*, 1912, **76**, 303.
[3] Moissan, *Compt. rend.*, 1896, **123**, 148.
[4] Balke and Smith, *J. Amer. Chem. Soc.*, 1904, **25**, 1229.

either as hydroxide or as oxalate, these being converted by ignition into the oxide. Lanthanum may be estimated volumetrically[1] by means of oxalic acid and potassium permanganate.

The atomic weight of lanthanum has been obtained at various times by many chemists, but with varying results. The most recent experiments, however, yield fairly concordant numbers. Thus Brauner and Pavlíček[2] found the atomic weight to be 139·04, Jones[3] 138·77, Baxter, Tani and Chapin[4] 138·91 and Hopkins and Driggs[5] 138·89; the number at present (1922) adopted is 139·0, which is probably slightly too high.

CERIUM. Ce = 140·25. At. No. 58.

361 The sources of this metal, which always occurs along with the rare earths, have already been mentioned, as well as the means by which it is separated (p. 797). The metal itself was first prepared by Mosander in the form of powder by heating the chloride with sodium. Wohler afterwards obtained it in the coherent state, and Hillebrand and Norton[6] have prepared it in large quantity by the electrolysis of the chloride, whilst Winkler prepared it by heating the dioxide with magnesium powder. It possesses the colour and lustre of iron, and is tolerably permanent in dry air, but in moist air tarnishes, becoming first of a yellow, then of a blue, and finally of a green colour. It is as soft and malleable as lead, and can be hammered and rolled, and, when warm, drawn into wire. The electrolytically prepared metal has a specific gravity of 6·628 (Hillebrand and Norton), 7·0124 (Muthmann and Weiss), 6·920 (Hirsch).[7] Cerium melts at 623° (Muthmann and Weiss). It takes fire more easily than magnesium, and when scratched with a wire or scraped with a knife the particles of finely-divided metal which are rubbed off take fire. The same phenomenon is observed when the metal is struck with a piece of flint, sparks of the metal flying off and burning with great brilliancy. The metal also burns in the flame with a much more brilliant light than magnesium. It reacts with the elements of the chlorine group, water, and acids

[1] Druschel, *Amer. J. Sci.*, 1907, [4], **24**, 197.

[2] *Journ. Chem. Soc.*, 1902, **81**, 1243.

[3] *Amer. Chem. J.*, 1902, **28**, 23; *Zeit. anorg. Chem*, 1903, **36**, 92.

[4] *J. Amer. Chem. Soc.*, 1921, **43**, 1080. [5] *Ibid.*, 1922, **44**, 1927.

[6] *Pogg. Ann.*, 1875, **155**, 631; 1875, **156**, 466; see also Muthmann, Hofer, and Weiss, *Annalen*, 1902, **320**, 231; 1904, **331**, 1.

[7] *Trans. Amer. Electrochem. Soc.*, 1911, **20**, 57.

in a similar way to lanthanum, but concentrated nitric acid converts it into a brown substance, which is probably chiefly cerium dioxide. The alloys of cerium with other metals are generally hard and brittle, but that with antimony is soft. The alloys with iron, nickel, tungsten, manganese, cadmium, zinc, and several other metals yield sparks when struck.[1] With tin,[2] definite compounds of the formulæ Ce_2Sn, Ce_2Sn_3, and $CeSn_2$ have been isolated, and with aluminium[3] compounds of the formulæ Ce_3Al, Ce_2Al, CeAl, $CeAl_2$, and $CeAl_4$ are obtained; copper, bismuth, and magnesium also form well-defined intermetallic compounds with cerium. The salts of cerium find a limited application in medicine as a remedy for sickness.

According to Schützenberger[4] and Brauner[5] the cerium compounds prepared from cerite invariably contain small quantities of the derivatives of an element of lower atomic weight; this has, however, been disputed by other workers, and the question still requires investigation.[6]

CERIUM COMPOUNDS.

Cerium and Oxygen.

362 Cerium forms three oxides: (1) a dioxide, CeO_2, (2) a sesquioxide, Ce_2O_3, and (3) a peroxide, CeO_3. The sesquioxide and the dioxide are basic, and yield corresponding series of salts known as the *cerous* and *ceric* salts, but the dioxide, like the corresponding lead compound, acts in many respects as a peroxide.

Cerous Hydroxide, $Ce(OH)_3$, is formed as a white precipitate when ammonia or potash is added to solutions of the cerous salts. On exposure to air it oxidises very rapidly, and becomes coloured reddish-violet. Cerium sesquioxide is not formed by heating the dioxide in a stream of hydrogen as was formerly stated, but in this way a dark blue oxide is obtained which has a composition[7] approximating to Ce_4O_7. A hydroxide

[1] *Trans. Amer. Electrochem. Soc.*, 1911, **20**, 57.

[2] Vogel, *Zeit. anorg. Chem.*, 1911, **72**, 319.

[3] *Ibid.*, 1912, **75**, 41.

[4] *Compt. rend.*, 1895, **120**, 663, 962.

[5] *Chem. News*, 1895, **71**, 283.

[6] Boudouard, *Compt. rend.*, 1897, **125**, 772; Brauner, *Proc. Chem. Soc.*, 1898, **14**, 69; Wyrouboff and Verneuil, *Compt. rend.*, 1897, **125**, 1180; Drossbach, *Ber.*, 1900, **33**, 3506.

[7] Meyer, *Zeit. anorg. Chem.*, 1903, **37**, 378; Sterba, *Ann. Chim. Phys.*, 1904, [8], **2**, 193.

roughly corresponding to this last substance has also been obtained by allowing cerous hydroxide to oxidise partially in air.[1] According to Burger the dioxide is reduced by calcium to the sesquioxide. This is a yellowish-green powder, which absorbs oxygen when preserved, and burns in the air to form the dioxide.[2]

Cerium Dioxide, CeO_2, is formed when a cerium salt of a volatile oxy-acid is heated in the air, and is thus obtained as a white [3] or pale straw-coloured powder, which assumes a reddish tinge on ignition. If obtained by the ignition of the hydrated oxide it has a salmon colour. It may be obtained in the crystalline form by igniting cerous chloride with borax in a wind furnace.[4] It dissolves in concentrated sulphuric acid, forming a dark yellow solution which has powerful oxidising properties, and evolves considerable quantities of active oxygen.

When the acid sulphate is heated with caustic potash, or when chlorine acts on cerous hydroxide suspended in water, the hydrated dioxide, $CeO_2,3H_2O$, is formed as a sulphur-yellow powder, whilst, if the hydroxide precipitated by the action of ammonia on a solution of cerium sulphate is dried at 385°, a bright yellow hydroxide, $CeO_2,2H_2O$ or $Ce(OH)_4$, is obtained, which does not lose water to any considerable extent until heated to 600°.[5] The hydroxides dissolve in hydrochloric acid, yielding a deep yellow solution which on heating yields the trichloride, chlorine being simultaneously evolved. The dioxide behaves therefore both as a basic oxide and a peroxide. A higher hydrated *peroxide*, CeO_3,xH_2O, is also known.[6]

Cerium dioxide [7] when heated to high temperatures with chromium sesquioxide forms the compounds $CeO_2Cr_2O_3$, $3CeO_2,4Cr_2O_3$, $CeO_2,2Cr_2O_3$ and $CeO_2,5Cr_2O_3$.

Cerium dioxide is used in the manufacture of mantles for incandescent gas burners. Mantles composed of thoria

[1] Wyrouboff and Verneuil, *Compt. rend.*, 1899, **128**, 501; see also *Ann. Chim. Phys.*, 1906, [8], **9**, 289.

[2] *Ber.*, 1907, **40**, 1652.

[3] Spencer, *Journ. Chem. Soc.*, 1915, **107**, 1265; Wyrouboff and Verneuil, *Compt. rend.*, 1897, **124**, 1230; 1898, **127**, 863; 1899, **128**, 501; Sterba, *ibid.*, 1901, **133**, 221; Brauner, *Zeit. anorg. Chem.*, 1903, **34**, 207.

[4] Nordenskiold, *Pogg. Ann.*, 1861, **114**, 612; see also Sterba, *Compt. rend.*, 1901, **133**, 294; *Ann. Chim. Phys.*, 1904, [8], **2**, 193.

[5] Carnelley and Walker, *Journ. Chem. Soc.*, 1888, **53**, 84.

[6] de Boisbaudran, *Compt. rend.*, 1885, **100**, 605.

[7] Veil, *Compt. rend.*, 1920, **170**, 939.

alone give only a dull light when heated in the Bunsen flame, whereas the addition of a small quantity of cerium oxide causes a brilliant incandescence. The maximum brilliancy is obtained when the mantles contain 99 per cent. of thoria and 1 per cent. of ceria, whilst a greater or a smaller amount of ceria causes a marked diminution in the intensity of the light. No fully satisfactory explanation of this phenomenon has as yet been given.

Cerous Compounds.

363 *Cerous Hydride*, CeH_3, is prepared by passing hydrogen over metallic cerium heated at 250–270°. It is a dark-blue or black powder, and takes fire spontaneously in air [1]; in moist air it decomposes very rapidly; it is decomposed also by acids with evolution of hydrogen [2] and formation of cerous salts.

Cerous Chloride, $CeCl_3$, is formed as a yellowish-white sublimate when the metal is heated in chlorine, or when an intimate mixture of the oxide and carbon is heated in this gas. It may also be prepared by heating the sulphide first in a stream of carbon dioxide and then in hydrogen chloride. Prepared in this way it is a white, crystalline mass which dissolves in water with a hissing noise.[3] The boiling point of the solution in alcohol points to the formula $CeCl_3$. The hydrated salt, $2CeCl_3,15H_2O$, remains behind in ill-defined crystals when a solution of cerous oxide in hydrochloric acid is allowed to evaporate over sulphuric acid, and the hydrate, $CeCl_3,7H_2O$, has also been obtained in rhombic crystals. On heating, it decomposes with evolution of hydrogen chloride and formation of a basic chloride CeOCl. When treated with hexamethylene tetramine [4] a compound is formed of the formula $CeCl_3,14H_2O,2C_6H_{12}N_4$. Cerous chloride is hydrolysed [5] to the extent of 0·14 per cent. in a 1/32 normal solution. Cerous chloride forms double chlorides with the chlorides of mercury, antimony, bismuth, tin, platinum, and gold.

Cerous Bromide, $CeBr_3$, is obtained as a hygroscopic, snow-white, crystalline powder by passing hydrogen bromide over

[1] Dafert and Miklauz, *Monatsh.*, 1912, **33**, 911.

[2] Muthmann and Kraft, *Annalen*, 1902, **325**, 261, 281; Kellinberger and Kraft, *ibid.*, 279.

[3] Muthmann and Stutzel, *Ber.*, '898, **31**, 1829; 1899, **32**, 3413.

[4] Barbieri and Calzolari, *Atti. R. Accad. Lincei*, 1911, [5], **20**, i, 164.

[5] Denham, *Zeit. anorg. Chem.*, 1908, **57**, 378.

heated cerium sulphide.[1] The anhydrous bromide [2] may also be prepared by heating the oxide in a mixture of sulphur chloride and hydrobromic acid. It is a very deliquescent substance, dissolving in water to form a faintly acid solution from which no crystalline hydrates have as yet been isolated. It forms double bromides with the bromides of antimony, bismuth, tin, and gold.

Cerous Iodide, $CeI_3,9H_2O$, forms transparent, easily soluble crystals which readily decompose with evolution of iodine.

Cerous Sulphide, Ce_2S_3, is formed when the metal is burnt in the vapour of sulphur, when the oxide is heated in carbon disulphide vapour, and when cerous sulphate is heated in a current of sulphuretted hydrogen.[3] It is a brown or purple-black powder of specific gravity 5·1. When the oxide is fused with three parts of sodium pentasulphide, and the fused mass lixiviated with water, cerous sulphide is obtained in small crystals resembling mosaic gold, which do not undergo alteration on exposure to the air.[4]

Cerous Sulphate, $Ce_2(SO_4)_3$, dissolves in water at 0° to the extent of 40 parts [5] in 100, whilst at 100°, 100 parts of water dissolve only 0·775 part. The solution yields crystalline hydrates with 12, 9, 8, 5, and 4 molecules of water respectively. With stannic sulphate [6] a double salt of the formula $CeHSn(SO_4)_4$ is formed as a microcrystalline powder. Crystalline derivatives are formed by cerous sulphate with pyridine [7] and quinoline sulphates.

Potassium Cerous Sulphate, $3K_2SO_4,Ce_2(SO_4)_3$, is formed when an equal or greater weight of potassium sulphate is added to a solution of cerous sulphate. It dissolves in about 56 parts of water at 20°, and is almost insoluble in a concentrated solution of potassium sulphate. It dissolves readily, however, in acidified water, and on slow evaporation a double salt, $Ce_2(SO_4)_3,2K_2SO_4,3H_2O$, crystallises out. If less than the above proportion of potassium sulphate is added to a solution of cerous

[1] Muthmann and Stutzel, *Ber.*, 1899, **32**, 3413.

[2] Burton, *Compt. rend.*, 1907, **145**, 243.

[3] Muthmann and Stutzel, *Ber.*, 1899, **32**, 3413; Sterba, *Ann. Chim. Phys.*, 1904, [8], **2**, 193.

[4] Compare Muthmann and Stutzel, *Ber.*, 1899, **32**, 3413; Sterba, *Ann. Chim. Phys.*, 1904, [8], **2**, 193.

[5] Muthmann and Rolig, *Zeit. anorg. Chem.*, 1898, **16**, 450; compare Brauner, *Journ. Chem. Soc.*, 1888, **53**, 357.

[6] Weinland and Kuhl, *Zeit. anorg. Chem.*, 1907, **54**, 244.

[7] Kolb, Melzer, Merckle, and Teufel, *Zeit. anorg. Chem.*, 1908, **60**, 123.

sulphate, another salt having the composition $Ce_2(SO_4)_3,K_2SO_4$ is formed as a granular, crystalline mass.

Sodium, ammonium and thallium sulphate also form sparingly soluble double salts with cerium sulphate.[1] An acid sulphate,[2] $CeH_3(SO_4)_3$, is formed by dissolving the normal sulphate in concentrated sulphuric acid and crystallising.

Cerous Nitride, CeN, is readily prepared by heating cerium in a current of nitrogen. According to Dafert and Miklauz [3] pure cerium nitride cannot be got by the foregoing method; the pure substance is obtained by heating the hydride at 800–900°, in a current of nitrogen. It is a lustrous yellow or bronze substance, stable in dry air, and is decomposed by water with formation of ammonia, hydrogen, and cerium dioxide.[4] A further nitride,[5] CeN_2, is formed as a greyish-black powder by heating cerium in a closed copper tube with a limited supply of air.

Cerous Nitrate, $Ce(NO_3)_3,6H_2O$, is a crystalline mass, obtained by the action of barium nitrate on a solution of cerous sulphate, or by the action of nitric acid on cerium dioxide in the presence of hydrogen peroxide, which begins to decompose about 200°. It is easily soluble in water and in alcohol, and forms crystalline double salts with ammonium,[6] sodium, potassium, rubidium,[7] cæsium, and thallium nitrates, and also with the nitrates of pyridine, quinoline, and piperidine.[8] A series of double nitrates [9] of the general formula $2Ce(NO_3)_3,3M(NO_3)_2,24H_2O$ is formed with the nitrates of magnesium, nickel, zinc, cobalt, and manganese.

Cerous Phosphate, $CePO_4$, occurs in the mineral monazite. This mineral often contains thorium, tin, manganese, and calcium in varying quantities. It crystallises in brownish, hyacinth-red, monoclinic crystals, and occurs in the Urals, in Norway, and in several localities in the United States and South America. It may be prepared by fusing cerium dioxide with sodium meta-

[1] Wolff, *Zeit. anorg. Chem.*, 1905, **45**, 89; Barre, *Compt. rend.*, 1910, **151**, 871.

[2] Wyrouboff, *Bull. Soc. chim.*, 1889, [3], **2**, 745.

[3] *Monatsh.*, 1912, **33**, 911.

[4] Muthmann and Kraft, *Annalen*, 1902, **325**, 261.

[5] Farabon, *Ann. Chim. anal.*, 1919, [2], **1**, 156.

[6] Wolff, *Zeit. anorg. Chem.*, 1905, **45**, 89.

[7] Wyrouboff, *Bull. Soc. franç. Min.*, 1907, **30**, 299; Jantsch and Widgorow, *Zeit. anorg. Chem.*, 1911, **69**, 221.

[8] Kolb, Melzer, Merckle, and Teufel, *Zeit. anorg. Chem.*, 1908, **60**, 123.

[9] Jantsch, *Zeit. anorg. Chem.*, 1912, **76**, 303.

phosphate, when it is obtained in rhombic prisms varying in colour from yellow to greenish-grey.

Cerous Carbonate, $Ce_2(CO_3)_3$, occurs in lanthanite, and may be obtained by precipitating a solution of cerous sulphate with ammonium carbonate. The precipitate thus obtained has the composition $Ce_2(CO_3)_3,5H_2O$, and on standing assumes the form of small, silky needles. Cerous carbonate forms double carbonates with sodium, potassium, and ammonium carbonate.

The nitrite,[1] bromate,[2] $Ce(BrO_3)_3,9H_2O$, perchlorate,[1] $Ce(ClO_4)_3,9H_2O$, dithionate,[1] $Ce_2(S_2O_3)_3,12H_2O$, selenate,[3] $Ce_2(SO_4)_3,4H_2O$, ammoniomolybdate,[4] $(NH_4)_6Ce_2Mo_{14}O_{48},24H_2O$, silicotungstate,[5] $2(12WO_3)2SiO_2,3CeO,H_2O,27H_2O$, and the complex ferrocyanide,[6] $NH_4CeFe(CN)_6$, have all been prepared.

Ceric Compounds.

364 *Ceric Fluoride*, CeF_4,H_2O, is obtained by acting on hydrated cerium dioxide with hydrofluoric acid, and on heating yields water and then hydrofluoric acid and free fluorine.[7] Ceric fluoride forms double compounds [8] with the fluorides of cadmium, copper, cobalt, nickel, and zinc which have the general formula $MF_2,2CeF_4,7H_2O$.

Ceric Chloride, owing to its extreme instability, has not yet been isolated, but if a ceric compound is dissolved in cold hydrochloric acid a dark red solution is obtained which in all probability contains the hypothetical acid, H_2CeCl_6. This solution, on keeping, or on warming, loses chlorine and a cerous compound is formed. Although the chloride is not known, a number of double compounds of it have been isolated, which include *ceric pyridinium chloride*, $(C_5H_5NH)_2CeCl_6$, *ceric quinolinium chloride*, $(C_9H_7NH)_2CeCl_6$ [9] and well defined crystalline derivatives with the hydrochlorides of caffeine, theobromine, quinine, and triethylamine.[10]

Ceric oxychloride, $CeOCl_2,10H_2O$,[11] is produced by the electro-

[1] Morgan and Cahen, *Journ. Chem. Soc.*, 1907, **91**, 475.
[2] James and Langelier, *J. Amer. Chem. Soc.*, 1909, **31**, 913.
[3] Cingolani, *Atti R. Accad. Lincei*, 1908, [5], **17**, 254.
[4] Barbieri, *Atti R. Accad. Lincei*, 1908, [5], **17**, 540.
[5] Wyrouboff, *Bull. Soc. franç. Min.*, 1905, **28**, 201.
[6] Robinson, *Journ. Chem. Soc.*, 1909, **95**, 1358.
[7] Brauner, *Monatsh.*, 1882, **3**, 8.
[8] Rinbach and Kilian, *Annalen*, 1909, **368**, 101.
[9] Koppel, *Zeit. anorg. Chem.*, 189°, **18**, 305.
[10] Stefano, *Annali Chim. appl.*, 1919, **12**, 130.
[11] Arnold, *Zeit. Elektrochem.*, 1918, **24**, 137.

lysis of slightly hydrated molten cerous chloride at 900°. It is deliquescent and is hydrolysed by water to form ceric hydroxide and cerous chloride.

Ceric Sulphate, $Ce(SO_4)_2$.—When cerium dioxide is heated with concentrated sulphuric acid it is converted without dissolving into ceric sulphate.[1] The salt, after washing with acetic acid and drying in a vacuum over potash, is obtained as a yellow, crystalline powder. It is very soluble in water, and the solution deposits a basic salt on warming. The hydrated salt, $Ce(SO_4)_2,4H_2O$, is obtained by dissolving the dioxide in dilute sulphuric acid and evaporating the salt in a vacuum over sulphuric acid. It is then deposited in the form of reniform masses consisting of fine crystals. In the moist state these are brown, whilst when dried they are yellow. When an excess of concentrated sulphuric acid is poured on the dioxide and the solution, diluted with water, gradually allowed to evaporate, *ceri-cerohydrosulphate* is deposited in fine, red, hexagonal crystals. Some doubt exists as to the exact composition of this compound, which is given by Brauner [2] as $2Ce(SO_4)_2,Ce_2(SO_4)_3,H_2SO_4,24H_2O$. On further evaporating the mother-liquor, yellow crystals of $Ce(SO_4)_2,4H_2O$ are deposited.

Ceric sulphate forms double sulphates with the sulphates of the alkali metals, such as $Ce(SO_4)_2,2K_2SO_4,2H_2O$, a compound which is deposited in small, yellow, monoclinic crystals. Ceric sulphate is decomposed by water with formation of basic salts, the composition of which varies according to the quantity of water present.

Ceric Nitrate.—The normal salt is not known, but when a solution of the hydrated dioxide in nitric acid containing calcium nitrate is evaporated, long red crystals of a *basic nitrate*, $Ce(NO_3)_3OH,3H_2O$, are obtained.[3] If potassium nitrate be added to the acid solution, and the liquid allowed to crystallise in a vacuum over lime, yellow, glistening, six-sided prisms are deposited, having the composition $2Ce(NO_3)_4,2KNO_3,3H_2O$. Ceric nitrate also forms double salts with other nitrates.

Ceric Ammonium Nitrate,[4] $Ce(NO_3)_4,NH_4NO_3,2H_2O$, is prepared by the electrolytic oxidation of a mixture of cerous

[1] Meyer and Aufrecht, *Ber.*, 1904, **37**, 140.

[2] *Zeit. anorg. Chem.*, 1904, **39**, 261, where a summary of the literature is given; see also Wyrouboff and Verneuil, *Ann. Chim. Phys.*, 1906, [8], **9**, 289.

[3] Meyer and Jacoby, *Zeit. anorg. Chem.*, 1901, **27**, 359.

[4] Plancher and Barbieri, *Atti R. Accad. Lincei*, 1904, [5], **14**, i., 119.

and ammonium nitrates. This compound has a colour very similar to that of potassium bichromate; it is fairly soluble in water, and on boiling or heating at temperatures above 60° is partially reduced with the formation of cerous nitrate.

Cerium Carbide, CeC_2, is obtained by heating cerium dioxide with sugar charcoal in the electric furnace, and forms a reddish-yellow, transparent, crystalline substance. On treatment with water it yields a mixture of 75 per cent. of acetylene, 4 per cent. of ethylene, and 21 per cent. of methane.[1] When cerium carbide is heated to 1250° in nitrogen [2] it is converted into the nitride.

Cerium Silicide, $CeSi_2$, is obtained when cerium dioxide is heated with silicon in the electric furnace.[3] It forms small crystals having a steely lustre and a specific gravity of 5·67.

Ceric Selenite,[4] $Ce(SeO_3)_2$, ceric dihydrogen arsenite,[4] $Ce(H_2AsO_4)_4,4H_2O$, ceric iodate,[5] and ceric monohydrogen arsenite,[4] $Ce(HAsO_4)_2,6H_2O$, have been prepared.

Detection and Estimation of Cerium.

365 The spark spectrum of cerium contains a number of bright lines, of which the brightest and most characteristic lie in the green and blue. A characteristic reaction for the cerium compounds is the precipitation of red ceric hydroxide when sodium hypochlorite is added to a colourless cerous salt; this dissolves in warm hydrochloric acid with evolution of chlorine. The other reactions have already been described.

In order to estimate cerium quantitatively, the solution is precipitated with caustic potash, and the washed and dried precipitate is heated in the air in order to convert it into the dioxide, or it is precipitated as the oxalate and converted into the dioxide by heating. Cerium may be estimated volumetrically [6] by means of oxalic acid and potassium permanganate, and also by means of potassium ferricyanide and potassium permanganate.[7]

The Atomic Weight of cerium has been determined by several

[1] Moissan, *Compt. rend.*, 1896, **122**, 357; 1897, **124**, 1233; Muthmann, Hofer, and Weiss, *Annalen*, 1902, **320**, 231.

[2] Fichter and Scholly, *Helv. Chim. Acta*, 1920, **3**, 164.

[3] Sterba, *Compt. rend.*, 1902, **135**, 170.

[4] Barbieri and Calzolari, *Ber.*, 1910, **43**, 2214.

[5] Barbieri, *Atti R. Accad. Lincei*, 1907, [5], **16**, i, 644.

[6] Meyer and Schweitzer, *Zeit. anorg. Chem.*, 1907, **54**, 104.

[7] Browning and Palmer, *Amer. J. Sci.*, 1908, [5], **26**, 83.

chemists. The early work of Bunsen[1] and Rammelsberg[2] gave low values; later, Brauner[3] and Robinson[4] found 140·2. Still more recently Brauner,[5] by the analysis of cerium oxalate and sulphate, obtained the number 140·25, which at present (1922) is accepted.

PRASEODYMIUM. Pr = 140·9. At. No. 59.

366 The substance originally described as didymia by Mosander (p. 794) was found by Lecoq de Boisbaudran in 1879 to contain the oxide of another element, named by him samarium, from which it was separated by repeated fractional precipitation with ammonia. Didymia, freed from samaria, was then looked on as an individual substance until in 1885 Welsbach[6] succeeded in resolving it into the oxides of two distinct elements, which he termed praseodymium and neodymium. This was accomplished by the oft repeated crystallisation, from strong nitric acid solution, of the double nitrate of the metal with ammonium, or, in the last stage of the process, sodium nitrate. The separation can also be effected by means of the double magnesium nitrate (Drossbach), or the sulphate.[7]

These two substances have not up to the present been further resolved and appear to be true elements, although Chroustschoff[8] states that he has isolated a third element, with bluish coloured salts, which he terms *glaucodidymium*. They resemble one another closely in their chemical properties, but their salts differ very strikingly in colour, those of praseodymium being green, and those of neodymium rose-coloured. The proportions present in the old didymium are about 1 of praseodymium to 2 of neodymium.

Praseodymium has been prepared by Muthmann and Weiss by the electrolysis of the chloride. It has a yellowish colour and is unaffected by air, melts at 940°, and has the sp. gr. 6·4754.

[1] *Annalen*, 1853, **86**, 265; 1858, **105**, 40.
[2] *Pogg. Ann*, 1859, **108**, 40.
[3] *Journ. Chem. Soc.*, 1885, **47**, 879; *Chem. News*, 1895, **71**, 283.
[4] *Proc. Roy. Soc.*, 1884, **37**, 150.
[5] Brauner and Batěk, *Zeit. anorg. Chem.*, 1903, **34**, 103; Brauner, *ibid.*, 207.
[6] *Monatsh.*, 1885, **6**, 477.
[7] Muthmann and Rölig, *Ber.*, 1898, **31**, 1718.
[8] Chroustschoff, *J. Russ. phys. Chem. Ges.*, 1897, **29**, 206; Kruss and Nilson, *Ber.*, 1887, **20**, 2134, 3067.

When heated in the air praseodymium burns, forming a mixture of oxide and nitride.

Praseodymium and Oxygen.—This metal readily forms a *dioxide*, PrO_2, which is obtained pure[1] by heating the nitrate with potassium nitrate at 400–450°. It is a black powder which yields chlorine with hydrochloric acid, is reduced by hydrogen peroxide, and in acid solution oxidises cerous to ceric salts and manganous salts to permanganic acid. No stable salts derived from this oxide are known.

The *sesquioxide*, Pr_2O_3, is obtained by heating the dioxide or one of the intermediate oxides in hydrogen as a yellowish-green amorphous powder which readily dissolves in acids, forming characteristic green salts. When this oxide or a salt of the metal with a volatile acid is heated a dark coloured oxide is formed, the composition of which is intermediate between Pr_2O_3 and PrO_2 and varies with the conditions of formation. Various formulæ have been ascribed to this substance, such as Pr_4O_7, Pr_5O_9 and Pr_6O_{11}.

The *hydroxide*, $Pr(OH)_3$, is a light green, amorphous powder. A hydrate of a peroxide, Pr_2O_5, is also known.

Praseodymium Chloride, $PrCl_3$, is a pale green, crystalline mass, melting at 818°, density at 18° 4·017; it is very readily soluble in water and alcohol, and yields a hydrate with $7H_2O$.

The *fluoride*, PrF_3, is obtained[2] as a gelatinous precipitate when hydrofluoric acid is added to a solution of the nitrate; on warming it yields yellow, glistening crystals.

The *bromate*, $Pr(BrO_3)_3,9H_2O$, is formed in the same way as cerous bromate.

Praseodymium Sulphate, $Pr_2(SO_4)_3$, crystallises with $8H_2O$ and forms green, monoclinic crystals. Hydrates with 5, 12, and $15\frac{1}{2}$ H_2O are also known. It forms sparingly soluble double sulphates with the sulphates of the alkali metals.

Praseodymium Nitrate, $Pr(NO_3)_3,6H_2O$, crystallises in long needles, and forms the double ammonium salt,

$$Pr(NO_3)_3,2NH_4NO_3,4H_2O.$$

It also forms double nitrates with the nitrates of rubidium,[3] magnesium,[4] nickel, cobalt, zinc, and manganese.

[1] Brauner, *Proc. Chem. Soc.*, 1901, **17**, 66.
[2] Popovici, *Ber.*, 1908, **41**, 634.
[3] Jantsch and Widgorow, *Zeit. anorg. Chem.*, 1911, **69**, 221.
[4] Jantsch, *Zeit. anorg. Chem.*, 1912, **76**, 303.

Praseodymium Carbonate, $Pr_2(CO_3)_3,8H_2O$, is formed by passing carbon dioxide into an aqueous suspension of the hydroxide, or by adding ammonium carbonate to a solution of the chloride. It is thus obtained in sparingly soluble, silky plates. It forms green double carbonates with the carbonates of the alkali metals.

The hydride, carbide, sulphides, and nitride resemble those of lanthanum in chemical properties.

Praseodymium is best detected by means of its absorption spectrum, which contains 5 bands, the maxima of which are situated at wave-lengths 596·8, 589·5, 481·2, 469·3, and 444·7 (Brauner). The oxide acts as an exciter of the phosphorescence of colourless oxides such as lanthana and yttria.

Praseodymium compounds colour the borax bead [1] yellowish-green in the oxidising flame and green in the reducing flame.

NEODYMIUM. Nd = 144·3. At. No. 60.

367 Neodymium salts are very difficult to prepare free from samarium, but this was accomplished by Demarçay [2] in 1898.

Neodymium is prepared by the electrolysis of the fused chloride, using a very thin carbon cathode and a current of 90–100 amperes. It has a yellowish colour and slowly tarnishes in the air. It is slowly attacked by cold water, and rapidly by hot water and acids. It melts at 840°, and has the sp. gr. 6·9563.

Neodymium and Oxygen.—The only stable oxide is the *sesquioxide*, Nd_2O_3, which is a blue powder, and is not affected by ignition in the air. The *hydroxide* [3] is prepared by precipitating a solution of a neodymium salt with an alkali hydroxide. If the dried product is heated to 310° a greyish-brown substance, $2Nd_2O_3,3H_2O$, is formed, whilst at 525° Nd_2O_3,H_2O, a grey compound, is formed. The unstable *dioxide*, NdO_2, is formed by the action of heat on the oxalate and nitrate in an atmosphere of oxygen.

The salts of neodymium are derived from the sesquioxide and are of a rose to a violet-red colour.[4] The *chloride* melts at 785°. It forms hydrates with $1H_2O$ and $6H_2O$, and derivatives with alcohol and pyridine. With gaseous ammonia the anhy-

[1] Milbauer, *Zeit. anal. Chem.*, 1907, **46**, 457.

[2] *Compt. rend.*, 1898, **126**, 1039.

[3] Joye and Garnier, *Compt. rend.*, 1912, **154**, 510.

[4] See Matignon, *Ann. Chim. Phys.*, 1906, [8], **8**, 243; *Compt. rend.*, 1906, **142**, 276; Matignon and Trannoy, *ibid.*, 1042.

drous chloride forms derivatives with 1, 2, 4, 5, 8, 11, and 12 molecules of ammonia. The bromide[1] is prepared in the same way as cerous bromide, and the fluoride[2] as praseodymium fluoride. The *sulphate* is much less soluble than that of praseodymium, whilst the *double ammonium nitrate* is more soluble than the corresponding praseodymium salt. Double nitrates[3] corresponding with those of praseodymium are formed by neodymium nitrate.

The absorption spectrum contains more than 20 bands, one of which, of wave-length 469·1, almost coincides with one of the praseodymium bands. Neodymium salts impart a violet colour to the borax bead[4] when heated in the reducing flame, but no colour in the oxidising flame. Like praseodymia, the oxide excites phosphorescence in other colourless earths. The oxide when heated, especially in presence of other oxides, glows with light which yields a discontinuous spectrum, a phenomenon which was also observed with the old didymium oxide.

SAMARIUM. Sa = 150·4. At. No. 62.

368 This element was discovered in samarskite by Lecoq de Boisbaudran in 1879, but its compounds were first obtained quite free from europium and gadolinium in 1904 by Urbain and Lacombe[5] by the fractional crystallisation of the double magnesium nitrates to which the corresponding bismuth salt had been added. In addition to the salts of the type SaX_3, samarium forms a subchloride, $SaCl_2$. It and europium are the only elements of the rare earth metals to form compounds of this type.

Metallic samarium is of a whitish-grey colour, melts at 1,300–1,400°, has a sp. gr. of about 7·7, and tarnishes in the air. The *oxide*, Sa_2O_3, has a faint yellow colour and does not form a higher oxide when heated in the air. The salts are topaz-yellow coloured and show a faint absorption spectrum, most of the bands being in the blue or violet. A large number of them have been described by Cleve.[6] The *chloride*, $SaCl_3$, is almost

[1] Burion, *Compt. rend.*, 1907, **145**, 243.
[2] Popovici, *Ber.*, 1908, **41**, 634.
[3] Jantsch and Widgorow, *Zeit. anorg. Chem.*, 1911, **69**, 221; 1912, **76**, 303.
[4] Milbauer, *Zeit. anal. Chem.*, 1907, **46**, 457.
[5] *Compt. rend.*, 1904, **138**, 1166.
[6] *Bull. Soc. chim*, 1885, [2] **43**, 53.

white, melts at 686°, and forms a hydrate with $6H_2O$, which crystallises in large yellow tablets. The anhydrous salt is soluble[1] in alcohol and pyridine, and with the latter substance forms a gelatinous substance on heating which redissolves on cooling. On heating in hydrogen it is reduced to samarous chloride, and on heating in oxygen it yields an oxychloride, SaOCl. When treated with ammonia,[2] derivatives containing 1, 2, 3, 4, 5, 8, 9·5, and 11·5 molecules of ammonia are formed. The *subchloride*, $SaCl_2$, is formed when the chloride is heated in dry hydrogen or ammonia, or with aluminium powder.[3] It is a reddish-brown, crystalline mass which dissolves in water, forming a reddish-brown solution which decomposes with evolution of hydrogen and becomes colourless. A corresponding subiodide, SaI_2, has also been prepared by reducing the tri-iodide at high temperatures with gaseous hydrogen iodide. It is a yellow compound which dissolves in water to form a brown solution, and this on keeping loses its colour and deposits gelatinous samarium hydroxide.

EUROPIUM. Eu = 152·0. At. No. 63.

369 The salts of this element were originally obtained from Lecoq de Boisbaudran's samarium by Demarçay (1896), and were first prepared pure by Urbain and Lacombe (1904). The separation from samarium is effected by the prolonged fractional crystallisation from nitric acid of the magnesium double nitrates in presence of bismuth nitrate, the double magnesium nitrate of which is intermediate in solubility between the other two. It has been shown recently[4] by the spectrum analysis of europium–samarium fractions that it is likely there is an element in this fraction which has not previously been discovered. This has been termed *eurosamarium*. The oxide, Eu_2O_3, and most of the salts have a faint pink colour, and the latter show a faint absorption spectrum. *Europium chloride*, $EuCl_3$, is formed in fine needles by heating the hydrated chloride in a mixture of chlorine and sulphur monochloride. It is soluble in water and the hydrated chloride, when heated to 600° is converted into the oxychloride EuOCl. This element, like samarium, forms a lower chloride,[5] $EuCl_2$, by

[1] Matignon, *Ann. Chim. Phys.*, 1906, **8**, 402.
[2] Matignon and Trannoy, *Compt. rend.*, 1905, **140**, 141.
[3] Matignon and Cazes, *Ann. Chim. Phys.*, 1906, [8], **8**, 417.
[4] Eder, *Sitzungsber. Akad. Wien*, 1917, IIa, **126**, 473.
[5] Urbain and Bourion, *Compt. rend.*, 1911, **153**, 1155.

heating the higher chloride in hydrogen. This compound is soluble in water without change, but on boiling the solution, oxidation occurs and the oxide is precipitated

$$12EuCl_2 + 3O_2 = 8EuCl_3 + 2Eu_2O_3$$

The spark spectrum is brilliant and characteristic. Europium occurs in very small quantities, monazite sand containing only 0·02 per cent. Its presence has been detected in the sun and certain stars.[1]

GADOLINIUM. Gd = 157·3. At. No. 64.

370 This element was discovered in 1880 by Marignac[2] in samarskite, and its salts were first prepared free from europium and terbium by Urbain and Lacombe.[3] The oxide, Gd_2O_3, is white and the salts are colourless and do not show absorption bands.[4] The oxide is hygroscopic, absorbs carbon dioxide from the air, and dissolves slowly in acids. It darkens in colour on heating and has a specific gravity 7·41. The *chloride*, $GdCl_3,6H_2O$, forms deliquescent, prismatic crystals. The *sulphate*, $Gd_2(SO_4)_38H_2O$, is isomorphous with the corresponding sulphates of the other rare earths. It forms double sulphates with the sulphates of sodium and potassium. *Gadolinium nitrate*, $Gd(NO_3)_3,6H_2O$, is similar to the other rare earth nitrates. It forms double nitrates with alkali nitrates and certain divalent nitrates.

TERBIUM. Tb = 159·2. At. No. 65.

371 The existence of the earth originally called erbia by Mosander was denied by Berlin (1860), and by Bahr and Bunsen (1866), but was confirmed by Delafontaine (1878) and by Marignac. It then received the name of terbia, the designation erbia having been in the meanwhile applied to the rose-red earth described below. It was afterwards found that all these preparations consisted mainly of gadolinium, and pure terbium compounds were first obtained by Urbain[5] by fractionating the nickel double nitrates, the ethyl sulphates, or a mixture

[1] Lunt, *Proc. Roy. Soc.*, 1907, **79**, [*A*], 118.

[2] *Ann. Chim. Phys.*, 1880, [5], **20**, 535.

[3] See also Urbain, *Compt. rend.*, 1905, **140**, 583.

[4] Benedicks, *Zeit. anorg. Chem*, 1900, **22**, 393; Popovici, *Ber.*, 1908, **41**, 634.

[5] *Compt. rend.*, 1905, **141**, 521; 1906, **142**, 957; *J. Chim. phys.*, 1906, **4**, 31, 105.

of bismuth nitrate with the nitrates of the terbium earths. According to Urbain, terbium forms a white oxide, Tb_2O_3, and a dark brown peroxide, which appears to have the composition Tb_4O_7, and is obtained by igniting the oxalate. The sesquioxide is strongly magnetic.[1] The salts[2] are colourless and show no absorption spectrum. *Terbium chloride*, $TbCl_3,6H_2O$, *terbium sulphate*, $Tb_2(SO_4)_3,8H_2O$, and *terbium nitrate*, $Tb(NO_3)_3,6H_2O$, are prepared in the same way and have similar properties to the corresponding compounds of the other yttrium earths. The presence of terbia in gadolinia renders the latter yellow.

DYSPROSIUM.	Dy = 162·5.	At. No. 66.
HOLMIUM.	Ho = 163·5.	At. No. 67.
ERBIUM.	Er = 167·7.	At. No. 68.
THULIUM.	Tm = 168·5.	At. No. 69.

372 The terbia originally isolated from crude yttria by Mosander subsequently received the name of *erbia* (Berlin), and has been shown by Soret, Cleve, Thalén and Lecoq de Boisbaudran to consist of at least four earths, the true *erbia*, *holmia*, *thulia*, and *dysprosia*. The salts of all these show absorption bands, but it is doubtful whether any one of the four, with the possible exception of dysprosia,[3] is an individual substance.[4] Thulium, according to Auer von Welsbach,[5] consists of at least three elements, which he names thulium I, II, and III respectively. Erbium forms a rose-coloured oxide which dissolves in acids to form intensely red salts, which in solution show absorption bands, whilst the salts[6] of dysprosium are green or yellow. Dysprosium oxide is pure white and very strongly magnetic,[7] being 12·8 times as strong as ferric oxide. Holmia is yellow in colour[8] and the salts are pale yellow with an orange tint.

Solutions of the salts when concentrated give a characteristic absorption spectrum containing about 15 bands.

Thulium oxide, Tm_2O_3, is quite colourless, whilst the salts are all green or bluish-green and in solution yield an absorption spectrum containing seven characteristic absorption bands.

[1] Urbain and Jantsch, *Compt. rend.*, 1908, **147**, 1286.

[2] Potratz, *Chem. News*, 1905, **92**, 3; Urbain and Jantsch, *Compt. rend.*, 1908, **146**, 127.

[3] Urbain, *Compt. rend.*, 1906, **142**, 785; **143**, 592.

[4] Compare *Zeit. anorg. Chem.*, 1892, **3**, 353, 407.

[5] *Monatsh.*, 1911, **32**, 373.

[6] Jantsch and Ohl, *Ber.*, 1911, **44**, 1274.

[7] Urbain, *Compt. rend.*, 1908, **146**, 922.

[8] Holmberg, *Arkiv Kem. Min. Geol.*, 1911, **4**, No. 2, 1.

NEO-YTTERBIUM. Yb = 173·5. At. No. 70.
LUTECIUM. Lu = 175·0. At. No. 71.

373 The element known as ytterbium was discovered by Marignac in gadolinite in 1878,[1] and was separated from scandium by Nilson in 1880. It forms one oxide of the type M_2O_3, which is white; the salts are colourless and yield no absorption bands, but the spark spectrum is characteristic (Thalén). Urbain,[2] by fractional crystallisation of the nitrate of pure ytterbia, has resolved it into two elements, which he terms lutecium and neo-ytterbium; of the three characteristic absorption bands of the "old" ytterbium, the α and β bands belong to neo-ytterbium and the γ band to lutecium. The atomic weights[3] were determined by analysis of the hydrated sulphates prepared from the nitrates which had been subjected to 15,000 recrystallisations. Auer von Welsbach,[4] by the fractional precipitation of ytterbium oxalate, has also resolved ytterbium into two components which he terms *aldebaranium* and *cassiopeium*; these elements are identical with neo-ytterbium and lutecium. Welsbach is of the opinon that a third element also is present, since some of the lines present in the spectrum of the old ytterbium do not appear in the spectra of either of the new elements. The compounds of the two elements are indistinguishable chemically, and have been investigated by Urbain, Bourion, and Maillard.[5]

CELTIUM. Ct = (?) At. No. 72 (?).[6]

In the isolation of lutecium from the gadolinite earths Urbain[7] obtained a small quantity of an uncrystallisable mother-liquor, which contained an element the oxide of which had a magnetic susceptibility 3-4 times less than that of lutecia. The name *celtium* was assigned to the element. The arc spectrum of this oxide is rich in lines, the most intense being λ=2685·2, 2765·8, 3080·7, 3118·6, and 3197·9. The oxide is less basic than lutecia, but more basic than scandia.

[1] *Compt. rend.*, 1878, **87**, 578.
[2] Urbain, *Compt. rend.*, 1907, **145**, 759.
[3] *Compt. rend.*, 1908, **146**, 408.
[4] *Monatsh.*, 1908, **29**, 181.
[5] *Compt. rend.*, 1909, **149**, 127.
[6] Dauvillier, *Compt. rend*, 1922, **174**, 1347, supports the claim of Celtium to the position 72 from the results of X-ray spectroscopy, but the discovery of Hafnium by Coster and Hevesy, *Nature*, 1923, **113**, 79, also of At. No. 72, throws doubt on this claim (p 858.)
[7] *Compt. rend.*, 1911, **152**, 141.

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