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PRACTICAL METALLURGY

AND ASSAYING

A TEXT-BOOK FOR THE USE OF TEACHERS, STUDENTS, AND ASSAYERS

By ARTHUR H. HIORNS

HEAD OF METALLURGY DEPARTMENT, BIRMINGHAM MUNICIPAL TECHNICAL SCHOOL

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To

PROFESSOR W. CHANDLER ROBERTS-AUSTEN, K.C.B., F.R.S.

IN RECOGNITION OF HIS EMINENT SERVICES IN DEVELOPING
THE TEACHING OF METALLURGY,
AND IN APPRECIATION OF HIS KINDNESS
AND OF
HIS UNFAILING SYMPATHY WITH ALL STUDENTS,
THIS BOOK IS DEDICATED
BY HIS OLD PUPIL

THE AUTHOR.

PREFACE.

THE aim of the book is to teach the principles of Practical Metallurgy by means of a series of experiments, which have been chosen, partly on account of their practical utility, and partly as affording a valuable course of instruction for students preparing for, or engaged in metallurgical pursuits.

The first part is specially intended for persons having little or no knowledge of the scientific principles underlying the subject: it will also lay a foundation for the study of the higher branches of any particular section of Metallurgy.

The second part consists of a treatise on Assaying by "dry" methods and is intended, in conjunction with the first part, to meet the wants of students desirous of making a complete study of the subject of dry assaying.

The third part deals with wet methods, and is designed to form a suitable course of study for students who have mastered the principles involved in the first and second parts, though it is hoped that the information will be useful to many who, possessing only a limited knowledge of the subject, wish to practise methods of analysis and assaying beyond their own particular branch. For convenience of study, this part is treated under three

heads—(1) Division of metals and acids into groups, with methods of separating and estimating each constituent; (2) Analysis of various ores, fluxes, slags, products and alloys; (3) Volumetric methods of assaying.

The Author has devoted special attention to the analysis of iron and steel, explaining the most trustworthy methods with which he is acquainted; but simple and rapid methods by which approximate results may be obtained have not been overlooked. Great care has also been exercised in giving detailed directions for the assay of gold, silver, copper and other useful metals.

Although the work mainly consists of a number of examples for the student to work out in a scientific manner, information is also given for the guidance of the operator in his manipulations and in explanation of the character of the bodies which should be obtained. A chemical equation is given where necessary, to show the changes which occur and to enable a calculation to be made for finding the quantity of a flux, reducing agent, etc., requisite in each case, and to verify the weight of the product obtained.

As Electro-Metallurgy now forms an important branch of this subject and is probably destined to still greater expansion in the near future, it has been thought advisable to introduce a few elementary experiments illustrative of its employment in connection with metals, such experiments forming the groundwork of the course of practical instruction given in the Electro-Metallurgical Laboratory of the Birmingham Municipal Technical School.

The short description which is given of a metallurgical

laboratory with its necessary fittings and appliances, will, it is thought, prove useful in the formation of new classes.

The Author cordially acknowledges the assistance he has received in the preparation of this work from Dr. Percy's Manuals on Metallurgy; Fresenius' Quantitative Analysis; Watts' Dictionary of Chemistry; Mitchell's Assaying; Crookes' Select Methods in Chemical Analysis; Sutton's Volumetric Analysis; Gruner's Traité de Métallurgie, and various papers in the pages of *Iron*, *Engineering* and *The Chemical News*. He is specially indebted to Professor Chandler Roberts-Austen, the notes on whose lectures at the Royal School of Mines form the basis of the experiments quoted, and whose kindly help was invaluable in the inauguration of the School of Metallurgy with which the author is associated. To Mr. G. C. Marks, C.E., for executing the drawings; to Mr. T. J. Baker for contributing the section on Electro-Metallurgy; and to Mr. Enoch Evans for the section on Gas Analysis, grateful acknowledgments are also tendered.

October 1888.

PREFACE TO SECOND EDITION.

ADVANTAGE has been taken of the issue of another edition to introduce some new matter, and also to make certain alterations which have been suggested by the increased experience of the last three years. The Author gratefully acknowledges his indebtedness to Mr. J. H. Stansbie for his kindness in reading the proofs.

BIRMINGHAM MUNICIPAL TECHNICAL SCHOOL,
February 1892.

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PART I.

INTRODUCTORY.

§ 1. Metallurgy in its fullest sense treats of metals in their natural state, the mode of their extraction from the ore, and their application to various manufacturing purposes.

It is a chemical art requiring a knowledge of the laws of Chemistry, and a metallurgical training is not complete without some acquaintance with that special branch known as Analytical Chemistry, by which the amount of every individual constituent of a compound may be determined. In fact, Metallurgy is the application of Chemistry, Physics and Mechanics to the treatment of metalliferous materials with a view to the extraction of the metals and their conversion to workable forms.

To certain groups of metals different modes of treatment are applicable, which vary from each other as much as the metals do themselves. All these methods rest on general principles, and in many cases the same reagents, the same apparatus, and the same processes are employed.

§ 2. The term metal has long been applied to a certain number of the chemical elements which have well-defined physical characters in common, by which they may be readily recognised. Gold and silver were formerly regarded as the types, on account of their high specific gravity, brilliant lustre, and superior conductivity for heat and electricity. But these properties are by no

means distinctive of metals, as there are many bodies, not classified among the metals, which have some of these physical characteristics.

Of the metallic elements there are about seventeen which may be called "useful" metals, viz.: silver, aluminium, arsenic, gold, bismuth, cobalt, copper, iron, mercury, manganese, nickel, lead, platinum, tin, antimony, zinc, and magnesium.

§ 3. Mercury, Caesium, and Gallium are the only metals liquid at the ordinary temperature, all the rest being solid and opaque except in extremely thin sheets. Copper is red, gold is yellow, the others white or greyish white.

The behaviour of the metals under the influence of heat is very varied. Tin, antimony, bismuth, lead, and zinc melt below a red heat. Gold, silver, and copper require a bright red. Iron, manganese, nickel, and cobalt, an intense white; while platinum will only melt in the oxy-hydrogen flame or by the agency of an electric current. With the exception of arsenic,* all are capable of becoming liquid when heated under ordinary conditions, and at high temperatures volatilised. Arsenic, antimony, mercury, zinc, and cadmium are readily volatile. There appears to be no relation between volatility and fusibility, for zinc and antimony require a much higher temperature than tin to fuse them, yet tin requires a strong heat to volatilise it.

§ 4. One of the most distinctive features of a metal is an internal mobility, in virtue of which its shape may be altered by pressure without disruption of the mass. This property is possessed by metals in varying degrees so that the "malleability" or power of being extended by pressure without cracking, and "ductility," or the capability of

* Professor Mallet and other observers have proved that arsenic may be liquefied by heat when under pressure.

being permanently elongated by a tensile stress combined with lateral pressure, which allows most metals to be drawn into wire, are by no means equal in extent: nor is the order of their malleability the same as for ductility, for the former depends on the softness and tenacity, while the latter is much more dependent on tenacity. By tenacity is understood the strength with which metals resist an attempt to pull their particles asunder by the action of a tensile stress. The tenacity is generally diminished as the temperature is increased, while, within certain limits, the reverse is the case with regard to malleability and ductility. Some metals have a very feeble tenacity and are then said to be brittle. When a metal resists rupture by a bending or twisting force it is said to be "tough." "Elasticity" is the power a body possesses of resuming its original form after the removal of an external force which has produced a change in that form. The point at which the elasticity and the applied stress counterbalance each other is termed the limit of elasticity. "Sonorousness" is an attribute of the harder metals, and is very marked in some of their alloys. "Hardness" is the resistance offered by the molecules of a substance to their separation by the penetrating action of another body, and like all other physical properties is considerably modified by the presence of impurities, so that in many cases softness is a test of purity. All malleable metals become hardened by pressure, and require occasional annealing during the process of manufacture. The fractured surface of metals is often characteristic, being spoken of as fibrous, crystalline, granular, silky, columnar, conchoidal, etc. Crystalline structure is often accompanied by brittleness, and fibrous structure by high tenacity.

§ 5. With regard to conducting power for heat and electricity the metals occupy the first place, silver standing at the head of the list. No physical property

is more affected by even traces of impurities than conductivity; it is also diminished by a rise in temperature. The capacity of metals for heat extends over a wide range; iron, for example, being more than $\frac{1}{10}$th that of water, while lead is less than $\frac{1}{30}$th. For the most part metals are heavier than water, platinum occupying the highest position among the useful metals, being $21\frac{1}{2}$ times heavier than an equal bulk of water. The specific weight determines the value of a metal for many purposes, as gold, for instance, the specific gravity of which being $19\frac{1}{2}$, greatly increases its convenience as a circulating medium, and aluminium is suitable for making small weights on account of its lightness.

The metallic elements are usually basic in character when united with oxygen, but this property is only relative, as an oxide which is basic in one compound may become acid when allied with a stronger base.

§ 6. By uniting two or more metals in various proportions an almost infinite variety of combinations may be obtained, possessing to a greater or less extent the properties of their constituents. The effect of this union is generally to increase the hardness, lower the melting point, alter the specific gravity, and otherwise modify the character of the components. Many metals are capable of uniting with others in definite proportions forming true chemical compounds; but as such compounds can be dissolved by the molten metals, they may with few exceptions be mixed in almost all proportions. The similarity in basic character of the metals would lead one to suppose that such combinations would be held together by feeble degrees of affinity, which would make it difficult to isolate them from their solvent metals. That there is in many cases some kind of affinity is evidenced by the heat produced when some metals are alloyed together. Thus, aluminium and copper, platinum and tin, arsenic and antimony, bismuth and lead, gold and just melted

tin evolve heat when they unite; on the other hand, lead and tin absorb heat in their union. But there is no great alteration of properties which is the general distinctive feature of chemical combination, the change being chiefly limited to variations in colour, malleability, tenacity, etc., while the product is always decidedly metallic. In some cases a small amount of a malleable metal added to another highly malleable one, will produce a brittle alloy, such as lead in gold. It is possible that two metals may combine when melted and separate on cooling. Matthiessen considers it probable that the condition of metals in alloys when in the liquid state is one of the following:—1. A solution of one metal in another; 2. Chemical combination; 3. Mechanical mixture; 4. A solution or mixture of two or all of the foregoing; and 5. One or more of the metals in the alloy may be present in an allotropic form.* Alloys are usually formed by melting the metals together, but they may also be prepared by strongly compressing together the constituent metals previously reduced to a fine state of division.

a. The action of acids and other solvents on alloys varies with the relative quantities of the metals present. Silver when alloyed with much gold is not affected by nitric acid, but when the silver is in excess, it may be entirely dissolved. Platinum, which when alone is insoluble in nitric acid or sulphuric acid, is readily dissolved when united with much silver.

b. The separation of the constituents of some alloys may be brought about by raising them to the temperature at which the most fusible melts, which then "liquates" out. In this way silver is removed from copper by means of lead; tin from iron and arsenic; mercury from gold, etc.

* See author's work on "Mixed Metals," p. 43. Macmillan & Co, Ltd.

LABORATORY APPLIANCES.

§ 7. A Metallurgical Laboratory requires as much space as is usually occupied by a Chemical Laboratory, and, in

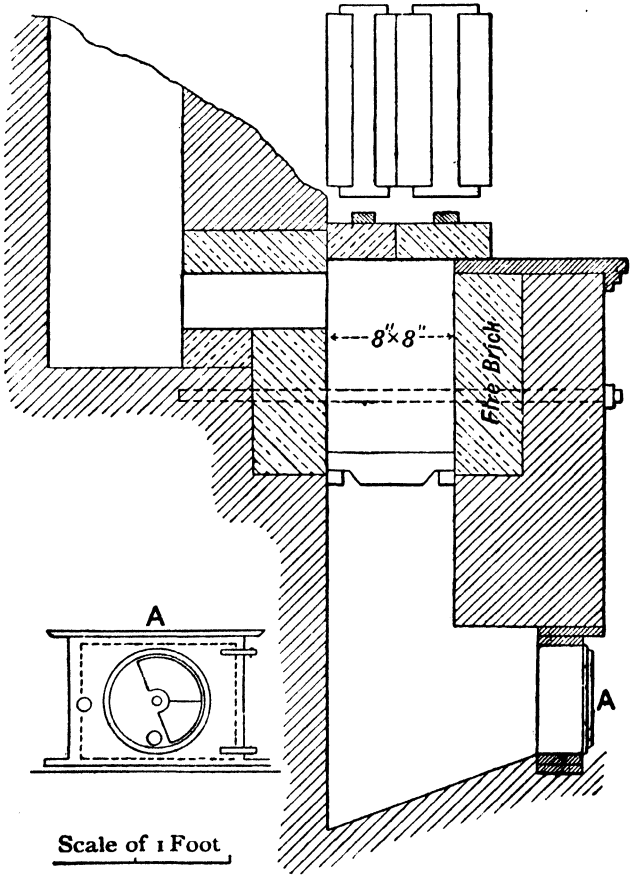


Fig. 1.

addition, necessary room for furnaces and muffles, proper

space being allowed for students to work at the fires, this being generally the busiest and most crowded part. The basement of a building is the most convenient, so that a good height of chimney may be obtained. The floor should be of brick or stone near the furnaces; all other parts may be boarded, or, if a brick floor extends all over the laboratory, it is advisable to have wooden stages in front of the work benches, so as to avoid damp, which is an usual accompaniment of basement rooms.

§ 8. The work benches should be fitted with drawers and cupboards, and with shelves above for reagents and fluxes. The tops of the benches require to be made of hard wood such as teak, or American walnut, to admit of the various hammering and pounding operations required in treating the products of the crucible, and the preparation of the tests for the furnace.

§ 9. The proper construction of the furnaces is a matter of the first importance, as a slight difference in the arrangement of the flues will considerably affect the draught, and prevent that high temperature requisite in melting such metals as iron, steel and nickel. The small wind furnaces used at the Royal School of Mines, and recommended by the Science and Art Department, are 1 foot deep and 8 inches square (Fig. 1). The draught hole is 6 inches by 3 inches, and the ashpit should have

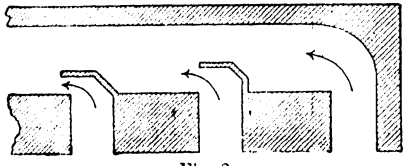


Fig. 2.

a capacity at least equal to that of the furnace. The bars are 9 inches long, $1\frac{1}{4}$ inches wide at top, and gradually tapering to the bottom. These are rather

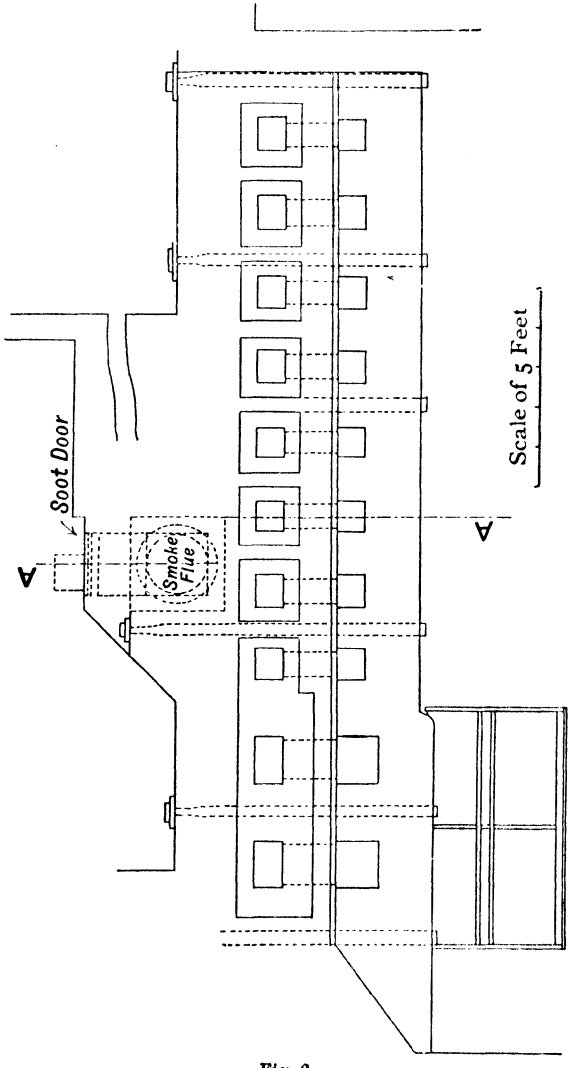


Fig. 3.

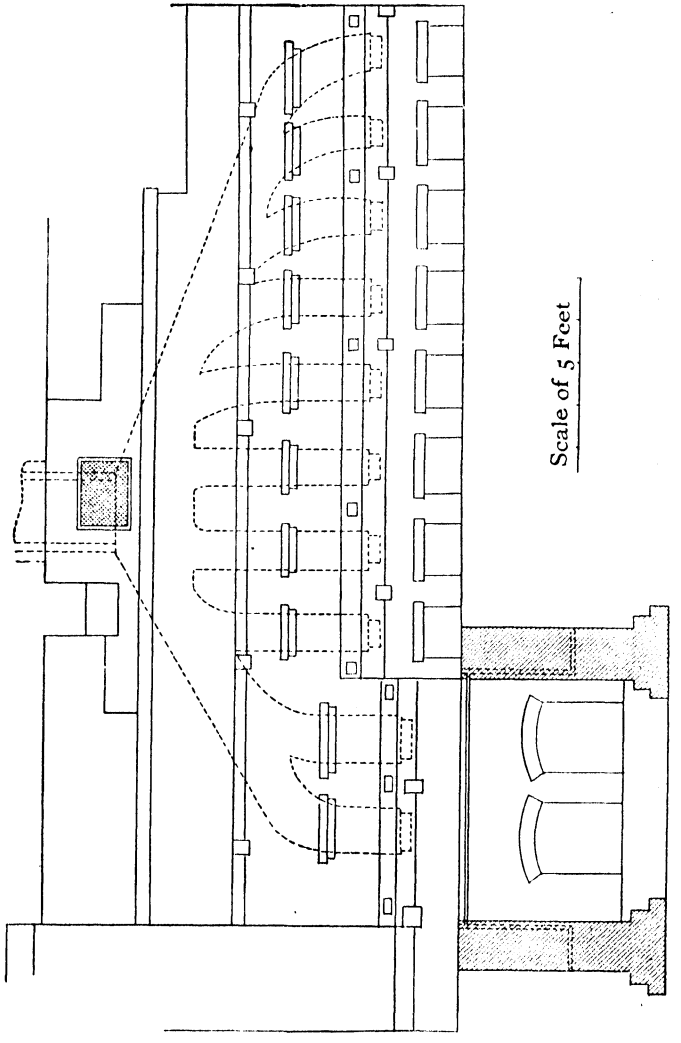


Fig. 4.

small for some operations, and furnaces about 10 inches square and 15 inches deep are preferable.

§ 10. The flue of a furnace is generally horizontal, and will vary in length according to the distance of the chimney from the furnace. The section of the flue has a great influence on the working, for, if too narrow, the friction is great and the draught too sluggish. For an active and strong draught the flue must be wide and the chimney large and high. The section of the flue should be from one-sixth to one-fourth that of the fireplace. Defective draught very often arises from the bad arrangement of the flue, for when the draught holes from several furnaces open into a common conduit, the currents, being continued beyond their orifices, modify each other. In a laboratory with which the author was acquainted, eight wind furnaces were connected with one horizontal flue, each opening into it at right angles, the chimney being at one end of the flue. Those near the stack drew fairly well, but in the farther ones the draught was so feeble that only a low temperature could be maintained, the products from one furnace acting as a damper on the next. Such an arrangement might be remedied by building brickwork as shown in Fig. 2, so as to divert the separate currents into one horizontal stream.

In the laboratory of the Birmingham Municipal Technical School, eight small wind furnaces and two full-sized casting furnaces are connected with one chimney, the flues, which were designed by Mr. Frederick Martin of the firm of Messrs. Martin & Chamberlain, Birmingham, being admirably adapted for producing an equally high temperature in each of the similar furnaces, and acting as well as if each were connected with a separate chimney. The arrangement is shown in plan and elevation (Figs. 3 and 4).

§ 11. Another essential structure connected with a

wind furnace is the stack or chimney, which is used for creating a draught and for carrying off the products of combustion. Now if the chimney be connected with several furnaces having an arrangement of flues as in Fig. 2 so as to produce a current in one direction, a single opening will be sufficient; but if furnaces are arranged on each side of the stalk, and the flues open into it at right angles, the shaft must be divided for a certain distance so as to divert the two streams into one vertical direction, as shown in the accompanying figure (Fig. 5), otherwise they will interfere with each other and check the draught.

The chimneys of the Birmingham laboratory are 70 ft. high, and built with double channels, as seen by the

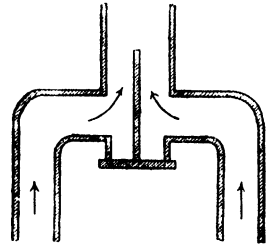
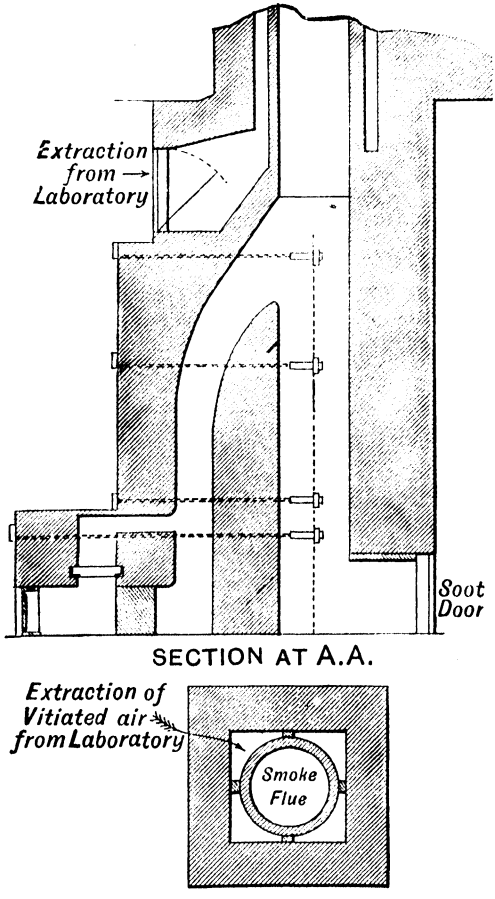


Fig. 5.

plan (Fig. 6) and section (Fig. 7). The smoke flue A is circular, built with fireclay pipes, 1 foot 8 inches internal diameter, and surrounding this is a rectangular space for extracting the vitiated air from the laboratory. Into this space the pipes from the fume chambers also discharge the vapours produced from the various operations conducted therein.

§ 12. Another appliance indispensable to a metallurgical laboratory is that known as a "Muffle" furnace, which is used chiefly for operations requiring the passage of a current of air, as in roasting and cupellation; its special

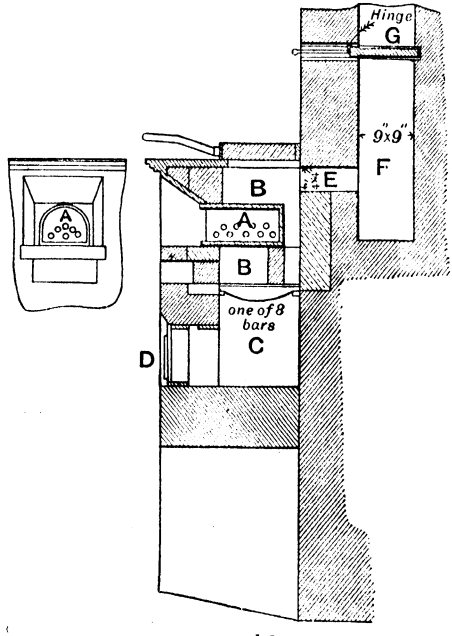
feature consisting of a device for isolating the materials operated upon, from both the fuel and the products of



Figs. 6 and 7.

combustion. The muffle proper is a ⌂ shaped fireclay vessel closed at one end, and fixed in such a manner that

its back and sides can be surrounded by the flame. It is perforated at the sides with a number of holes through which the air is drawn, the gaseous products passing into the flue. Fig 8 shows a vertical section through a muffle furnace. A is the muffle, B B the fireplace, C the ashpit, D the door of the ashpit, fitted with a register for opening or closing, E the draught hole, F the flue leading to the chimney, G the movable damper to regulate the draught. A front view of the muffle opening is seen in figure 8A.



Figs. 8 and 8A.

§ 13. *Gas Furnaces.*

The use of gas instead of solid fuel has many advantages to recommend it, the chief drawback being the great cost where illuminating gas is burned, as such fur-

naces are useless for metallurgical purposes without a good pressure and a large supply pipe. When this is secured, the muffle type will be found very convenient for laboratory use; but the air furnace burning coke is preferable to a gas furnace for ordinary crucible work.

When coal gas is used as a source of heat, the combustion should be as complete as possible, so as to prevent smoke and to obtain the maximum temperature. This is secured by using a burner on the Bunsen principle, and surrounding the flame with a jacket of fireclay or other refractory and non-conducting substance.

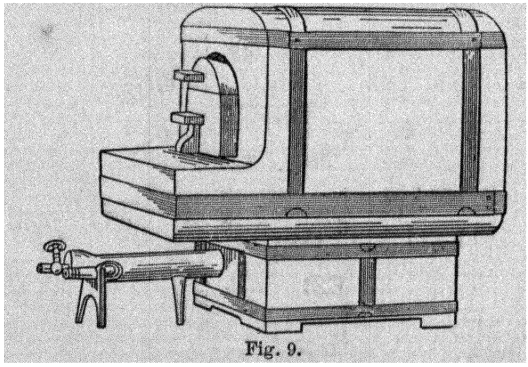


Fig. 9.

Perhaps the most successful worker in this direction is Mr. Thomas Fletcher of Warrington, several of whose furnaces have been in use in the Birmingham laboratory for some years.

An illustration of one of Fletcher's muffle furnaces is given in Fig. 9, which represents an external viewarranged for a "Blast" so as to produce a very elevated temperature. When worked by draught, the gas supply tap must be large and clear, so as to give as great a pressure of gas as possible at the burner nozzle. The india-rubber tubing must be smooth inside, the tubing made on wire not being suitable. If the gas supply is insufficient, the burner plate will become red hot. It is very important

that a light should be put to the burner before turning

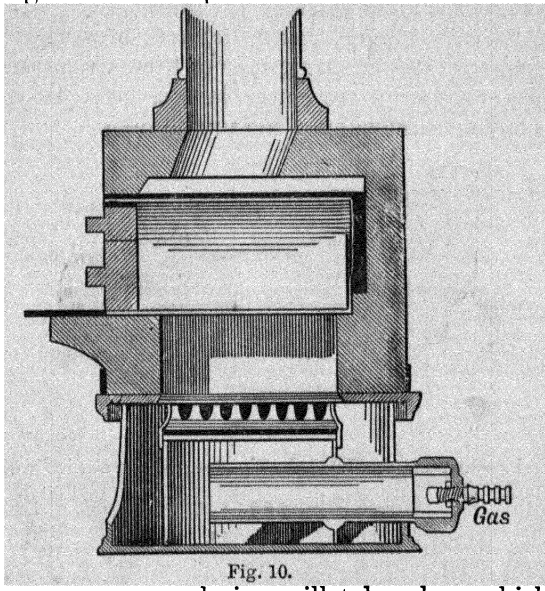


Fig. 10.

on the gas, or an explosion will take place which may

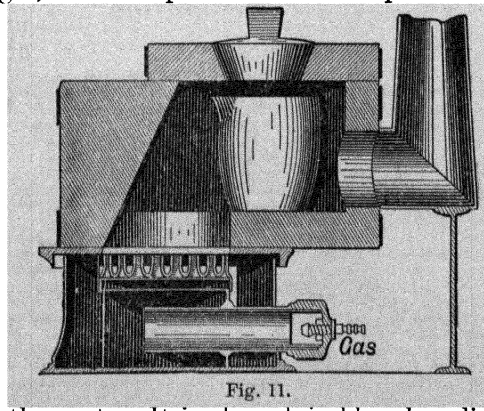


Fig. 11.

damage the parts. It is also advisable when lighting, to

cover the air opening round the gas entrance, to prevent the flame descending through the gauze.

Fig. 10 is a draught muffle furnace showing internal arrangement. Where a number of these are arranged in a laboratory, it is more convenient to have the gas entrance on the same side as the muffle door.

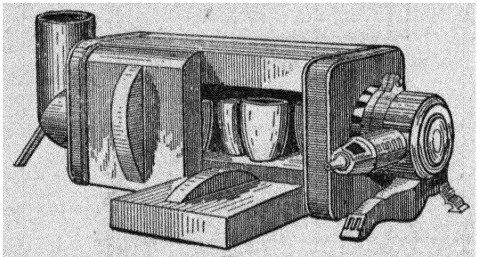


Fig. 12.

Fig. 11 represents Fletcher's draught crucible furnace to which the same remarks apply as to the muffle furnace.

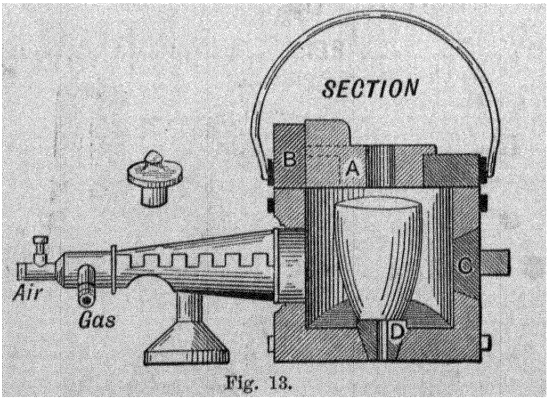


Fig. 13.

Fig. 12 shows Fletcher's reverberatory furnace for crucibles, muffles, cupels, etc. It is stated that one of these furnaces will do most of the work of an ordinary

laboratory. They work with a chimney draught to about the fusing point of silver, and with a blast, to that of cast iron. The furnace can be made to take two muffles, or one muffle and crucibles at the same time. The opening may be at the side or on the top. The burner is at one end out of the way of injury in the case of accident to a crucible, etc.

In special cases where it is desirable to raise metalliferous matter rapidly to a high temperature in a crucible, Fletcher's injector furnace (Fig. 13) is very useful, the blast being obtained from the foot bellows (Fig. 14). With $\frac{1}{2}$ inch gas pipe and the smallest foot blower, Mr. Fletcher claims for this furnace that a crucible full of cast steel may be melted in it in 7 minutes, tool steel in 12 minutes, and nickel in 22 minutes, beginning with all cold.

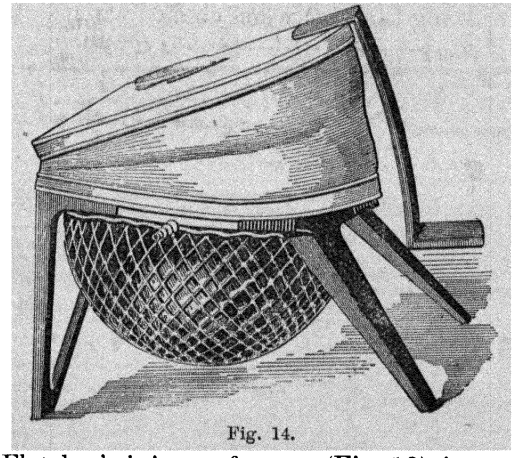


Fig. 14.

To adjust a new furnace to its highest power, put the nozzle of the burner tightly up against the hole in the side of the casing, turn on the full gas supply, light the gas in the furnace, and commence blowing before putting on the cover of furnace, with the airway full open.

If when the cover is replaced, the flame comes out of the hole in the cover about 2 inches, the adjustment is right. If the flame is longer, enlarge the hole in the air jet until the proper flame is obtained, or reduce the gas supply. Before stopping the blower, draw the burner back from the hole.

§ 14. *Furnace appliances.*

Stout iron pokers 3 feet long are used for stirring the fire and opening the bars when choked with clinkers and

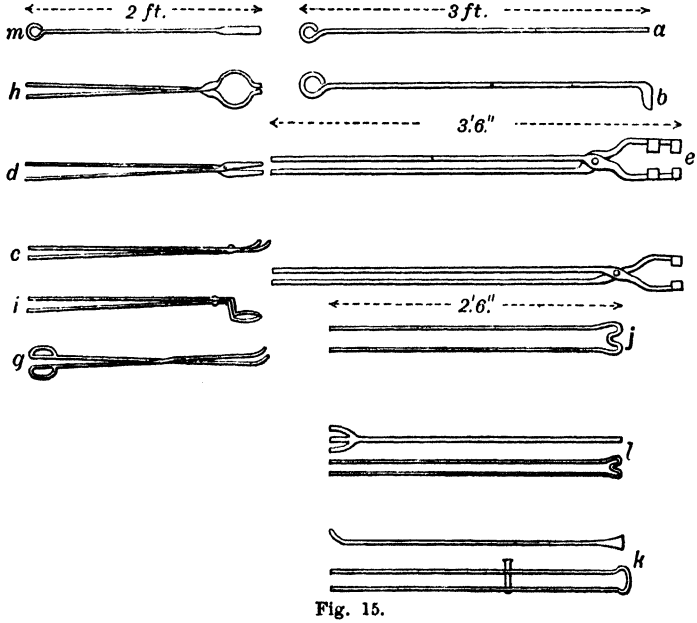


Fig. 15.

ashes (Fig. 15 *a*). For the purpose of cleaning the bars from underneath a poker bent at the end is advisable (Fig. 15 *b*). Each furnace should be provided with a pair of tongs having bent jaws (Fig. 15 *c*), and one pair with straight jaws (Fig. 15 *d*). For large crucibles the

basket tongs (Fig. 15 *e* and *f*) are used. The scissor tongs (Fig. 15 *g*) will often be found useful for packing coke round a pot. The forms (Fig. 15 *h* and *i*) are also occasionally required.

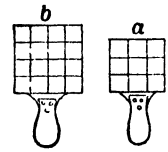


Fig. 16 *a* and *b*.

For use with a muffle the shape Fig. 15 *k* is employed, and those in Fig. 15 *l* for introducing and removing scorifiers. Another form shown in Fig. 15 *j* is generally used for

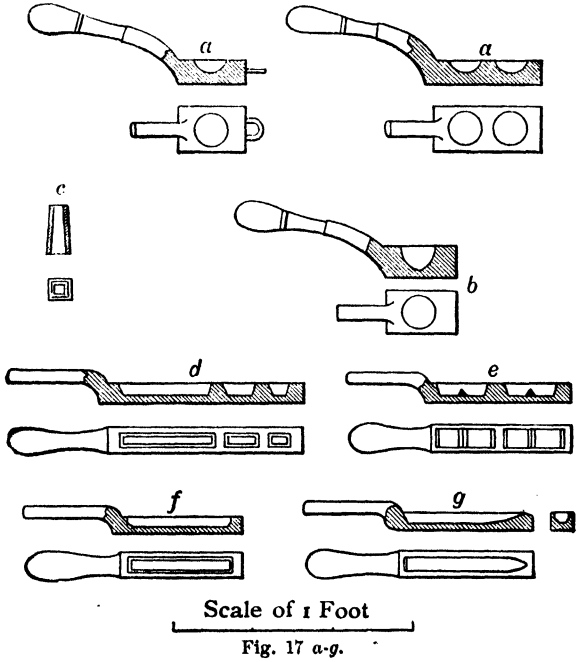


Fig. 17 *a-g*.

manipulating cupels. Fig. 15 *m* represents a stirring rod used in roasting operations.

For holding cupels in carrying to or from the muffle, sheet iron trays divided into nine or sixteen compartments are most useful (Fig. 16 *a* and *b*).

Moulds for receiving the contents of crucibles, scorifiers, etc., are of various shapes. Some are hemispherical, some conical, some pyramidal, others rectangular (Fig. 17 *a–g*). When the metal requires to be cast in a thin flat sheet, a closed mould, the parts of which are detachable, and can be regulated for different sizes, is used (Fig. 17 *h* and *i*).

Fig. 18 represents a copper scoop with wooden handle used for charging crucibles; it should always be kept smooth and clean.

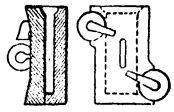


Fig. 17 *h* and *i*.

§ 15. *General Apparatus.*

(*a*) Pestles and mortars made of cast-iron of various sizes are required, and should be sufficiently deep to prevent loss when materials are being crushed in them. The shape shown in Fig. 19 is perhaps the most useful, although for some purposes the simple bowl shape is more convenient (Fig. 20). A Wedgwood ware pestle and mortar should be included among the set of apparatus required for each individual. When the material requires to be reduced to an impalpable powder, the agate mortar and pestle is called into requisition. When small portions of metallic or mineral matter of a very hard nature are to be reduced to a fine state of division, or when it is desirable that no portion should be lost, a steel mortar of the shape shown in Fig. 21 is most useful. *a* is the pestle which fits perfectly into the cylinder *b* which has a rim around the bottom outer edge by which means it is held firm by the cap *c* containing a hole whose diameter slightly exceeds the outside diameter of the cylinder which it encloses. This cap

Fig. 18.

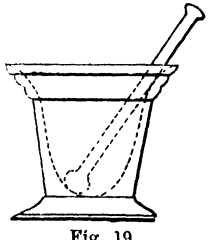


Fig. 19.

Fig. 20.

screws on to the base *d*, which is made of hardened steel, surrounded by a gun-metal rim screwed to fit the cap *c*.

(*b*) The operation of sifting is advantageous in ensuring that uniform fineness of the particles of a substance which is so essential to effect the solution of difficultly soluble bodies. This sameness of size also causes regularity in working, all portions being acted upon to the same degree when fused in a crucible with various fluxes. Also by the aid of the sieve, a rough mechanical separation of the gangue from the metalliferous matter may be effected

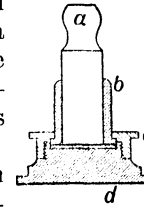


Fig. 21.

Two kinds of sieves are used. The open sieve is a wooden cylinder with a meshwork of brass wire gauze stretched over one end (Fig. 22). In the coarser ones iron wire is used. The box sieve is used when it is desirable to prevent loss. It consists of three parts: the sieve, a cover which fits tightly on the top, and a similar receptacle for receiving the sifted powder.

Fig. 22.

(*c*) *Washing and Vanning.*—Many ores contain small quantities of mineral matter associated with a large amount of earthy matter, such as tin stone, native gold, silver, etc., and when such materials are crushed to powder, the lighter portions may be washed away by running water, or made to float to the top when agitated in a vessel with water; the different constituents arranging themselves according to their specific gravities provided all the particles are of uniform size. For the purposes of the assayer, an iron

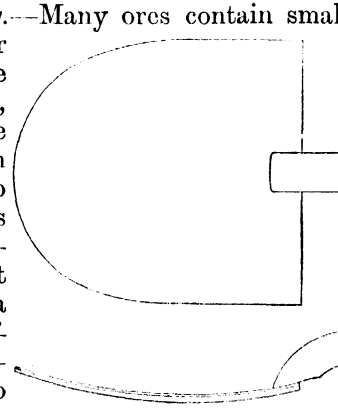


Fig. 23.

vanning shovel, or copper ladle renders useful service (Figs. 23 and 24). The powdered material is mixed with water, and a circular shaking motion is given to the tool, causing the separation mentioned above. The excess of water is then poured off, and the same motion imparted with the addition of a peculiar twist at each revolution, by which the heavier portions are thrown to the outer edge at the upper end, while the lighter non-metallic portions flow to the front and may occasionally be washed away by fresh water being added from a tap.

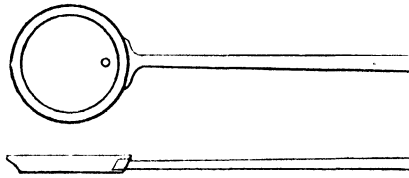


Fig. 24.

(*d*) One or two strong rectangular boxes, 13″ × 9″ × 9″, are useful for granulating easily fusible metals such as lead and tin. The inside is blackleaded, and the metal, when just on the point of solidifying, is poured in and subjected to a vigorous shaking, by which means it is broken up into fine powder.

(*e*) Two circular blocks of some hard wood having an iron band near top, 2 feet 6 inches high, and 16 inches in diameter, will be found very useful for odd work. One of these may be capped with a circular block of iron of the same diameter and 3 inches thick, which will answer the purpose of an anvil in many cases.

(*f*) Besides the range of students' work-benches already mentioned, a rough bench with a stout top about 3 inches thick for all such operations as pounding, sifting, crucible and cupel making, etc., is necessary. To one of the supports should be fixed a strong vice for general use. A pair of large vice shears for cutting thick pieces of metal is also indispensable.

(*g*) A Rolling Mill of the ordinary jeweller's kind is required for rolling out metals, such as lead for cupellation purposes, or metals from which a portion has to be taken for analysis. A pair of 2-inch rolls will be found a convenient size, connected with handles and fixed on an iron or wooden stand bolted to the floor (Fig. 25).

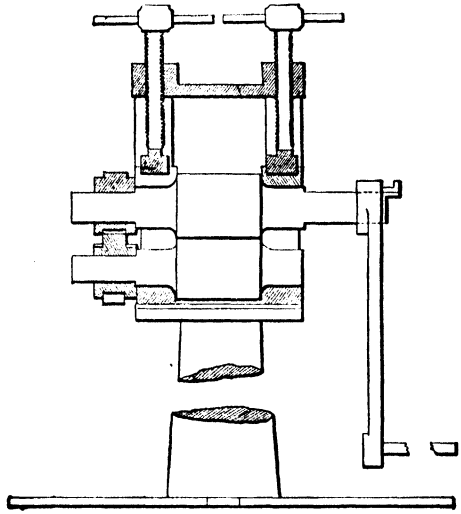


Fig. 25.

(*h*) A steel anvil should be fixed to a small but stout support for flattening buttons of gold and silver previous to rolling. This must be covered up when not in use and kept bright. In connection with this a hammer is used, weighing about 7 lbs., with a slightly convex face and rounded edges, to be also kept smooth and bright by enclosing in wash-leather when not in use.

§ 16. A fume chamber should be provided for every six students engaged in wet assaying, with a ring gas burner

at the origin of the flue pipe to create sufficient draught to remove obnoxious fumes. In the Birmingham laboratory the pipes from the different chambers are connected with an annular space (Fig. 6) which envelopes the central stack through which the products of combustion from the furnaces pass.

A very convenient method of utilizing a fume chamber where several flasks have to be heated at a time, is to provide an iron plate about 18 inches square, standing on four legs, and having two large Bunsen burners fixed underneath to supply the requisite heat.

§ 17. *Balances.*—Nothing in a laboratory is more liable to be deranged by dirt and acid fumes than chemical balances, so that a separate room for them is necessary, in which all the weighings should be made. This room, if possible, should be *outside* the laboratory.

Three kinds of balances are required in a metallurgical laboratory.

(1) A delicate balance capable of carrying 1000 grains and turning distinctly with $\frac{1}{1000}$ of a grain. Such an instrument is described in Watt's Dictionary as follows:

"The balance (Fig. 26) consists of a metal beam with two almost equal and similar arms suspended near its centre on a pivot, the weights to be compared are also suspended from two pivots at nearly equal distances from the central pivot. In its most perfect form it consists of a perforated brass beam cast in a single piece, combining great strength and perfect inflexibility, with comparatively small weight. It is suspended at the centre on a knife edge of agate about an inch long, and turns on a single polished plane of agate fixed on a projecting brass support, which enters a perforation of the beam and does not impede its motion. The agate knife edge is firmly embedded in a wedge-shaped piece of brass, and being once adjusted at right angles to the plane of the beam, is then permanently fixed. At each end of the

beam is a smaller agate prism with its edge uppermost, fixed in a brass setting which is capable of a little lateral movement, but slides on a brass plane in such a manner that the two extreme edges and the centre edge are all appreciably in one plane. The extreme edges may be moved to and from the centre edge by little adjusting screws, and fixed in the desired position by two clamping screws."

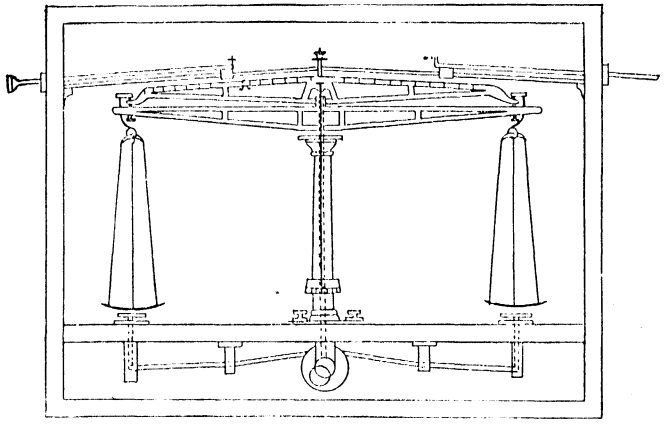


Fig. 26.

"Upon these extreme edges are balanced two agate planes from which by the bent wire, and a series of hooks and light wires, the pans are suspended."

"Except, however, when a weighing is being actually made, the agate planes and edges are never in contact, but the beam and pan suspensions are supported by a frame or movement having in the centre two Y's which catch projecting pins close to the centre edge, and lift the beam about $\frac{1}{100}$ of an inch off the plane, while steel points (shown in dotted outline, Fig. 27) entering hollows in the lower surface of the pan suspensions likewise raise these planes off the edges and retain them in

exact positions for the new experiment. The movement of the brass frame is governed by a rod descending through the pillar of the balance and resting on a single

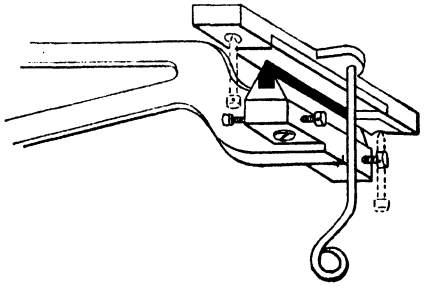


Fig. 27.

eccentric, by the turning of which it is gradually raised or lowered."

"Most of the weight of the beam and frame is usually borne by a spiral spring in the interior of the column. An index moving over an ivory scale, 1 inch long, divided into twenty parts, indicates the movement of the beam. The index should, of course, point to the central division. The balance is enclosed in a glass case with convenient windows. Two spirit levels, or a circular level and levelling screws are attached, by which the whole instrument must be adjusted to horizontality. Above the centre of the beam is a small weight called the gravity bob, which being screwed up or down regulates the stability of the balance, while a small vane being turned to the right or left adjusts the beam to equilibrium. In the figure, too, will be seen an arrangement of rods by which a small rider weight may be placed on any part of the beam, the balance case remaining closed."

(2) A rough assay balance, which should take 1000 grains in each pan, and turn with $\frac{1}{10}$ of a grain, suitable for elementary work, is shown in Fig. 28. The

pillar is fixed on a mahogany stand having a drawer containing the weights to be used from 1000 grains to $\frac{1}{10}$ of a grain. It will be more convenient and durable if the pans are of brass and movable.

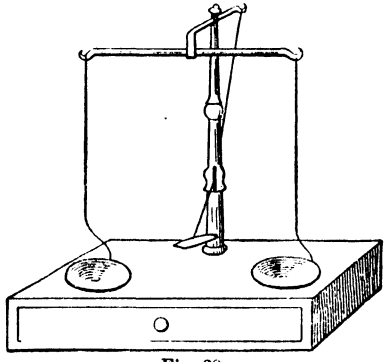


Fig. 28.

(3) A balance similar to the above for heavier weights capable of carrying 7 lbs. and turning readily with a grain, is also necessary.

REFRACTORY MATERIALS AND VESSELS.

§ 18. *Crucibles, etc.*—(*a*) Earthen crucibles are made of fire-clay mixed with sand, burnt clay, or other infusible matter, so as to counteract the tendency which raw clay possesses of shrinking when heated. The bodies thus mixed with the clay expand, or do not contract on heating, having been already shrunk when burnt, and therefore act in an opposite manner to the clay. Such a composition must be able to resist a high temperature without softening, must not be friable when hot, and be capable of withstanding sudden changes of temperature without cracking, as, for example, when a white hot crucible is brought out of a furnace into cold air.

Some crucibles are required to resist the corrosive action of metallic oxides in the material operated upon, and in the ashes of the fuel, so that a crucible should be selected which is best adapted to the special purpose to which it is to be applied.

The component parts of crucibles are first crushed to a fine powder and passed through a sieve, the fineness of whose meshes will vary with the desired fineness of the grain in the pot, the plasticity being closely connected with the fineness of the particles, at any rate for small crucibles this closeness of grain appears to be indispensable; then the fine powder is mixed with water and kneaded to the right consistence for use. The best results are obtained by using a mixture of different fire-clays, the most infusible being those containing the largest amount of silica and the minimum of oxides of iron and lime. The presence of potash or soda in small quantity sensibly increases the fusibility, but they act advantageously in soldering the particles together. Iron pyrites, which is frequently disseminated through clays, especially those from the coal measures, is perhaps the most injurious constituent. A crucible made from such clay will become indented with small cavities, and even holes, when exposed to a prolonged high temperature. It follows then that the most refractory crucibles are those made from pure clays, the nearest approach to which is presented by some French clays.

(*b*) The fitness of a clay for making crucibles may be determined by moulding a portion into the shape of a prism or any form containing sharp edges, carefully drying, baking, and exposing to a high temperature in a covered crucible for some time. If very refractory, the test will show no signs of fusion. If the edges are rounded it is a proof of incipient fusion, and if melted, the clay is useless.

(*c*) Clay vessels of all kinds may be tested to ascertain their power of resisting corrosion by melting in them a

mixture of litharge, red oxide of copper, and borax, and noticing the time this mixture will take to permeate them. Those which resist this destructive action the longest will of course be the best. Most crucibles are by this means eaten away irregularly, showing the necessity of uniformity of grain to resist perforation.

(*d*) All crucibles should be cautiously annealed before use by placing them in an inverted position over the furnace, otherwise they are liable to split when plunged into a red hot fire. I have noticed this tendency with the best plumbago crucibles.

(*e*) Small crucibles may be made by hand in the laboratory by using a mould as shown in accompanying Fig. 29. "*a* is a short, hollow, slightly conical piece, open at both ends, made of gun metal; *bb* are short pins of iron inserted one on each side of *a*, near the bottom or narrower end; *c* is a round block of wood, in the centre of which, on the upper surface, is a circular cavity large enough to receive the lower end of *a*, including the projecting pins *bb*; through the middle of this cavity is a hole *h*, and upon the bottom lies a disc of gun metal, as seen in Fig. 29, which also has a hole in the centre, of the same size as *h*; around the edge of this cavity is screwed a flat ring of brass *dd*, which projects inwards to the extent shown by the dotted line (Fig. 30); *cc* are notches to allow the pins, *bb*, to pass through, so that *a* may be turned in the position seen in Fig. 30, when the pins, *bb*, will hold it firmly under the projecting edge of the brass ring; *f* is a wooden circular plug, in the bottom of which is fixed the iron pin *g*; by means of this pin the plug is kept upright exactly in the centre of

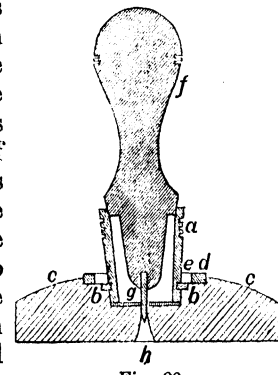
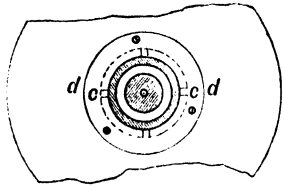


Fig. 29.

the mould. Fig. 31 is another wooden plug without a pin, but having an oblique groove *i*; the inner surface of *a* is very slightly oiled, and also the outer surface of *f* where it passes into *a*—*a* being adjusted as shown in Fig. 30. A small lump of well-tempered clay is put into *a*, when the plug *f* is forced down and turned round; the excess of clay escapes from the upper edge of *a*; *f* is now withdrawn and a small bit of clay dropped in, when *f'* (Fig. 31) is forced down and turned round and round, the excess of clay escaping by the groove *i*; *f'* is then taken out and *a* with the contained crucible detached."



Scale of 6 Inches

Fig. 30.

(*f*) "The covers are made with the mould (Fig. 32). *a* is a cylindrical piece of wood upon which is placed a cylinder of brass *bb*, perforated with several holes *cc*, etc. *d*, a cylindrical plug of wood hollowed out at the bottom. This plug fits into the brass cylinder *bb*, upon the top of which it is supported by a shoulder, so as to leave a space *e*. A small lump of clay being put into the cylinder, the plug *d* is pressed down and turned round, when a cover is moulded in the space *e*, the excess of clay being expelled through the holes *cc*, etc." (Percy's *Metallurgy*, pp. 228-9.)

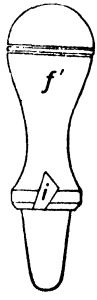


Fig. 31.

(*g*) Plumbago or black lead pots are made from varying proportions of fire-clay mixed with powdered graphite or coke dust. Good graphite is neither altered nor fused by exposure to the highest temperatures (air being absent), so that it is an admirable substance for crucibles. The graphite is powdered, sifted, and mixed with sufficient clay to render it plastic. Good plumbago crucibles, after a careful preliminary annealing, withstand the

greatest changes of temperature without cracking, and may be used many times in succession.

(*h*) When an ordinary crucible requires to be protected from the corrosive action of metallic oxides, or when small amounts of metallic compounds have to be reduced, the inside is coated with a lining of charcoal. This is done by first mixing the charcoal with sufficient starch paste, or treacle to make it adhere when pressed. The crucible is then loosely filled with the brasque, and a cavity of the desired size made by boring with a triangular-shaped piece of wood, and then made smooth with a round elongated wooden tool, whose size and shape is apportioned to the capacity of the cavity desired. (Fig. 33 *a*, *b*.) The brasqued crucible is shown in Fig. 34.

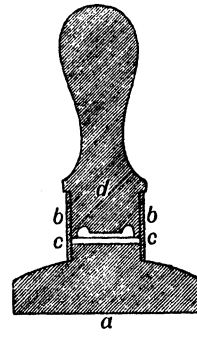


Fig. 32.

The atmosphere in such a crucible will always be reducing at an elevated temperature, and in some cases a compound may be reduced without any additional carbon.

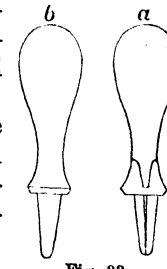


Fig. 33.

§ 19. The crucibles used in a metallurgical laboratory may be conveniently classified under the following heads :—

Fig. 34.

(*a*) *London Crucibles.*—These are round in shape, of a reddish brown colour, close in grain, but liable to crack with sudden changes of temperature. They resist the corrosive action of metallic oxides remarkably well. (Fig. 35 *a*–*d*.)

(*b*) *Cornish Crucibles.*—These are also round and used in two sizes; they are course in grain and of a greyish white colour, fairly refractory, but very liable to be corroded with metallic oxides. They are chiefly used in copper assaying. (Fig. 36 *a*, *b*.)

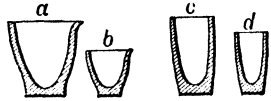


Fig. 35.

Fig. 36.

(*c*) *Hessian Crucibles.*—This kind is triangular in shape, so that the metal may be readily poured from each edge, fairly refractory, not very liable to corrosion with oxides, but very prone to crack with sudden changes of temperature, and to break when held with the tongs. (Fig. 37.)

(*d*) *French Crucibles.*—The quality of these is excellent, being smooth and carefully made, though somewhat brittle; they withstand high temperatures without softening, and resist corrosion by molten litharge exceedingly well. They are used in melting such metals as gold, silver, copper, etc. (Fig. 38 *a*, *b*.)

Fig. 37.

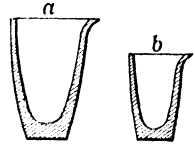


Fig. 38.

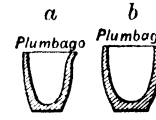


Fig. 39.

(*e*) *Plumbago Crucibles.*—These pots resist sudden changes of temperature, are highly refractory, and the least corroded by metallic oxides, but they are inconvenient when a reducing atmosphere is not desired. (Fig. 39 *a*, *b*.) To enable them better to withstand great changes of temperature, they are coated with a mixture of borax and lime, dried, and then another coating of slaked lime and linseed oil is brushed on.

(*f*) *Iron Crucibles.*—These are employed in assaying certain selenides and sulphides, such as galena, etc.

(*g*) *Lime Crucibles.*—Deville first introduced the use of crucibles cut out of solid blocks of pure lime, so as to avoid the introduction of carbon and silicon into metals during fusion, with very satisfactory results, the bodies melted therein, such as manganese, iron, nickel, etc., being purer, more malleable, and more ductile than when fused in clay crucibles. As large blocks of pure lime are difficult to obtain, Mr. David Forbes introduced the following plan :—

A clay crucible of somewhat larger dimensions than the desired lime one is filled with lamp black and well pressed down. The central portion is then removed with a knife, leaving a thin lining firmly adhering to the sides, which is then rubbed smooth with a glass rod. The hole is then filled with finely powdered lime, and a cavity made by cutting away the inner portion as before, leaving a shell of lime which becomes firm and compact after heating. The layer of carbon prevents it acting on the outer crucible.

(*h*) *Alumina Crucibles.*—Pure alumina is infusible at the highest furnace temperatures, will not unite with bases to form readily fusible compounds, and is eminently adapted for lining crucibles used for melting metals. But pure alumina is rare, so that other means have been devised for obtaining it. The following method is described in Mitchell's Assaying, page 12 :—"Ammonia alum is ignited at a white heat, when it leaves alumina in a dense compact form : this is then finely powdered. To a solution of another portion of ammonia alum in water, ammonia is added, when alumina is precipitated in a gelatinous state : this is washed till free from sulphate of ammonia. The alumina is then mixed with water and worked up

paste, the precipitated gelatinous alumina being kneaded in from time to time; this gives coherency, and when sufficient has been added (which may be ascertained experimentally) the mass may be moulded into shape. Such crucibles require careful annealing, and are infusible at the highest furnace temperatures."

(*i*) *Platinum Crucibles.*—These crucibles are indispensable in wet assaying where speed and accuracy are desired, yet they require great care in using, as many substances will corrode and otherwise injure them. They cannot be used for any substances containing easily reducible oxides, such as those of silver, lead, etc. Many oxides, sulphides, and phosphides also affect them, as does the naked flame of a Bunsen burner. They should be heated preferably on a platinum triangle, although pipe-clay is a good substitute. Brass and iron tongs, unless perfectly clean, will leave a dark stain where they touch when red hot, so that the tongs should be capped with platinum.

Platinum crucibles should be cleaned after each operation by scouring them with wet sea sand and a little dilute hydrochloric acid. Stains may often be removed by heating with acid sulphate of potassium or borax, then washing and scouring with sea sand, the particles of which, not being sharp, do not scratch like ordinary sand.

§ 20. *Roasting dishes* are small shallow vessels made of fire-clay, used for roasting or calcining ores, regulus, speise, etc., also for oxidising metals in a muffle. Fig. 40.

Fig. 40.

21. *Scorifiers* are small cup like fire-clay vessels of an acid character, the silica of which readily unites with metallic oxides forming fusible scoriae. These vessels are largely employed ging-off metals like tin and antimony, in silver

and gold ores, and compounds which cannot be perfectly removed by direct cupellation. Fig. 41.

§ 22. *Cupels* are vessels somewhat resembling scorifiers in shape, made of boneash, which has the property of absorbing molten oxide of lead; the latter dissolves other oxides which may be present, carrying them with it into the pores of the cupel. Base metals may thus be separated from the unoxidisable metals by a prolonged heating of the alloy with an excess of lead in the cavity of a cupel. Fig. 42 *a–c*.

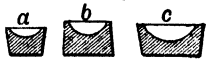


Fig. 42 *a-c*.

To make cupels the boneash must be in fine powder, otherwise it requires to be passed through the meshes of a fine sieve to remove any lumps. It is then moistened with sufficient water to make it adhere firmly when tightly pressed in the hand.

The apparatus in which the cupels are made consists of two parts. The mould in which the boneash is placed and the plug which produces the desired cavity and presses the boneash into a compact vessel. The latter is removed, dried, and is then ready for use. Fig. 43 *a*, *b*.

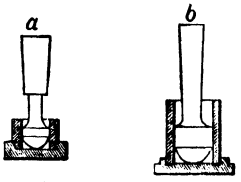


Fig. 43 *a* and *b*.

The wood tray (Fig. 44) is used for mixing the bone-

Fig. 44.

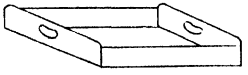


Fig. 45.

ash, and the iron tray (Fig. 45) for holding cupels whi,s drying.

METALS, FLUXES, REDUCING AGENTS, RE-AGENTS, ETC., USED IN A METALLURGICAL LABORATORY.

§ 23. The following bodies should be provided for the use of students, but they need not be of a high degree of purity. Re-agents for analysis will be described in another part.

Fluxes may act as true solvents, and probably in many slags true solution occurs. More generally a flux is used for the purpose of forming a fusible compound with the earthy constituents of an ore, or to take up impurities from metals after oxidation. The gangue or earthy matter of an ore is usually a silicate of lime, alumina, magnesia, or oxide of iron; or a carbonate of lime and magnesia. Silica, and the silicates of lime, alumina, and magnesia are practically infusible when alone, but the addition of lime, or oxide of iron, or an alkali to silicate of alumina causes the formation of a fusible double silicate. Similarly the addition of oxide of iron or alumina or alkali to silicate of lime renders the latter fusible. Thus a body which is infusible in itself may be used as a flux to make another otherwise infusible body fusible. Most earthy bodies are either acid or basic in their properties and therefore require a flux of opposite properties to themselves, that is, an acid gangue requires a basic flux and *vice versa*. For operations performed in clay crucibles it is advisable not to form too basic a slag, as it rapidly corrodes them, since they are made of fire-clay and silica which unite readily with lime, soda, and most bases. Slags from which metals are to be separated should not be too acid, unless in the case where the metal is already in the metallic state mixed with dross or dirt. In the case when the metal is easily fusible and liable to oxidation or volatilisation, it should be covered with a layer of resin or fat or common salt.

(See § 23, No. 22.) In most cases the fusion of a metal, when reduced from its oxide, should be accompanied with a basic slag, as it is difficult to completely liberate the whole of a metal from acid slags such as borates and silicates. When the object is to separate one metal, say copper, without reducing an unnecessary amount of another, say iron, at the same time, a slag with much borax is an advantage, but it will contain some copper and require to be cleaned. In some cases it is advisable to treat an ore or metalliferous matter so as to form a sulphide first instead of reducing to the metallic state. Such sulphide is termed a "regulus." (See § 59.) It is usually brittle, dark in colour, and crystalline. A regulus is often reduced to metal by strongly heating it with an oxide. (Expt. 178.) Sulphide of iron and some other sulphides formed during an assay will remain diffused through the slag, instead of fusing into a button of regulus, if the slag contain sulphide of sodium and the temperature is not too high. Use is sometimes made of arsenic, in a similar way to that of sulphur, to form an arsenide, which is termed a speise. It is chiefly employed in the metallurgy of nickel, cobalt, and tin, forming brittle and easily fusible compounds.

(1) *Antimony.* Sb. Atomic weight, 120. Specific gravity, 6·75. Melts at 440° C. The commercial metal has a fern-like appearance on its surface, and may contain varying amounts of sulphur, potassium, arsenic, lead iron, and copper. It may be purified from sulphur, iron arsenic, and copper, by fusing with sulphide of antimon and carbonate of soda in a crucible for an hour; fro sulphur and potassium by fusion with nitre. Fineness grain is a test of purity.

(2) *Arsenic.* As. Atomic weight, 75. Specific gr 5·62, vaporises under ordinary conditions without ing. It exists in two forms:—1. The compact va obtained by condensing the metal at a tempera

little below its melting point, so that it solidifies in an atmosphere of its own vapour. It is then white, having a strong lustre and little tendency to oxidise in air below 80° C. even when powdered. 2. When reduced from its oxide by carbon, being mixed with other gases, or when condensed on a cold surface, it is a dark grey crystalline substance less dense than the former variety, and readily oxidisable. When heated it emits an odour like garlic, and in presence of air or oxygen forms As_2O_3.

(3) *Aluminium.* Al. Atomic weight, 27. Specific gravity, 2·6. It is a white metal with a faint tinge of blue, takes a fine polish, and may be frosted like silver by plunging into a weak solution of soda, well washing, and digesting in strong nitric acid. It is very malleable and ductile, as soft as silver, and highly sonorous. Its melting point is 625° C., but it is not volatile when heated out of contact with air; it exhibits a crystalline structure when heated and slowly cooled; does not oxidise in air even at a red heat; does not combine with sulphur, and not blackened with sulphuretted hydrogen; is not soluble in dilute nitric or sulphuric acid, but soluble in hydrochloric acid. It may be fused with nitre without oxidising, so that impurities may be removed by this means. Its tensile strength in the cast state is 7 tons per square inch, but this may be considerably increased by cold hammering. It unites with other metals to form valuable alloys.

(4) *Bismuth.* Bi. Atomic weight, 207·5. Specific gravity, 9·80, but this is "diminished" by pressure. Melts at 268° C. This metal is greyish white with a reddish tinge, a bright lustre, not sensibly oxidised at ordinary temperatures, but when heated in air burns with a bluish flame emitting yellow fumes. When pure, crystallises more readily than any other metal; is

more dense in the liquid than in the solid form; is the most diamagnetic of all metals, and its best solvent is nitric acid. When mixed with lead and tin it forms fusible alloys.

(5) *Gold.* Au. Atomic weight, 196·2. Specific gravity, 19·5. Melts at about 1045° C. It possesses a characteristic yellow colour; is the most malleable and ductile of metals; has high conductive power for heat and electricity; is unaffected by air; is nearly as soft as lead; is a feeble base, and therefore readily separated from its states of combination; its best solvent is moist chlorine, generally obtained by heating the metal with two parts hydrochloric acid and one part nitric acid.

(6) *Iron.* Fe. Atomic weight, 56. Specific gravity, 7·8. Melts at above 1600° C. when pure. The pure metal is seldom required, but may be obtained by the electrolysis of a solution of its chloride, or in the dry way by melting pianoforte wire with oxide of iron and pure glass in a lime crucible. Hoop-iron, filings, turnings, and the purest kind of soft iron wire, are the forms most useful in a metallurgical laboratory. It should be soft, malleable, tenacious, practically infusible, but should soften at a white heat; should not be sensibly hardened when made red hot and plunged into cold water.

(7) *Steel* is iron containing varying proportions of from 0·15 to 1·8 per cent. of carbon and usually some manganese. It may be hardened by sudden cooling from a red heat, the hardness being in proportion to the carbon or other bodies which have a similar effect. It may be permanently magnetised. Its colour is greyish white, of a uniform granular texture, very close grained, and whiter when hardened than when soft; has very high tenacity: melts at about 1300° to 1500° C.; and is less oxidisable than soft iron at ordinary temperatures.

(8) *Cast iron* is a variety with a greater proportion of carbon and other bodies than is contained in steel. Three kinds are known in commerce, viz. :—"Grey," in which the carbon is chiefly free ; "White," in which the carbon is for the most part combined ; and "Mottled," which is a combination of the other two. A white variety is also used, combined with manganese, called ferro-manganese ; and with phosphorus, called ferro-phosphorus, etc. ; the effect being to harden, and to render it more fusible and brittle. A grey variety of pig-iron, containing about 4 per cent. of silicon, is used to produce softness in other brands of pig-iron, as the silicon induces the separation of carbon in the graphitic form. Cast-iron melts at 1100° to 1300° C.

(9) *Lead.* Atomic weight, 206·4. Symbol Pb. Specific gravity, 11·45. Melting point, 325° C. The commercial variety is sufficiently pure for laboratory purposes, except for exact assays of gold and silver. It is a bluish grey, soft, malleable metal, with feeble tenacity, tough, and may be welded by pressure. The property of viscous flow is well exhibited by lead, so that it may be forced through perforations, as in making piping and bullets. It enters into the composition of many useful alloys.

(10) *Magnesium.* Mg. Atomic weight, 24. Specific gravity 1·75. It is a malleable white metal, oxidising in moist air ; melts at 750° C., and volatilises like zinc. When ignited in air it burns with a bright light, forming magnesium oxide MgO. It is a strong base, and replaces zinc, iron, etc., from their solutions.

(11) *Mercury.* Hg. Atomic weight, 200. Specific gravity, 13·6. It is a white metal, liquid at the ordinary temperature ; freezes at – 39°·44 C., forming a tin-white ductile mass ; is not affected by air unless heated ; dis-

solves in nitric acid; boils at 350° C.; combines with silver, gold, tin, lead, bismuth, cadmium, zinc, but not so readily with copper and iron. The commercial metal often contains zinc, bismuth, lead, antimony, and tin. When pure, a globule of the metal will roll down a slight incline as a sphere; if impure, the particle elongates somewhat; also, when shaken in an open flask will tarnish after a time. It is used in the extraction of gold and silver.

(12) *Nickel.* Ni. Atomic weight, 58·6. Specific gravity, 8·3. Little more fusible than iron. It is a white, malleable, ductile, tenacious metal; welds like iron; does not easily oxidise; combines with sulphur to form regulus, and with arsenic to form speise. May be reduced from its oxide by carbon, carbonic oxide, and hydrogen, and takes up varying proportions of carbon like iron.

(13) *Platinum.* Pt. Atomic weight, 194·3. Specific gravity, 21·5. Melts only by aid of the electric current or by means of the oxy-hydrogen blow-pipe at a temperature of 1775° C. It is a white unoxidisable metal, malleable and ductile, very tenacious, softer than silver; an inferior conductor of heat and electricity; soluble in aqua-regia, but when alloyed with much silver it is dissolved by nitric acid, and may thus be separated from gold.

(14) *Silver.* Ag. Atomic weight, 107·6. Specific gravity, 10·5. Melts at 945° C. It is a pure white metal with a brilliant lustre, very malleable and ductile, soft; has considerable tenacity; is the best conductor of heat and electricity; is hardened by alloying with copper; does not oxidise, but mechanically absorbs oxygen when melted, and gives it out again on cooling, this is termed "spitting"; it combines directly with sulphur to form sulphide; is soluble in strong sulphuric and dilute nitric acids, and forms useful alloys with copper, gold, and other metals.

(15) *Tin.* Sn. Atomic weight, 117·4. Specific gravity, 7·3. Melts at 227° C. Commercial tin is seldom pure, the metal being generally associated with arsenic, lead, iron, copper, and occasionally with tungsten, manganese, antimony, zinc, and molybdenum. It is a white metal, with a characteristic smell when warm, and makes a peculiar crackling sound when bent, known as the "cry"; it is malleable, but has low tenacity; does not oxidise at ordinary temperatures.

(16) *Copper.* Cu. Atomic weight, 63·2. Specific gravity, 8·82. Melts at 1050° C. It is red in colour, highly malleable, ductile, tough, and tenacious, not sensibly volatile, and is one of the best conductors of heat and electricity. The common impurities are iron, arsenic, silver, antimony, and cuprous oxide; sometimes bismuth, tin, sulphur, and lead. Of these antimony and bismuth are the most injurious. It is soluble in acids, and forms with many metals useful alloys.

(17) *Zinc.* Zn. Atomic weight, 65. Specific gravity, 7·15. Melts at 415° C. It is a bluish white metal with a bright lustre; commercial zinc is brittle in the cast state with a highly crystalline structure, but becomes malleable at 100° to 150° C., above this point it again becomes brittle; the pure metal is malleable at the ordinary temperature and volatile at a bright red heat. It is soluble in acids and alkalies; is a strong base, and displaces most metals from their solutions. The chief impurities in commercial zinc are lead, iron, arsenic, and sometimes silver. Its chief alloys are formed with copper.

(18) *Carbon.* C. Atomic weight, 12. This substance in its different forms, more or less pure, is largely employed as a reducing agent, chiefly as charcoal and anthracite. In the form of coke and charcoal it is used as a fuel, and as graphite in making crucibles.

(19) *Phosphorus.* P. Atomic weight, 31. When pure it is transparent and nearly colourless; melts at 44° C.; shows a crystalline structure when broken, is very inflammable, burning with a brilliant white flame, so that it must be kept in water. Phosphorus assumes several different forms, one of which is amorphous, and red in colour. This kind may be heated to 250° without alteration; does not ignite by moderate friction, and may be handled without danger. It unites readily with most metals when heated with them, making them, as a rule, crystalline and brittle.

(20) *Sulphur.* S. Atomic weight, 32. At ordinary temperatures is yellow, brittle, solid, tasteless, and almost inodorous; melts at 120°, and boils at 440°; combines directly with most metals when heated with them, forming sulphides and evolving great heat. It is used in the laboratory in the form of powder, and as roll sulphur.

(21) *Ammonium Chloride* (AmCl) called sal-ammoniac. This substance is decomposed by several metals forming metallic chlorides and liberating ammonia, which property is taken advantage of in purifying gold. A similar reaction occurs with several metallic salts

(22) *Sodium Chloride* (NaCl) or common salt, is employed in metallurgical operations for preserving the substance beneath from the action of the atmosphere, and to moderate the action of bodies which cause violent ebullition. It melts and volatilises at a red heat in an open crucible, but requires a white heat to vaporise it in a closed vessel. When heated to redness with silica it forms a readily fusible silicate. It forms fusible compounds with antimony and arsenic, thus removing them from other metals during the process of refining. As the crystals decrepitate when heated, common salt should be powdered before using as a flux. Under

certain circumstances it has a tendency to form volatile chlorides with a consequent loss of metal.

(23) *Borax* ($B_4O_7Na_2$). In the crystalline form it may contain 5 or 10 molecules of water, which are given off on heating, causing an enormous increase in volume, so that the vitrified form is much more suitable for assaying. It forms fusible compounds with silica, and nearly all bases, being especially useful in uniting with metallic oxides, sulphides, and arsenides. The commercial salt is adulterated with common salt and alum.

(24) *Sodium Carbonate* (Na_2CO_3) has the property of oxidising many metals, as tin, iron, zinc, etc., by the action of its carbonic acid, and as a consequence of this action it acts as a desulphuriser. It forms fusible compounds with silica and many metallic oxides; it also melts at a low temperature, absorbing many infusible substances, such as lime, alumina, charcoal, etc. In some cases it acts as a reducing agent, as in the case of silver chloride. When mixed with carbonate of potash a double salt is formed, which fuses at a lower temperature than either taken alone, a property very useful in the fusion of silicates, etc.

(25) *Potassium Nitrate* (KNO_3), also called nitre and saltpetre, is largely used as an oxidising agent. It fuses below redness, and at a higher temperature decomposes, yielding a large volume of oxygen, whereby the sulphur of metallic sulphides is converted into sulphurous acid, and the metals into oxides. Sodium nitrate acts in the same way.

(26) *Potassium Bitartrate* ($\overline{T}HoKo$), known also as cream of tartar or tartar. When pure this substance is white, but the variety chiefly used by assayers is coloured, and sold as red "Argol," which is cheaper, and contains other carbon-

aceous matters, which give it greater reducing power than pure cream of tartar. This reagent is very valuable in assays requiring much carbonaceous matter.

(27) *Potassium Chlorate* ($KClO_3$). This substance is sometimes used with nitre as an oxidising agent in dry assays, but much more frequently in wet assays.

(28) *Potassium Cyanide* (KCN). This flux is valuable on account of the facility with which it fuses, and the readiness with which it reduces many metallic compounds when mixed with carbonate of soda. For the purposes of dry assaying, common cyanide is preferable as a reducing agent, because it contains carbonate of potash.

(29) *Calcium Oxide* (CaO), or lime, is used in the caustic state, or combined with carbonic acid in the form of carbonate. It is a useful flux for silica and silicates, with which it combines to produce a double sillicate, being in this form more fusible. It is also used to remove sulphur and phosphorus from metals, and their compounds.

(30) *Calcium Chloride* ($CaCl_2$) is useful as a desiccating agent.

(31) *Calcium Fluoride* (CaF_2) or Fluor-spar. This substance acts as a flux in two ways—1, by combining with silicates, forming fusible compounds; 2, by reacting on silicates and evolving silicon fluoride. It also forms fusible compounds with sulphates of lime and baryta, and with phosphates of lime. It should be free from pyrites, blende, and galena, with which it is likely to be contaminated.

(32) *Phosphate of Lime* ($Ca_3P_2O_8$). This substance is obtained from the calcination of bones, preferably those

of sheep and horses, until they become white; and is chiefly used in the laboratory for the manufacture of cupels. For this purpose the boneash should be of good quality and in fine powder; lime and other substances with which it is adulterated greatly interfering with its absorbent properties.

(33) *Barium Nitrate* ($Ba2NO_3$). A solution of this salt is used as a test for soluble sulphates in the presence of lead or silver.

(34) *Barium Chloride* ($BaCl_2$) is used for the same purpose as the nitrate in the absence of lead and silver.

(35) *Cupric Oxide* (CuO), Black Oxide of Copper. This oxide forms the base in ordinary copper salts; melts at a white heat; is decomposed by heat, giving up oxygen and forming the lower oxide Cu_2O, thus acting as an oxidising agent; is readily reduced to metallic copper by reducing agents; when heated strongly with silica a silicate of the suboxide is formed; when heated with copper in suitable proportion it forms cuprous oxide (Cu_2O).

(36) *Cuprous Sulphide* (Cu_2S). This body is formed when copper and sulphur are heated together. It is a dark bluish grey substance, breaking with a conchoidal fracture; when heated in air a mixture of oxide and sulphate is formed; when heated with sufficient oxide of copper it is completely reduced to the metallic state.

(37) *Copper Sulphate* ($CuSO_4$) in the crystalline state contains 5 molecules of water, becoming anhydrous at 200° C. Copper is precipitated from a solution of this salt by certain metals, such as iron and zinc. When a solution of copper sulphate is submitted to electrolysis, the copper is deposited in a practically pure state.

(38) *Plumbic Oxide* (PbO) is produced when lead is heated in a current of air or oxygen. At a temperature of about 300° C. more oxygen is taken up, forming red lead; when the temperature is sufficiently high to melt the oxide, a yellow or reddish yellow crystalline mass is formed, known as litharge. Both oxides are reduced by carbon or hydrogen, producing metallic lead. Lead oxide when melted oxidises nearly all the metals, except mercury, gold, silver, platinum, etc. With other oxides it forms easily fusible compounds. With sulphur it forms sulphurous acid, metallic lead being isolated. When oxide of lead in sufficient quantity is melted with an infusible silicate a fusible double silicate is formed.

(39) *Plumbic Sulphide* (PbS). Lead and sulphur unite directly when heated together, forming a lead-grey crystalline substance known as artificial galena. It melts at a red heat, and at a higher temperature may be sublimed. Heated in air it is oxidised to sulphate or oxide, according to the temperature. It is reduced by iron. When one molecule of PbS is heated with 2 molecules of PbO the whole of the lead is isolated.

(40) *Manganese Dioxide* (MnO_2). This substance is black in colour, opaque, and a good conductor of electricity. When heated alone it is infusible, but gives off oxygen, forming Mn_2O_3 or Mn_3O_4 according to the degree of heat employed: heated with charcoal it is reduced to MnO. The facility with which it gives up oxygen makes it a valuable oxidising agent. With hydrochloric acid it is extensively used for generating chlorine. When strongly heated in a crucible lined with a paste of carbon it is reduced to the metallic state.

(41) *Silica* (SiO_2). This body occurs in crystalline and amorphous forms; it is white; infusible, except at the very highest temperatures; non-volatile; insoluble in water

and acids, except hydrofluoric; after ignition, is decomposed by carbon in the presence of iron, copper, or silver at a white heat, forming silicides of those metals. The amorphous and gelatinous varieties are slightly soluble in alkaline carbonates, but readily soluble in caustic alkalies. It combines with all the bases forming silicates, and is therefore frequently employed to effect the fusion and separation of gangues in ores; the best forms to use being pure white sand and quartz. If the silica is coloured, it should be digested with hydrochloric acid before use.

(42) *China Clay* is essentially a hydrated silicate of alumina, and when pure may be represented by the formula $(2Al_2O_3, 3SiO_2) + 3OH_2$; but the clay is generally mixed with other silicates. China clay is white, and infusible in an ordinary furnace when heated alone, but readily unites with earthy and metallic gangues to form a fusible slag, and therefore forms a useful flux for assaying ores like those of iron.

(43) *Glass* is a mixture of silicates of sodium and potassium with some insoluble silicate, such as silicate of calcium, magnesium, aluminium, iron, or lead. Being a compound silicate it fuses easily at a high temperature, and readily combines with lime and other bases containing little or no silica, so that it is often preferred to pure silica, and serves to economise borax. It is also employed as a covering in melting metals, so as to exclude the air. Plate or window glass or green bottle glass is the most useful, but flint glass, which contains much oxide of lead, would be detrimental in many cases.

(44) *Ferrous Sulphide* (FeS) is chiefly used as a source of sulphuretted hydrogen. Roasted with easily decomposable sulphides as that of silver, it converts them into sulphates. Heated with oxides of copper, nickel, etc., it

forms regulus. Heated in air it is oxidised to sulphate, and at a high temperature to oxide.

(45) *Iron Pyrites* (FeS_2). This body loses half its sulphur at a white heat, forming ferrous sulphide, and is used for similar purposes to that compound. It is chiefly employed in the metallurgy of copper, nickel, and cobalt.

(46) *Ferric Oxide* (Fe_2O_3). This oxide is very stable, non-volatile, and of a red colour. At a white heat it gives up oxygen, forming the magnetic oxide (Fe_3O_4). By heating with carbon, or carbonic oxide, it is reduced to the metallic state, but if much carbonic acid is present, ferrous oxide may be formed, which combines with any silica present, forming a fusible silicate. For this reason it is sometimes used as a flux in copper assaying. In refining iron it acts as an oxidising agent. In presence of sulphur it oxidises that element to sulphurous acid.

(47) *Zinc Oxide* (ZnO) is a powerful base; it forms combinations with alkaline earths and several bases, and has a strong affinity for alumina. It is reduced by carbon, carbonic oxide, and hydrogen.

(48) *Cinnabar* (HgS). This sulphide is red in colour, and is decomposed by heating in a current of air. It is also reduced by many metals, and forms a better sulphurising agent than sulphur itself, being less volatile.

(49) *Black Flux.* This substance is prepared by heating a mixture of 2 parts of tartar (argol) and 1 part or less of nitre to redness in a closed crucible. The resultant mixture of potassium carbonate and carbon is often used in copper and lead assaying. It must be kept in closed bottles to prevent absorption of moisture. When great reducing power is required, black flux is prepared by

heating the tartar alone, but the excess of carbon thus produced reduces the fusibility of the slag. A mixture of sodium carbonate and charcoal is frequently used instead of black flux. The following proportions are recommended :—

Sodium carbonate,	94	88	82
Charcoal, . .	6	12	18

PHYSICAL PROPERTIES OF THE USEFUL METALS AND THE INFLUENCE OF SMALL QUANTITIES OF IMPURITIES IN MODIFYING THESE PROPERTIES.

Note.—Before using a mould, it should be warmed and black-leaded to prevent the metal sticking. This is assumed to be done in all the succeeding experiments in which a mould is used.

§ 24. Experiment 1. Weigh out 1000 grains of commercial lead; melt at the lowest possible temperature with a little charcoal to prevent unnecessary oxidation; pour into a rectangular mould (Fig. 17 *e*) so as to produce an ingot about 2 inches long and $\frac{1}{2}$ an inch wide. When cold, place it half-way in the jaws of a vice, and bend it backwards and forwards with a hammer until it is broken. Notice the absence of any definite structure on the fractured surface, and the toughness as exhibited by the difficulty in producing rupture. Re-melt and cast in the same mould as before; remove from mould when set, and place the ingot across two iron supports about $1\frac{1}{2}$ inches apart; heat the centre with the flame of a Bunsen burner, held in the hand, so that the flame only is under the metal, until the lead begins to melt, then strike the centre one sharp blow with a hammer, when the ingot will break short, showing its brittleness at this point.

The fractured surface will now be entirely different, showing a transverse columnar structure, the size and clearness of the columns being in proportion to the purity of the lead.

Exp. 2. Weigh out 1000 grains of the same lead, and melt with 50 grains of sulphide of lead; pour into a rectangular mould, and fracture when cold. It will be observed that this impure lead breaks much more readily than pure lead, and a crystalline or partially crystalline structure has been induced. Now re-melt, cast into mould, and place the ingot across two supports; heat with Bunsen burner as before, and break when on the point of melting. The fractured surface will still show the transverse columns, but they will be much smaller than with pure lead.

Exp. 3. Take 1000 grains of lead, and alloy with 15 grains of antimony. Fracture cold, and also when on the point of melting as described in Exp. 1. Notice that it is both hot and cold short, and that the fractured surface is coarsely granular in both cases.

Exp. 4. Melt 1000 grains of lead with 15 grains of metallic arsenic, and repeat the experiments described in Exp. 1. Notice the same results as with antimony.

Exp. 5. Test the malleability of lead by rolling the ingots obtained in Exps. 1, 2, 3 and 4 into sheets as thin as possible without cracking. It will be observed that the presence of impurities considerably impairs the malleability.

Exp. 6. Cut a strip of sheet lead about one-eighth of an inch wide, and observe how little force is required to produce rupture by applying a tensile stress. Instead of this strip, lead wire may be used.

Exp. 7. Test lead to show its feeble elasticity and the absence of sonorousness when struck, if solid. When, however, lead is cast in the shape of a mushroom, it becomes sonorous.

§ 25. Exp. 8. Melt 500 grains of grain tin; pour into the rectangular mould (Fig. 17 *e*) at as low a temperature as possible, taking precautions to prevent any dross getting into the mould; allow to cool without shaking or vibration. Notice the white, clear, and bright surface of the ingot when cold, which is a test of purity, also its full and rounded sides. The ordinary quality remains full, and rounded on the sides until the instant of becoming solid, when a frosted appearance will shoot out from the middle towards the sides, and a slight longitudinal depression will be produced on the surface. With a still commoner quality the colour becomes yellowish on cooling, and the appearance of the frosted crystalline markings takes place sooner, and completely covers the whole surface.

Bend the ingot of tin close to the ear, when a peculiar crackling sound known as the "cry" will be heard; this characteristic effect will be more marked the purer the tin.

Exp. 9. Melt and cast 1000 grains of tin; cool and fracture by bending backwards and forwards with a hammer. Notice the toughness of the metal and the absence of a definite structure on the fractured surface. In this respect it is similar to lead.

Re-melt, cast, and fracture when on the point of solidifying or melting. Notice the indefinite crystalline structure with the peculiar fern-like markings on the ruptured surface.

Exp. 10. Alloy 950 grains tin, 30 grains copper, and 20 grains lead, by melting together in a crucible with a

little charcoal. When alloyed, remove crucible from the fire and scrape the surface with a piece of stick until the surface ceases to oxidise, pour into rectangular mould, and allow to cool without shaking. Notice the longitudinal depression of the centre and the frosted appearance of the whole surface.

Exp. 11. Melt 950 grains tin with 20 grains of thin sheet iron and 30 grains lead; cast and cool as before. Notice the dull spotted appearance, and the character of the fracture, which should be finely granular, grey in colour, and the metal cold short.

Exp. 12. Melt 400 grains of tin, 10 grains of arsenic, and 600 grains of iron in a crucible with the lid luted on with clay. Break the pot, re-melt the alloy, and cast into a rectangular mould. Observe that the surface has a dull grey appearance, and that the nature of the fractured surface is of a steel-grey colour, finely granular, hard, and brittle. This is known as "hard head."

Exp. 12A. Melt 1000 grains of tin, and pour into a crucible containing 75 grains of red phosphorus which has been well rammed down. Rapidly place the crucible in a furnace, and stir with an iron rod until the mixture is uniform. Pour into an iron mould, and allow to cool. Observe that the metal is brittle, and that the fractured surface is highly crystalline. It probably contains about 5 per cent. of phosphorus.

Exp. 13. Test the malleability of pure and impure tin by flattening the various ingots with a hammer, or by rolling, observing the effect of impurities in hardening, and reducing the malleability. Test for tenacity (as in Exp. 6), which will be found to be very low as was the case with lead. Warm some tin, and notice the characteristic odour.

§ 26. Exp. 14. Weigh out 1000 grains of tough pitch copper, place in a clay crucible, and cover with charcoal. Heat in a brisk fire until melted. If the surface of the metal can then be seen, add more charcoal, and keep it in the fire a few minutes longer. The top of the pot may be covered with a piece of coke to keep the air away. Remove the crucible from the furnace, scrape the charcoal to one side, and pour the metal carefully into a rectangular mould (Fig. 17 *e*). When cool, tip the ingot out, and notice the longitudinal ridge on the upper surface which is characteristic of overpoled copper. Nick the centre with a steel chisel, place in a vice, and strike with a hammer until it breaks. Observe that it breaks somewhat short, that the fractured surface has a bright pale red colour, and is coarsely granular with some transverse fibres. This brittleness or cold-shortness is probably due to oxides of foreign metals such as iron, antimony, arsenic, etc., which have been reduced to the metallic state by carbon, and have alloyed with the copper.

Exp. 15. Melt 1000 grains of ordinary copper in a crucible without any charcoal, and heat to whiteness. Remove the crucible from the furnace; expose to the air until a thin crust of oxide forms on the surface, then shake the contents, so that the oxide may be dissolved by the copper, and pour into a warm rectangular mould. Allow to cool, and remove from mould. Observe the longitudinal furrow on the upper surface. Place it in the vice and strike vigorously with a strong hammer, when the ingot will break short, showing it to be brittle. Notice the dull deep purplish red colour of the fractured surface, the uneven finely granular structure, and the absence of fibre. It is technically known as "dry" copper, and the degree of dryness will depend on the proportion of oxygen dissolved. It is also called "underpoled" copper.

Exp. 16. Re-melt the dry copper obtained in the last experiment, with the addition of charcoal. When melted, partially remove the crucible from the fire, and stir the copper for a short time with a stick: this is termed *poling;* then pour into a rectangular mould, when, if the metal has been poled sufficiently, the ingot will present a flat surface having neither ridge nor furrow. Nick the centre when cold with a chisel, place in vice, and hammer backwards and forwards until it breaks. Observe its great toughness as compared with the overpoled and underpoled samples, its even close-grained structure when broken, its freedom from fibres or cavities, its bright metallic lustre, and fine salmon-red colour.

Exp. 17. Melt 500 grains of copper, and add a small piece of phosphorus very expeditiously to the crucible held with the tongs just inside the furnace; replace in the fire till all the uncombined phosphorus has burnt off. Repeat this addition of phosphorus two or three times, and then pour into rectangular mould. Notice the full appearance of the ingot with its longitudinal ridge resembling overpoled copper, and its lead-like colour. Fracture when cold, and observe its extreme brittleness and the facility with which it may be crushed to a fine powder; its bluish-white, coarse, semi-crystalline structure, and its hardness when tested with a file.

Exp. 18. Melt 500 grains of copper mixed with 5 grains of thin sheet iron, and add a bit of phosphorus about the size of a nut, with the precautions mentioned in Exp. 17, and pour into rectangular mould. Notice the full, convex, and compact nature of the ingot; its cold shortness when struck with hammer; its reddish grey close-grained fracture, very much resembling bronze, and its moderate hardness when tested with a file.

Exp. 19. Melt 500 grains of copper, and add 20 grains of metallic arsenic. When mixed, pour into rectangular

mould. Observe the longitudinal furrow resembling dry copper; its cold shortness, and the dull, close-grained, light reddish-grey appearance of the fractured surface.

Exp. 20. Melt 500 grains of copper, and add 10 grains of antimony. Notice that the effect is much the same as with arsenic. Some of the arsenic is lost by volatilisation in experiment 19, as is also some of the antimony in the present case.

Exp. 21. Place 500 grains of sheet copper in a crucible, well incorporate with an excess of white sand mixed with sufficient carbon to reduce the silica to silicon, lute on a lid and expose to a white heat for several hours. When cold, break open the pot, remove the metal which exists in several globules, and re-melt the whole so as to collect into one ingot. The surface will be slightly indented, and resembling gun metal in colour when filed. It can be rolled and hammered out in the cold; is much harder than copper, and fairly tough. If the temperature is too low, or not sufficiently prolonged, only a very little silicon will be reduced, and the metal will simply resemble slightly underpoled copper.

Exp. 22. Melt 500 grains copper with 10 grains of lead and cast into rectangular mould. Notice the longitudinal furrow, the cold shortness, and all the appearances of dry copper.

Exp. 23. Melt 500 grains of copper and add 25 grains of sulphide of copper; cast into rectangular mould. The surface of the ingot may be very rough, and the fractured surface very vesicular from the escape of gases. The structure may be partly crystalline and partly granular, while the colour and lustre may be bright in some parts and dull in others, resembling overpoled and underpoled copper. On re-melting and pouring, the ingot assumes the appearance and properties of moderately dry copper.

Exp. 23A. Mix 500 grains of sheet copper with 100 grains of black oxide of manganese and 25 grains of carbon, place in a crucible, cover with a layer of carbon, lute on lid, and heat strongly for two hours. When cold break open the crucible, collect any globules of metal, and re-melt the whole metal so as to collect into one ingot. The copper is whitened in proportion to the manganese alloyed with it.

§ 27. Exp. 24. Place 1000 grains of iron in a crucible and raise it to white heat, then drop in cautiously a bit of phosphorus, and repeat this at intervals until the iron melts. Remove from fire; cool; break the crucible, and detach the button of metal. Fracture and observe its brittleness, its white close-grained metallic appearance, inclining to crystalline, and its great hardness as tested by a file.

Exp. 25. Mix 1000 grains of iron with 20 grains of arsenic; place in clay crucible; lute on the lid with clay, and expose to the highest temperature of a wind furnace for an hour. Remove; cool; break the crucible, and extract the button of metal. Observe that it is brittle, hard, and that the fractured surface has a grey, granular appearance, resembling grey cast iron.

Exp. 26. Heat strongly for an hour in a covered crucible 1000 grains of iron mixed with 25 grains of ferrous sulphide. Allow to cool; break the pot, and remove the button of metal. Place the latter in a vice, and break with hammer and chisel. Notice its brittleness, hardness, and the white, granular appearance of the fractured surface, resembling white cast iron. There will probably be black patches on the surface, and also on the fractured part, which are characteristic of sulphur in iron.

Exp. 27. Place 1000 grains of hoop iron in a crucible and raise to a white heat, then add small bits of sulphur at intervals, until the whole is melted; then pour into half-round mould (Fig. 17 *a*); cool; fracture, and notice its brittleness, its coarse, stony appearance, its bronze-like colour, and generally its vesicular structure.

Exp. 28. Mix together in a crucible 400 grains of hoop iron and 300 grains of cast iron; lute on a lid, and expose to a white heat for an hour; allow to cool; break open the crucible, and extract the button of metal. Test the hardness with a file; observe the white granular texture, somewhat coarse, tending to crystalline, its general appearance resembling very hard coarse-grained steel.

Exp. 29. Cut up 1000 grains of hoop iron into small pieces, and thoroughly embed them in charcoal in a clay crucible; lute on the lid; place in a wind furnace, and keep the whole at a white heat for two hours; then allow the fire to burn down, remove the crucible, and when cold break open to detach the button of metal. Place the latter in a vice and break by means of a hammer and chisel. The substance will probably be a soft grey cast iron, with a medium sized granular fracture.

Exp. 30. Repeat experiment 29, with the addition of 200 grains of white sand mixed with the carbon. Keep the crucible at a white heat for three hours; allow to cool in the furnace; detach button of metal, and break in the vice as before. The substance will be harder than the former when tested with a file; of a light-grey or mottled appearance, a fine granular structure, and more compact than with carbon alone. Such a compound would probably contain about 5 per cent. of silicon.

Exp. 31. Heat strongly for an hour or two in a covered crucible, 500 grains of hoop iron cut up small, and embedded in white sand, and observe that the iron remains unaltered; showing that carbon or some other reducing agent is necessary to decompose the silica.

Exp. 32. Cut up 1000 grains of hoop iron; mix 100 grains of black oxide of manganese with carbon in excess; place the whole in a clay crucible. Lute on lid, and expose the whole to a very high temperature for two hours; allow to cool in the furnace, break crucible, detach metal, and break in vice as before. The fractured surface may present a white ground work, with almost regular concentric rings of dark stars, giving the whole the characteristic appearance of mottled cast iron. The iron, moreover, is soft when tested with a file.

§ 28. Exp. 33. Melt 10 grains of silver by placing in a red-hot cupel heated in a muffle, and keep in the molten condition for fifteen minutes. Observe that the metal does not tarnish in contact with the air. Now urge the muffle to a white heat, and maintain at that temperature for some time; the metal volatilises; cool out of contact with air very slowly; notice the clear surface; weigh and determine the loss due to volatilisation.

Re-melt and cool quickly in contact with air, when the oxygen, which has been mechanically absorbed, is disengaged on the metal solidifying, raising a blister on the surface, or covering the same with a number of small excrescences, giving it a frosted appearance. This action is called "spitting."

Exp. 33A. Re-melt the silver with 2 grains of copper, cool in air as before, and notice that the copper prevents "spitting."

Exp. 33B. Melt 10 grains of silver with sufficient

sodium chloride to cover the bead of silver, so that the metal cools under a layer of salt, and notice the even surface.

Exp. 33C. Re-melt with a quantity of nitre, instead of salt; cool as before, and observe the frosted appearance.

Exp. 33D. Re-melt the silver with ½rd its weight of gold, and notice that the phenomenon of "spitting" takes place.

Exp. 33E. Now alloy with more than ½rd of gold, cool in air, and notice that no "spitting" occurs.

Exp. 34. Melt 10 grains of silver in a cupel; add a little sulphur, and allow the bead to cool. Fracture, and notice the bluish-grey granular structure. Re-melt and heat to expel the greater part of the sulphur, cool, and observe that the metal cracks on the edges when rolled. Re-melt in a small crucible, with the addition of a bit of iron wire; pour into mould, and detach the iron regulus by striking the sides with a hammer, and prove that the silver now rolls without cracking.

Exp. 35. *To Prepare Pure Silver.*—Dissolve 100 grains of standard silver in dilute nitric acid in a beaker of about one pint capacity, then add distilled water till three parts full; heat nearly to boiling, and carefully add a hot saturated solution of common salt, until the whole of the silver is precipitated as chloride, stirring at the same time with a glass rod; allow to stand in a warm place until the liquid is clear, then decant off the greater part of the solution; add hot water; allow to settle; again decant the clear liquid, and repeat this three or four times. Now wash the precipitate on to a filter paper; wash two or three times with hot water,

and dry the whole. When dry, transfer paper and precipitate to a clay crucible; add twice the bulk of carbonate of soda, and fuse at a good red heat for about fifteen minutes; then pour into a rectangular mould, cool, and detach the slag, the last remnants of which may be removed by dissolving in hot water. Now roll out into a thin strip ready for use in other experiments.

§ 29. Exp. 36. Strongly heat 10 grains of fine gold in a muffle for some time, and observe that no oxidation takes place; remove; cool in air, and notice that there is no alteration of the surface due to liberation of oxygen, as is the case with silver under similar circumstances. Roll out the gold into a strip, and prove its great malleability. Cut with a knife to ascertain its softness.

Exp. 36A. Re-melt the gold in a small crucible with the addition of $\frac{1}{20}$th of a grain of lead, and roll out as before. Notice that it now cracks on the edges, showing that this small amount of lead makes it brittle and alters its colour.

Exp. 37. Melt 10 grains of gold with $\frac{1}{10}$th of a grain of iron. Cut with knife to test its hardness. Roll out thin, and notice that it cracks on the edges.

Exp. 38. Melt 10 grains of gold with $\frac{1}{20}$th of a grain of antimony, and observe the same effect as with lead. (See Exp. 36A.)

Exp. 39. Melt 10 grains of gold in a small crucible; drop in a little sulphur; pour into mould, and observe that no change has taken place, the colour, softness, and malleability remaining unaltered.

Exp. 40. Dissolve a few grains of gold in aqua regia; evaporate to dryness to remove acid; re-dissolve in about a pint of distilled water; add a solution of sulphate of iron and heat, when the gold will be precipitated as a brown powder. Filter through a filter paper, wash residue with water, and warm till perfectly dry. Then carefully rub the brown powder with some smooth surface, when the ordinary yellow colour and lustre of gold will appear.

Exp. 41. The gold which has been rendered brittle in the previous experiments by alloying with lead, antimony, and iron, may be fused with a little nitre and double the quantity of carbonate of soda; pour into mould, cool, detach the slag, and roll out thin to test its malleability. In order to make it very tough use a little sal-ammoniac and charcoal, and fuse the metal for a few minutes. This flux should be added just as the gold is melting.

§ 30. Exp. 42. Take 500 grains of shot nickel containing about 99 per cent. of the metal; place in a clay crucible; lute on lid, and expose to a white heat for an hour. Remove crucible from fire; allow to cool; break open the pot, and examine the button of metal. Observe that it is white; malleable when hammered; hard, very tenacious, tough, and difficult to break. Also that the fractured surface is greyish white, and exhibits a mass of transverse fibres.

Exp. 43. Take 500 grains of the nickel used in the previous experiment; place in a blacklead crucible with 20 grains of carbon; lute on lid, and expose to a white heat for an hour. Remove; allow to cool; break open the pot, and extract the metal. Observe that the button is darker in colour, fairly malleable, hard, and moderately tenacious. The fractured surface is of a dark grey colour,

and granular, the fibrous structure having been destroyed by the union with carbon.

§ 31. Exp. 44. Take a portion of pure mercury; observe its silvery white colour; that it is tasteless and odourless; that it is liquid at ordinary temperatures; that it boils when heated to 350° C., and then begins to oxidise, forming HgO. Heat a portion strongly in a muffle, and observe that it completely volatilises. Rub together mercury and each of the following metals: Silver, gold, tin, lead, bismuth, zinc, iron, and copper. Notice that the iron and copper are less readily amalgamated than the others.

Exp. 45. Weigh out about 50 grains of mercury and add a little powdered zinc and antimony, but not sufficient to destroy the liquid character of the mercury, and cause the globule to roll down a slight incline. Observe that the spherical shape is not maintained as would be the case with pure mercury, but that the globule elongates, carrying a tail with it. Shake up the impure mercury in a flask, and observe a thin film of oxide on the surface impairing its lustre. Dissolve the metal in nitric acid, evaporate to dryness, and boil up with water, when a residue will be left owing to impurities.

Exp. 46. Rub together a portion of mercury and sulphur in a clear porcelain mortar for some time, when black sulphide will be formed. Place this in a porcelain crucible; cover; and heat gently for some time; cool, and observe the red crystals of vermilion. Place some of the sulphide in the centre of a hard glass tube open at both ends; rest the latter in a horizontal position on the ring of a retort stand; heat the portion containing the sulphide by means of a Bunsen burner, and notice the globules of mercury on the cooler portions of the tube,

showing the decomposition of this sulphide by the combined agency of heat and air.

Exp. 47. Take a hard glass tube about a foot long closed at one end, and introduce a little mercury, then draw out the open end with a table blowpipe to a fine point thus—

Heat the end containing the metal till it has volatilised, and observe the condensed mercury at the narrow part, proving that mercury may be readily distilled.

§ 32. Exp. 48. Melt 1000 grains of zinc, and pour into a rectangular mould; cool down to about 150° C.; place on two supports, and strike the centre several times with a hammer, when it will bend but not break. Hammer out one end of the ingot on the anvil; cut it off with a chisel; warm again if necessary, and roll into a thin sheet. It may require annealing once or twice by heating to about 200° C. during the process. The other half of the ingot will by this time have cooled down to the ordinary temperature; place it in vice, and strike with hammer, when the metal will break off short, showing its crystalline structure, and brittleness at the ordinary temperature. Heat a portion to a temperature of 200° to 300° C., and prove the brittleness at that point as well as when cold. Hammer out another portion at 150° C.; allow to cool, and then break in the vice. Notice that the crystalline structure has been destroyed by forging, the metal having become close-grained and minutely crystalline.

Exp. 49. Heat 500 grains of zinc with 20 grains of clean iron filings in a covered crucible for an hour at a moderate temperature; remove from fire, and pour into

an iron mould; fracture, and observe that the crystals are much smaller than in pure zinc, being partly replaced by a granular groundwork, and that the lustre is less bright.

Exp. 50. Mix together in a crucible two parts of lead and one of zinc, well melt together, and pour into the upright taper mould (Fig. 17 *c*), which should have been previously heated and blackleaded. When cold, knock out the ingot of metal. By close inspection of the exterior, a line will be observed where the two metals have separated; place in vice up to this mark as near as possible, and give it a few sharp blows with a hammer, when it will break off short. Notice the dull grey granular appearance of the fractured surface interspersed with a number of small crystals; also that the lower end of the ingot consists of lead which is very malleable, and the upper end of zinc which is highly crystalline and brittle.

Exp. 51. Melt 500 grains of zinc, drop in two or three bits of phosphorus, and cast into rectangular mould (Fig. 17 *e*). The phosphorus increases the brilliancy and lengthens the crystalline plates which are arranged transversely at an angle of 30 to 40 degrees in a definite manner, while the zinc before adding the phosphorus appears more irregularly crystalline.

Exp. 52. Melt 500 grains of zinc and then drop in 20 grains of arsenic—the effect is much the same as with phosphorus.

Exp. 53. Melt 50 grains of zinc in an open crucible so that air may have free access, using a hot fire; observe that the zinc is volatile, burning with a brilliant bluish white flame, forming a very light white powder, which is oxide of zinc.

§ 33. Exp. 54. Melt 300 grains of antimony in a small crucible, and when partially cool, pour out the still liquid portion; cover with lid; allow to cool, and observe the rhombohedral crystals.

Exp. 55. Melt 300 grains of antimony in a crucible; remove from fire; scrape the surface with a piece of wood until it remains bright and no film of oxide forms; pour into iron mould, and observe the nature of the surface. Before melting, crush up the metal in a mortar to prove its extreme brittleness.

Exp. 55A. Raise 100 grains of antimony to a red heat; notice that it takes fire, burning with a white flame, and forming the white trioxide. If commercial antimony be used, it will probably exhale the characteristic garlic odour of burning arsenic with which it is contaminated.

Exp. 56. Roast 50 grains of powdered commercial antimony in a muffle, and observe the odour of sulphur dioxide, showing the presence of sulphur in the metal.

Exp. 57. Melt 100 grains of common antimony with a little hoop iron; pour into round mould; cool, and observe the crust of iron sulphide on the surface of the metal.

CLAYS, SILICATES, AND SLAGS.

§ 34. Exp. 58. Measure out four medium-sized crucibles full of good fire-clay and pound in an iron mortar until sufficiently fine to pass through a sieve with 40 to 60 meshes to the inch. Then take two measures of crushed clay, which has been previously baked, pass through the same sieve, and mix the two lots together. Now weigh out three lots of 1000 grains each and reserve them for

experiments 59, 60 and 61. To the remainder add water, and knead the whole to the consistence of dough. Then shape a piece in the form of a pyramid by cutting with a knife or spatula, also cut a rectangular base for the pyramid to rest on; dry them both at about 100° C.; place in a cold gas muffle; gradually increase the heat to redness, and maintain at that temperature for fifteen minutes. Remove; place in a crucible; cover with lid, and expose to the highest temperature of a wind furnace for half an hour; remove from fire; cool, and observe the character of the sharp edges. If they show no signs of fusion, the clay is very refractory; if incipient fusion only has occurred, the clay is moderately refractory.

Exp. 59. Mix with one of the 1000 grains of clay, reserved from Exp. 58, ten per cent. of lime or oxide of iron or five per cent. of each; make a pyramid as previously described, bake, and then heat strongly. Notice that the clay partially fuses.

Exp. 60. Repeat Experiment 59, but with the addition of five per cent. of sodium carbonate in place of the lime or oxide of iron, and notice that the clay completely fuses.

Exp. 61. Repeat Experiment 59, but with the addition of three to four per cent. of iron pyrites instead of the lime or oxide of iron. (See § 18 *a*.)

Exp. 62. From the clay prepared in Experiment 58, make a few small crucibles and lids as described (§ 18 *e*); carefully dry, and bake in muffle. Line three or four of these with the charcoal brasque mentioned in § 18 *h*; dry, and carefully heat with lid on in a muffle until all flame ceases; remove and cool with lid on, otherwise some of the carbon will burn away.

Exp. 63. Test the power of resisting corrosion of the unlined crucibles by observing how long 100 grains of

litharge can be kept melted without eating its way through the bottom of the crucible.

Exp. 64. Take one part of raw clay by measure and an equal amount of crushed coke; well knead together with water, and mould into crucibles, as in Experiment 62. Dry, bake, and test the refractory power as before. Instead of the coke powder, good native graphite may be used.

§ 35. Exp. 65. Take 200 grains of white sand; place in crucible; lute on the lid, and expose to a high temperature for two hours. Notice that it remains unmelted.

Exp. 66. Take 348·8 grains of silica * and 651·2 grains of lime; place in clay crucible lined with charcoal paste; lute on the lid; expose to a white heat for two hours, and observe that the mass is infusible at that temperature. These proportions correspond to the formula $2CaO.SiO_2$, the ratio of the oxygen in the acid to that of the base being as 1 : 1.

Exp. 67. Take 517·2 grains of silica and 482·8 grains of lime and expose in a covered and luted crucible as before to a white heat for two hours. Notice that the mass is well melted, compact, and has a glassy fracture. This silicate corresponds to the formula $CaO.SiO_2$, the ratio of oxygen in the acid to that in the base being as 2 : 1.

Exp. 68. Take 445·5 grains of silica and 554·5 grains of lime and proceed as before. The mixture melts and forms a compact slightly crystalline silicate, the formula of which is $4CaO.3SiO_2$, the oxygen ratio of acid to base being as 3 : 2.

Exp. 69. Mix together 211·3 grains of silica and 788·7

* Ca = 40 . O = 16 . Si = 28.

grains of lime; heat strongly for two hours as before. Observe that the mixture does not melt. This corresponds to the formula $4CaO.SiO_2$, the oxygen ratio of acid to base being as 1 : 2.

Exp. 70. Mix together 616·4 grains of silica and 383·6 grains of lime in a brasqued crucible; cover; lute on lid, and expose to a white heat for two hours. Observe that the mass is unmelted, or only partly melted into a compact glassy slag. This mixture when combined would have the formula $2CaO.3SiO_2$, the oxygen ratio of acid to base being as 3 : 1.

(*a*) From the foregoing series of experiments it will be observed that silicates of lime having a composition corresponding to $CaO.SiO_2$ and $4CaO.3SiO_2$ are fusible at the temperature of an assay furnace. That $2CaO.3SiO_2$ is partly fusible; and that $2CaO.SiO_2$ and $4CaO.SiO_2$ are infusible, which shows that an excess of silica is an advantage, and an excess of lime a disadvantage in inducing fusibility in slags.

§ 36. The fusibility or otherwise of the corresponding silicates of magnesia may be determined in a similar way to those of lime.

Exp. 71. Take 428·6 grains of silica and 571·4 grains of calcined magnesia (obtained by igniting the carbonate); place in a brasqued crucible; lute on lid, and expose to a white heat for two hours. Observe that the substances only partially fuse into a white hard semi-crystalline mass. These proportions correspond to $2MgO.SiO_2$, with oxygen ratio of acid to base as 1 : 1.

Exp. 72. Take 600 grains of silica and 400 grains of magnesia. Heat as above, and notice that the mass only just melts, or partly melts. The formula is $MgO.SiO_2$ and oxygen ratio of acid to base as 2 : 1.

Exp. 73. Take 529·4 grains of silica and 470·6 grains of magnesia. Heat as before. The mass is well melted and has a crystalline fracture. The formula is $4MgO,3SiO_2$, and oxygen ratio of acid to base as 3 : 2.

Exp. 74. Heat as before 272·7 grains of silica and 727·3 grains of magnesia. The mass does not melt, but frits together. The formula is $4MgO.SiO_2$ and oxygen ratio of acid to base is as 1 : 2.

Exp. 75. Heat as before 692·3 grains of silica and 307·7 grains of magnesia. The mass melts, forming a hard porous substance corresponding to the formula $2MgO.3SiO_2$; the oxygen ratio of acid to base is as 3 : 1.

(*a*) With regard to the above experiments on silica and magnesia, we find that those substances having a composition corresponding to $4MgO.3SiO_2$ and $2MgO.3SiO_2$ are fusible; that $MgO.SiO_2$ is just fusible; that $2MgO.SiO_2$ is partly fusible; and that $4MgO.SiO_2$ is infusible.

§ 37. No silicate of alumina is completely fusible at the highest temperature of an assay furnace, but the proportions requisite to form the compounds represented by the formulæ $Al_2O_3.3SiO_2$ and $2Al_2O_3.9SiO_2$ respectively soften at a high temperature, which may be verified by heating in brasqued crucibles, with lids luted on (Fig. 34), 643 grains of silica with 357 grains of alumina, and 730 grains of silica with 270 grains of alumina. The alumina may be obtained by strongly calcining sulphate of alumina.

(*a*) Although, as stated above, silicates of alumina are infusible alone, the addition of a small amount of another base greatly reduces their melting points. The substance commonly added for this purpose is lime. Magnesia may also be used, but it is much less fluxing than lime. The most fusible compounds of lime and alumina are comprised between those in which the oxygen of the

silica is double the sum of that of the lime and alumina, and those in which the oxygen of the silica is half the sum of that of the lime and alumina; and these compounds are fusible in proportion as the relation between the bases approaches that of $6CaO : Al_2O_3$. They still melt well when the relation is as $3CaO : Al_2O_3$; but they become much less fusible when the relation is as $3CaO : 2Al_2O_3$. The composition of clays, which are richest in alumina, may, with some exceptions, be expressed by the formula $2Al_2O_3.3SiO_2$. Hence it follows that by the addition of an amount of lime intermediate between 3CaO and 6CaO, or the equivalent in carbonate of lime, they ought always to melt well; and that the fusion ought to be still more easy when, in addition to lime, silica is added in a proportion ranging from SiO_2 to $4SiO_2$.

§ 38. Exp. 76. *To Prepare Silicate of Copper.*—Take 300 grains of the black oxide of copper (CuO) and sufficient white sand to give the reaction :—

$$* \underset{316}{4CuO} + \underset{60}{SiO_2} = \underset{344}{2Cu_2O.SiO_2} + O_2.$$

Well mix the two substances together, place in a scorifier, and heat strongly in a muffle for half an hour, when the ingredients will be fritted together without melting.

Exp. 77. Take 200 grains of the above silicate of copper, crush up fine, and mix with sufficient ferrous sulphide to give the reaction :—

$$2Cu_2O.SiO_2 + 2FeS = 2Cu_2S + 2FeO.SiO_2.$$

Place the mixture in a crucible; lute on a lid, and heat strongly for half an hour in a furnace. Remove from fire; allow to cool; then break the crucible, and describe the contents, which consist of a dark bluish grey fine-

* Cu = 63 : Si = 28 : Pb = 207.

grained copper regulus at the bottom, and a black glassy slag of silicate of iron on the top.

§ 39. Exp. 78. *To Prepare Silicate of Lead.*—Take 300 grains of litharge, mix with sufficient sand to give the reaction :—

$$* \quad 2PbO + SiO_2 = 2PbO.SiO_2.$$

Place the mixture in a roasting dish, and heat at a low temperature in a muffle, so as to frit the ingredients together, or melt together in a crucible and pour into a mould. Describe the result.

Exp. 79. Take 200 grains of the above silicate, 10 grains of charcoal, and sufficient iron, to give the reaction :—

$$2PbO.SiO_2 + 2Fe = 2FeO.SiO_2 + 2Pb.$$

Place in crucible, and heat for about 15 minutes, until all action ceases, then pour into mould, and describe the result.

§ 40. Exp. 80. *To Prepare Silicate of Iron.*—Take 300 grains of powdered hematite and sufficient sand to give the reaction :—

$$Fe_2O_3 + SiO_2 = 2FeO.SiO_2 + O.$$

Heat together in a crucible; allow to cool; then break the pot, and describe the result.

EXAMINATION OF FUELS.

§ 41. The industrial value of fuels depends on the combustibility, the length and volume of the flame, the purity, the calorific power, and the calorific intensity.

Exp. 81. The temperature at which a given fuel inflames may be determined by passing hot air over it at

* Cu = 63 : Si = 28 : Pb = 207 : Fe = 56.

different temperatures in a glass tube. In this way dry peat has been found to inflame at 225° C.; pine charcoal at 280° C.; pine wood at 300° C.; ordinary coal at about 350° C.; coke and anthracite at a nascent red heat. The igniting points of charcoal and coke depend upon the temperature at which they have been produced; the higher this point, the less inflammable they become. The most inflammable kinds of wood and coal are those which are richest in hydrogen.

Exp. 82. Weigh a lump of wood of a convenient size to go inside an ordinary clay crucible, cover with a lid, place inside a furnace, and observe the character of the flame produced from its decomposition. It will be voluminous, white, and mixed with dense fumes of tarry matter. When all flame ceases remove the crucible, taking care to keep the lid on until quite cold; then weigh the charcoal produced, and estimate the percentage obtained from the sample of wood taken.

This should be repeated with different kinds of wood.

Exp. 83. Repeat the last experiment with a weighed portion of compressed peat.

Exp. 84. Take a lump of lignite weighing about 2000 grains; crush to a powder in an iron mortar, and weigh 500 grains. Place in a clay crucible; cover, and heat in a furnace. Notice the long smoky flame, the disagreeable odour peculiar to itself, and very different from that of ordinary coal. Remove from furnace; cool with lid on, and weigh the carbon residue. This residue retains the form and colour of the lignite from which it has been produced.

Exp. 85. Weigh 500 grains of a sample of ordinary coal which has been crushed to powder, and treat as in Exp. 84. Observe that the flame is less voluminous, and the odour quite different; that the particles have caked

together, forming a more or less dense and compact coke according to the temperature and duration of the coking operation, and that a larger percentage of fixed carbon remains. Its colour will be greyish black, with a semi-metallic lustre, especially if a high and prolonged temperature has been employed. Notice also that coke is much less combustible than charcoal.

Exp. 86. Repeat Experiment 85 with 500 grains of powdered anthracite. Observe that the flame in this case is very short, and the powdered fuel presents much the same appearance at the conclusion as before the coking operation, still retaining its pulverulent form, showing that it is non-caking; also note that the amount of the fixed residue is greater than in any of the above cases.

Exp. 87. Take different samples of coal, crush to a fine powder, and pass through a sieve with 80 meshes to the inch; weigh out 50 grains of each; place in small scorifiers, and heat in a muffle until all the carbon is removed and a white or reddish white ash remains; cool and weigh to obtain the amount of ash, and as 50 grains were taken, the result, when multiplied by 2, will give the percentage.

Exp. 88. Weigh out 50 grains each of wood and peat, and decarbonise, as with coal, to determine the amount of ash present in each case.

Exp. 89. The estimation of moisture may be made by heating 25 grains of finely powdered coal in a water oven for an hour, cooling and weighing. First carefully dry a pair of watch glasses, having ground edges so as to fit accurately, and obtain their exact weight. Then weigh in one of them the coal to be examined, and expose the whole to a temperature of 100° C. for an hour; cool and weigh. Notice the loss; repeat the experiment for

another half hour; again weigh, and repeat until the weight is constant.

Exp. 90. To determine the amount of sulphur in coal; take 50 grains of finely powdered coal, and oxidise the sulphur present into sulphate; then precipitate the sulphuric acid with barium chloride.

1*st Method.* Powder a quantity of pure sodium chloride and nitre; dry at 100° for some time, then incorporate the 50 grains of dry coal with 500 grains of a mixture consisting of $\frac{2}{3}$rds sodium chloride and $\frac{1}{3}$rd nitre. Half fill a porcelain crucible with this mixture; partly cover with lid, and heat gently over a gas flame until the mass is completely deflagrated, which may be known by its white colour; then add more of the mixture, and repeat the heating until the whole of the coal has been oxidised. Allow the crucible to cool, place it in a large evaporating basin; cover with water; heat to boiling, and continue the ebullition until all soluble matter is dissolved. Remove the crucible and carefully wash it with hot water. Now add hydrochloric acid to the solution, and heat until all gases are expelled. Then filter off any insoluble matter, allowing the filtrate to run into a beaker; again boil and add a solution of barium chloride, stirring at the same time with a glass rod, until all the sulphate is precipitated; allow to stand in a warm place for the solution to clear; filter; well wash several times with hot water; dry; then brush off the precipitate on to a sheet of glazed paper; burn the filter paper completely in a weighed porcelain crucible; then add the precipitate and again ignite for some time; allow to cool in a desiccator, and weigh the barium sulphate ($BaSO_4$). If the paper be of the kind now sold as ashless, no deduction need be made for its ash. Then as 233 : 32 = weight of ppt. : the S present : and as 50 grains of the fuel were taken, the result when multiplied by 2 will give the percentage of sulphur present.

2nd Method. Mix 50 grains of coal with 100 grains of pure quick lime, place in a roasting dish, and cover the mixture with another 100 grains of lime, then strongly heat in a muffle for an hour, or until the mass is quite white. Digest the roasted mass with hydrochloric acid, filter off any insoluble residue, and treat the filtrate with barium chloride and proceed as in the former method.

Exp. 91. To determine the calorific power of a given fuel, carefully dry a quantity of finely powdered potassium chlorate and nitrate in separate dishes. Also a quantity of the fuel very finely powdered should be dried, for half an hour at least, in a water oven. Weigh out 30 grains of the dried coal, 225 grains of potassium chlorate, and 75 grains of nitre; well mix and introduce into the perfectly dry copper tube of what is known as Thompson's or Wright's calorimeter; ram it moderately tight; insert a small piece of "fuse" (prepared by soaking cotton wick in a solution of nitre and drying it), and place the tube in the stand ready for the experiment. Now take the temperature of the water in the large vessel; light the fuse; cover with the bell tube, taking care that the tap is closed, and put the whole in the water before the ignited fuse has had time to burn down to the mixture. When the combustion appears complete, open the tap so that the water may absorb the residual heat in the tube, and again take the temperature of the water. The increase of temperature, plus 10 per cent. added for loss, gives the evaporative power of the fuel.

EXAMPLE:

Temp. of water before the experiment	=	55° Fahr.
,, ,, after ,, ,,	=	66° ,,
,, produced by the combustion,	=	11
Plus 10°/₀	=	1·1
Total evaporative effect,	=	12·1

i.e., 1 lb. of the coal on perfect combustion will generate 12·1 lbs. of steam.

(*a*) The apparatus (Fig. 46) consists of a tall glass cylindrical vessel *a* capable of holding 60,000 grains of water. At a given distance a mark is scratched on the outside to indicate 29,010 grains of water, which equals 967 × 30 (the former figure being the latent heat of steam and the latter the weight of fuel taken). A copper vessel (*b b*) fitted at the top with a stopcock, and a perforated stand *c*, into the socket of which the copper crucible *d* fits. This stand has 3 springs *e* for keeping the cylinder *b* tightly fixed to the stand.

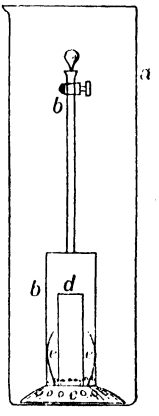


Fig. 46.

Note.—The quantity of water used is immaterial, provided its weight is known, and that there is sufficient to cover the lower portion of the copper vessel *b b*.

(*b*) The calorific value of fuel may be estimated in "calories" or in vapour units. The calorie represents the heat absorbed by the unit weight of water when its temperature is raised one thermometric degree, the centigrade scale being most generally employed. The vapour unit was proposed by Rankine, and corresponds to 537 calories if the Centigrade scale be used, and 967 calories for the Fahrenheit scale. In order to express calories in vapour units, divide by 537 or 967 respectively. To convert vapour units into calories multiply by these numbers. Take the example given above, viz., 12·1 vapour units; 12·1 × 967 = 11,700·7 calories.

SPECIFIC GRAVITY OF SOLIDS.

§ 42. By this term is understood the ratio of the weight of a body to the weight of an equal bulk of another body taken as a standard. Pure distilled water is almost invariably employed for this purpose. As the volume of bodies is altered by heat it is necessary to conduct the experiment at a known temperature, which is generally 15°·5 C. There are several ways by which the density may be determined, but the most useful and generally applicable is as follows :—

Exp. 92. The body is suspended by a horse hair from the pan of a specific gravity balance, and accurately weighed in air; then it is completely immersed in a beaker of distilled water placed underneath the pan and reweighed. The body will now appear lighter than before, the loss in weight being exactly equal to the weight of an equal volume of the water; so that a body immersed in water loses a portion of its weight equal to that of the displaced water. Now place weights in the short pan, *i.e.*, the one from which the body is suspended, to counterbalance this diminution and observe the amount added. Then divide the weight in air by the loss of weight in water, and the result gives the specific gravity.

Suppose the body is lighter than water. Take its weight in air as before, then the weight in water of a piece of lead sufficient to sink it, and the weight in water of the light substance with the lead attached. The density D is then obtained by the following equation.

$$D = \frac{\text{Weight of substance in air.}}{\text{Wt. of lead} - (\text{Wt. of lead} + \text{light subs.}) + \text{Wt. of substance in air.}}$$

In more accurate work it is usual to reduce the weight of the substance to its weight in vacuo, but for further information the student is recommended to refer to the "Theory and Use of a Physical Balance," by James Walker, M.A. (Clarendon Press, 1887.)

Exp. 93. Suppose the body to be soluble in water or decomposed by that liquid; then substitute for the water some liquid in which the body is insoluble, oil of turpentine or spirits of wine being generally applicable. Weigh in air as before, then note the difference when weighed in turpentine; this gives the weight of a volume of turpentine equal to that of the substance. The specific gravity of oil of turpentine compared with water is known, and as the specific gravity of turpentine is to the specific gravity of water, so is the weight of a bulk of turpentine equal to that of the body, to the weight of a bulk of water equal to that of the body. The weight in air of the body is then divided by the latter. Let A = the weight of body in air : A′ = the weight of body in turpentine. Then the weight of a bulk of turpentine equal to that of the body is $A - A' = A''$. Let S = the density of the turpentine, and S′ = the density of water; then $S : S' :: A'' : x$, and the specific gravity of the body $= \frac{A}{x}$.

The density of oil of turpentine varies from ·86 to ·88.
" " alcohol is ·794 at 15·5° C.

Exp. 94. The specific gravity of a metal or alloy may be determined approximately by removing the pan and suspension of an ordinary laboratory balance, carefully counterpoising by wrapping sheet lead round the end of the beam, and suspending the metal by means of a horse hair, weighing in air, then taking the weight when suspended in water, and calculating as described in Exp. 92.

Exp. 95. Determine by the above method the specific gravity of lead, iron, copper, zinc, tin, etc. Also various alloys, such as gun metal containing 900 parts by weight of copper and 100 parts of tin. Now calculate the density of the gun metal, and notice whether it agrees with the experimental determination thus :—

Let the weight of the above gun metal in air = 1000 grains. The amount of copper present in the alloy is therefore 900 grains and the tin 100 grains.

Weight of copper in air = 900
" " water = 900 − x

The difference between these weights = x

And $\frac{900}{x}$ = 8·8 = the specific gravity of copper.

Weight of tin in air = 100
" " water = 100 − y

The difference between these weights = y

And $\frac{100}{y}$ = 7·3 = the specific gravity of tin.

Now $x = \frac{900}{8{\cdot}8} = 102{\cdot}3$

And $y = \frac{100}{7{\cdot}3} = 13{\cdot}7$

116

Therefore 116 is the weight of an amount of water equal in bulk to 1000 grains of the alloy, and $\frac{1000}{116}$ = 8·62 = the specific gravity of the bronze.

The following formula for calculating the theoretical density on the assumption that the union of two metals

has been attended neither by contraction nor expansion will show whether the alloy has actually expanded or contracted :—

$$\frac{W}{D} = \frac{w}{d} + \frac{w_1}{d_1}.$$

W and D representing the weight and density of the resulting alloy, and w w_1 d d_1 the same with regard to the constituents.

ALLOYS.

Some general remarks respecting metallic alloys are given, §§ 5 and 6.

§ 43. *Copper-Tin Alloys.**

Exp. 96. Weigh out 842 grains of copper and 158 grains of tin; place the copper in clay crucible with a little charcoal; cover with lid, and place in hot fire. When melted add the tin; take out of furnace; remove lid; give a rotatory motion to crucible to well mix the contents, or stir with a charred stick, and pour into rectangular mould (Fig. 17 *e*). When cold fix the ingot in vice and strike with hammer until fracture occurs. Observe the reddish yellow colour, close fine-grained fracture, and moderate toughness. It corresponds to $Cu_{10}Sn$, and is fairly malleable.

Exp. 97. Take 828 grains copper and 172 grains tin. Melt with charcoal, as before. Notice that it resembles the alloy (Exp. 96) but is less malleable and tough, and may be represented by Cu_9Sn.

Exp. 98. Take 810 grains copper and 190 grains tin. Melt and cast as before. Notice the yellowish red colour and fine-grained fracture. It is still less malleable and tough than No. 96. Formula Cu_8Sn.

Exp. 99. Take 789 grains copper and 211 tin. Melt and cast into mould. Observe that the colour is similar to No. 98, that the fracture is vitreous and conchoidal and the metal feebly malleable. Formula = Cu_7Sn.

* Cu = 63; Sn = 118.

Exp. 100. Take 762 grains copper and 238 tin. Melt and cast as before. Notice the pale red colour, the fine-grained vitreous fracture, its brittleness in the cold and malleability at red heat. Formula = Cu_6Sn.

The alloys given in Exps. 96 to 100 are used for bell-metal.

Exp. 101. Take 727 grains copper and 273 grains tin. Melt and cast as usual. Observe its yellowish white cast of colour, its extremely fine-grained conchoidal fracture, its great brittleness and ready fusibility as compared with copper. Formula = Cu_5Sn.

Exp. 102. Take 681 grains copper and 319 grains tin. Melt and cast as usual. Observe that this alloy is also very fine grained, very brittle, easily pulverable, and has a conchoidal fracture. This mixture is termed Speculum Metal. Formula = Cu_4Sn.

Exp. 103. Take 616 grains copper and 384 grains tin. Melt and cast. Observe the dark bluish grey, crystalline structure, the brittleness, and that it may easily be pulverised in a mortar. The long crystalline plates run in a direction transverse to the longer axis of the ingot, producing a somewhat rough appearance, quite different from the preceding alloys. Formula Cu_3Sn.

Exp. 104. Take 516 grains copper and 484 grains tin. Melt and cast. Observe the greyish white colour, the vitreous and conchoidal fracture inclining to crystalline, and that it is very brittle. This may be termed white bronze. Formula Cu_2Sn.

Exp. 105. Take 348 grains copper and 652 grains tin. Melt and cast. Observe its whitish grey colour, and large crystalline plates, which give it a lamellar structure, and its brittleness. Formula CuSn.

Exp. 106. Take 211 grains copper and 789 grains tin. Melt and cast. Notice its irregularly crystalline fracture and tin grey colour; that it is whiter than the preceding one; moderately hard, and somewhat malleable. Formula $CuSn_2$.

Exp. 107. Take 151 grains copper and 849 grains tin. Melt and cast. Notice that the colour is whiter than the preceding alloys; that it is crystalline when cooled slowly; tough, fairly malleable, soft, and easily fusible. Formula $CuSn_3$.

Exp. 108. Take 96 grains copper and 904 grains tin. Melt and cast. Observe that it is as soft as tin, of a greyish white colour, partly crystalline and partly granular, giving a rough heterogeneous appearance to the fractured surface; and that it is tough and malleable. Formula $= CuSn_5$.

§ 43A. With regard to the foregoing series of copper-tin alloys, only $SnCu_3$ and $SnCu_4$ remain unchanged when solidified; all the others undergo a certain amount of liquation, causing a different composition at the top to that at the bottom of the ingot, so that in determining the mean specific gravity two experiments must be made—one with a piece from the top portion, and the other with a piece filed off the bottom. In alloys rich in tin expansion takes place, so that the specific gravity is less than the mean of the two metals, down to the proportion $CuSn_2$. Alloys rich in copper undergo a contraction which reaches a maximum at $SnCu_3$; therefore, the specific gravity is greater than the mean. The greatest density is found in the alloy $SnCu_3$, which is 8·91; even gun metal has only a density of 8·84.

The alloy $SnCu_3$ is distinguished from all the rest by several characters: it has the same homogeneous com-

position after repeated fusions; is peculiar in colour; has the greatest density, and is very brittle.

The hardness, reckoning from pure tin, increases with the proportion of copper up to CuSn. This and all alloys up to $SnCu_5$ are very brittle, and from this the hardness diminishes as the proportion of copper increases. It must be understood that the formula given with each does not imply that they are all true chemical compounds.

§ 43B. Exp. 109. Make the bronzes (Exp. 98 and 99) red hot, and cool by plunging into water; prove that the density has increased, and that they are comparatively soft when tested with a file. Repeat the heating, and allow to cool slowly; prove that the density is lowered and that the alloy is harder. It will be observed that this is the opposite of steel under the same conditions. These bronzes readily break when worked at the ordinary temperature; but at temperatures a little below dull redness they may be forged like bar iron, and easily hammered into thin plates. "Alloys containing 88 to 94 per cent. of copper, which are malleable at ordinary temperatures, are not increased in density by slow or sudden cooling." —*A. Riche.*

§ 44. *Copper-Zinc Alloys.**

The effect of small quantities of zinc on copper is to render its red colour paler; a larger quantity makes it yellow, the brightest yellow being obtained by the alloy containing equal parts of copper and zinc. Beyond this, when the zinc largely predominates, the colour gets paler; and when the proportions equal the alloy $CuZn_3$ the colour is bluish white, resembling impure zinc. With regard to this subject, Karsten makes the following remarks: "In certain proportions the alloy of copper and zinc is more ductile than copper at ordinary temperatures, but generally brittle at a red heat. Very small quantities of zinc do not impair the ductility of copper at ordinary temperatures, excepting that when thus alloyed it sooner becomes hard and brittle by hammering, and therefore requires to be oftener heated to redness; but even ·6 per cent. of zinc is sufficient to cause copper to crack when hammered at a red heat. The most ductile of the alloys of copper and zinc are those which contain 84·5 per cent. copper to 15·5 per cent. zinc (tombac), and 71·5 copper to 28·5 zinc (brass). The alloy formed of equal weights of the two metals cracks in rolling. Excess of zinc renders the alloy brittle, the most brittle being Cu_2Zn_3 and $CuZn_2$. Small quantities of lead in copper-zinc alloys diminishes the ductility; tin increases their hardness." Brass turns red when rubbed with hydrochloric acid, because zinc is dissolved in preference to copper; but when rubbed with ammonia it turns white, because the ammonia dissolves out the copper.

Exp. 110. Take 906 grains copper, 94 zinc. Place the copper in a clay crucible with a little charcoal, in sufficient quantity to cover the surface when melted;

* Cu = 63. Zn = 65.

place in a hot fire and melt. Now remove from furnace, and drop in the lump of zinc weighing 94 grains, and quickly mix the contents by stirring with a piece of wood. The crucible is by this means filled with flame and gases from the decomposition of the wood, keeping out the air to a great extent, and diminishing the oxidation of the zinc; then pour the alloy into a rectangular mould; allow to cool, and weigh. The loss of weight may be taken roughly to indicate the loss of zinc. Now calculate the proportion of copper to zinc on the above assumption, *i.e.*, if the metal has been poured clean from the crucible. If the above operation is not very rapidly performed, the metal will solidify and require remelting, in which case more charcoal should be added, but the loss of zinc will be considerable. It would be better in such a case to repeat the experiment. Suppose the alloy as above to weigh 990 grains. Assuming that 990 grains contain 906 grains copper and 84 grains of zinc, 1000 grains will contain :—

$$\frac{906 \times 1000}{990} = 915{\cdot}1 \text{ copper.}$$

The alloy then contains 91·51 grains copper to 8·49 grains of zinc per cent. Repeat the experiment, adding zinc in excess of the stipulated quantity. The alloy should have a reddish yellow colour when filed, a fracture resembling dry copper, partly granular, partly fibrous; be somewhat tough, and malleable. This may be termed red brass. The proportions given correspond to the formula $Cu_{10}Zn$.

Exp. 111. Take 829 grains copper and 171 grains zinc. Melt the copper first, and add the zinc with precautions as in Exp. 110. The colour should be yellowish red, with fine fibres running across the fractured surface; it should be malleable, tough, and correspond to the

formula Cu_5Zn. It is known as Princes metal or Bath metal.*

Exp. 112. Take 795 grains copper and 205 grains zinc. Melt copper and add zinc as before. Notice the yellowish red colour and fine fibred fracture, also that it is tough but less malleable than the preceding one. This is the composition of Tombac,* and when hammered into leaves is called Dutch metal. Formula = Cu_4Zn.

Exp. 113. Take 744 grains copper and 256 grains zinc. Melt copper and add zinc. Observe the pale yellow colour, and nature of the fractured surface with fine fibres. It is less tough than the preceding one, but more malleable, easily fusible, and moderately hard, the working qualities being about the same as common brass. It is known as Mosaic gold.* Formula = Cu_3Zn.

Exp. 114. Take 660 grains copper and 340 grains zinc. Melt and add zinc as before. Notice the deep yellow colour, the finely fibrous fracture. This forms English yellow brass. It is very malleable and ductile, moderately soft, tenacious, and melts at a medium temperature. Formula = Cu_2Zn.

Exp. 115. Take 492 grains copper and 508 grains zinc. Melt copper and add zinc as before. Observe the deep yellow colour, coarsely granular fracture, and that it is only moderately tough and malleable in the cold. Very flexible when hot, but not adapted for wire drawing. It is known as German brass.* It is also the composition for hard solder for braizing. Formula = CuZn.

Exp. 116. Take 326 grains copper and 674 grains zinc. Melt copper and add zinc as before. Notice the yellowish

* These names are used for alloys containing various proportions of copper and zinc. For further information see author's work on "Mixed Metals," pp. 90 and 102.

white colour, coarsely granular fracture, its brittleness and low fusing point. It is very tenacious, being far superior in this respect to several of the preceding alloys. It is said to be used by watchmakers. Formula = $CuZn_2$.

Exp. 117. Take 353 grains copper and 647 grains zinc. Melt copper and add zinc as before. Notice its white colour, conchoidal vitreous fracture, its great brittleness, hardness, and easy fusibility. This may be termed white brass. Formula = Cu_8Zn_{17}.

Exp. 118. Take 244 grains copper and 756 grains zinc. Melt and add zinc as before. Notice its bluish white colour, fine grained fracture, brittleness, hardness, and easy fusibility. Formula = $CuZn_3$.

§ 45. Besides the alloys of copper with zinc mentioned in the foregoing examples, many other preparations are in general use, thus :—

Muntz metal, formerly largely used for sheathing for ships, as it keeps them cleaner and is less costly than copper sheathing, consists of 600 copper and 400 zinc; but the proportions of copper vary from 56 to 63 per cent. according to the ideas of the manufacturer. In some cases 2 to 3 per cent. of lead is added.

Brass Solder.—Two parts by weight of ordinary brass, with one part of zinc. This corresponds to 44½ parts copper and 55½ parts zinc.

The following table shows the composition of some ancient and modern bell metals containing zinc :—

	Cu.	Sn.	Zn.	Ni.	Fe.
Modern English Bell Metal,	80·0	14·4	5·6	0	0
Darmstadt Chimes (1670), -	73·9	21·6	1·2	1·2	2·1
Bells of Rouen, 12th century,	70	26·0	1·8	·6	1·6

Useful Alloys of Copper and Zinc.

	Cu.	Zn.	Sn.	Pb.	Sb.	Fe.
Bronze for Statues,	91·4	5·53	1·7	1·37		
Brass for gilding,	82·16	17·48	·24	·12		
Do. do.,	80	16·5	2·5			
Sheet brass,	84·7	15·3				
Gilding metal,	83	17				
Pinchbeck,	90	10				
Prince's metal,	75	25				
Dutch metal,	80	20				
English wire,	70	30				
Gun metal,	90		10			
Muntz metal,	60	40				
Brass for turning and for machinery,	65	33		2		
Britannia metal,	3		90		7	
Brass for ship nails,	62·82	25·64	2·64	8·89		
Tombac,	80 to 90	20 to 10				
Bronze colour, pale yellow	83·33	16·66				
,, ,, deep ,,	84·6	15·3				
,, ,, orange,	98·9	1·1				
,, ,, copper red,	99	1				
,, ,, violet,	98·5	1·5				
,, ,, yellow,	84·62	15·37				
Aich metal,	60·0	38				2
Sterro metal,	58	38	2			2

Exp. 119. Calamine brass is a variety of brass made from calamine, instead of adding zinc direct to the copper.

Take 500 grains of oxide of zinc, 100 grains charcoal, and 330 grains of sheet copper, cut up fine. Place in clay crucible; cover with a layer of charcoal; cover with lid; lute on with clay, and heat very strongly for an hour. Remove from fire; allow to cool; break open the crucible, and examine the button of brass.

§ 46. *Other Alloys of Copper.*

* *Bronzes—(a) Phosphor bronze.* This is an alloy of copper, tin, and phosphorus prepared first by Dr. Künzel of Dresden, although other ingredients are now added. It may be made as ductile as copper and as hard as steel, by varying the proportions of the constituents. It forms a very fluid metal for castings, which are sound and uniform. It is stronger, tougher, and more durable than gun-metal or brass, and does not become crystalline with repeated shocks or bends; hence its use for wire rope. It is less acted on by sea water than copper. This alloy may be made by adding a rich alloy of phosphor tin to the right proportion of copper and tin, or a rich phosphor copper may be used. See Exps. 12*a* and 17 for the production of this substance. Although no phosphorus may remain in the bronze, it removes the oxygen, and promotes a more intimate mixture of the particles of copper and tin. With too much phosphorus, the alloy becomes very hard and brittle.

(*b*) *Silicon bronze.* This is a similar alloy to phosphor bronze, the phosphorus being replaced by silicon, which produces an alloy having a much higher conductivity than phosphor bronze, as the presence of phosphorus has a most injurious effect on electrical conductivity. Silicon bronze has great strength and durability, so that with this alloy the wires may be thinner than the ordinary wire, and yet have the same strength. Also when broken they coil up and spring back in consequence of their elasticity, instead of falling to the ground. This alloy may be prepared by strongly heating copper with sand and carbon, then alloying the silicon-copper with the necessary amount of tin. Or take 250 grains of potassium-silico-fluoride, 300 grains of glass, 125 grains of

* See author's work on "Mixed Metals," pp. 192 to 229.

common salt, 40 grains of carbonate of soda, 30 grains of carbonate of lime and 250 grains of dried calcium chloride. Heat in a plumbago crucible until they just begin to act on each other, then add molten copper or bronze as the case may be.

(*c*) *Manganese bronze.* This alloy is prepared by mixing a small proportion of rich ferro-manganese with copper and tin. The ferro-manganese is melted in a separate crucible and added to the molten copper. In this way the manganese unites with any oxygen in the copper, and rises to the surface as slag, so that its action resembles that of phosphorus; but a little manganese and iron alloy with the copper, which is then used for making alloys with tin and zinc. The toughness, hardness, and strength is thereby increased, which can be modified in different degrees by altering the proportion of ferro-manganese used, so that the amount of manganese can be regulated with great nicety. About four varieties of ferro-manganese are employed, containing 10 to 40 per cent. of manganese. The lower qualities are used for those copper alloys in which zinc exceeds the tin, and the higher qualities for those in which tin alone is used with copper. The amount of ferro-manganese added varies from 2 to 4 per cent. The bronze forms very sound and uniform castings, and is claimed to have the strength, toughness, and hardness of mild steel, without any of its defects. It also offers great resistance to pressure. Manganese bronze may be made by adding 10 per cent. of cupro-manganese to an alloy of 800 parts copper and 100 parts tin. See Exp 23*a*.

(*d*) *Delta metal.* This alloy, so named by Mr. Dick, is an alloy of copper, zinc, and iron, having a close analogy to the corresponding manganese bronze, but contains no manganese. Attempts were made some twenty-five years ago to utilise such a combination, but the alloys were

uncertain in their character from the amount of iron being very variable, and Mr. Dick set himself to discover a means of introducing a known and definite quantity of iron in each alloy. He does this by melting iron in zinc, till the latter is saturated, and using this ferro-zinc to alloy with the copper, with or without pure zinc. The alloy is liable to oxidise when re-melting for casting, thus altering the composition; to remedy this a little phosphorus is used in combination with the copper. In some special alloys a little manganese, tin, or lead is added to impart particular properties. Delta metal has a specific gravity of 8·4; is very liquid when melted, producing sound and fine grained castings. The cast metal resists a tensile strain of 20 tons to the square inch. When forged at a dark red heat, its breaking strain is raised to 35 tons, and when hammered cold, it reaches 40 tons to the square inch. It is stated that the iron in the alloy is chemically combined, as the metal does not rust in moist air nor does it affect the magnetic needle. The copper varies from 58 to 63, and the iron from 1 to 3 per cent., and the remainder is zinc.

(*e*) *Aluminium bronze and Aluminium brass.* This was originally composed of ninety parts copper and ten parts aluminium, and is stated to be a definite compound of the formula Cu_9Al. It has a gold colour; is extremely hard; takes a high polish; has a high tenacity (43 tons to the square inch), and is very malleable.

An addition of 2 to 3 per cent. of brass to aluminium bronze increases its strength, and renders it less susceptible to oxidation.

When the aluminium reaches 19 to 20 per cent. in a copper-aluminium alloy, a brittle compound is produced. Aluminium bronze may be made by melting the two metals together, but the aluminium must be placed at the bottom of the crucible and the metals covered with charcoal, as well as the crucible being covered with a lid,

so as to exclude the air. Other metals, such as zinc, tin, and iron, may be added for special purposes. Aluminium brass is manufactured by adding zinc or brass to aluminium bronze. The composition is between the following limits:—Copper 67 to 71, zinc 31¾ to 25½, aluminium 1¼ to 3½.

It is sometimes stated as an objection that some kinds of aluminium bronze contain no aluminium; still the small amount of this metal used in its manufacture may have a very beneficial effect on the resulting alloy in the same way as phosphorus has in phosphor-bronze, of which some varieties retain only a mere trace of phosphorus.

§ 47. *Alloys containing Nickel and Cobalt.*

The chief alloys of these metals are those with copper and zinc, known as German silver or nickel silver. The copper and nickel are first melted, then heated zinc is added as in making brass. Or sheet copper and nickel may be cut up small, mixed with zinc; placed in a crucible, covered with charcoal, the lid luted on, and the whole strongly heated together for half an hour; then removed from fire, allowed to cool, and the pot broken to recover the alloy. It has a white colour and crystalline structure, but after careful annealing may be rolled into sheet. When the crystalline structure has once been destroyed, German silver may be worked like brass. It is white like silver, harder, and admits of a fine polish.

(*a*) Weigh out 600 grains of copper and 80 grains of nickel, place in clay crucible with a little charcoal, cover with a lid and heat very strongly until the whole is melted, then add a lump of zinc weighing 340 grains, and quickly mix the contents by stirring with a piece of wood. (See Exp. 110.) Pour into a rectangular mould, cool, and weigh. Then break the ingot, and observe that

the colour is much paler than brass. Also notice that *it is very tough* and fairly malleable. It contains 8 per cent. of nickel.

(*b*) Repeat the previous experiment with 570 parts of copper, 120 parts of nickel, and 325 parts of zinc. Test its malleability and toughness as in previous case. Observe that it is also whiter in colour. It contains 12 per cent. of nickel.

(*c*) Repeat Experiment (*a*) with 540 parts of copper, 160 parts of nickel, and 315 parts of zinc. Observe that it is whiter than (*b*), also very tough and malleable. It contains 16 per cent. of nickel.

(*d*) Repeat Experiment (*a*) with 540 grains of copper, 200 grains of nickel, and 270 grains of zinc. Observe that this alloy is still whiter than the last, and that it is malleable and tough. It contains 20 per cent. of nickel.

(*e*) The following analyses give the composition of some higher qualities of German silver:—

Copper.	Nickel.	Cobalt.	Zinc.	Lead.
50	31	—	19	—
53	27	—	20	—
48½	24½	—	24	3
59	22	—	19	—
55	22	—	23	—
60	19	3	18	—

§ 48. Messrs. Wiggin & Co., of Birmingham, have introduced an alloy called "silveroid," consisting of copper, nickel and zinc, with tin, or lead in various proportions, which has great whiteness, closeness of grain, and great tensile strength.

Cobalt bronze is still whiter than silveroid, has a close grain, brilliant lustre, great toughness and tensile strength as well as hardness. It contains, in addition to the above, small quantities of cobalt

§ 49. *Lead Alloys.*

(*a*) Lead alloys with tin in all proportions, but the specific gravities are less than the mean of the constituents. Küpffer investigated this subject with the following results. The symbols represent atomic proportions :—

Alloy.	Specific Gravity.		Melting Point.
	Found.	Calculated.	
SnPb,*	9·426	9·437	241°C.
$SnPb_2$,	10·078	10·094	—
$SnPb_3$,	10·387	10·412	239°
$SnPb_4$,	10·555	10·600	—
Sn_2Pb,	8·745	8·752	196°
Sn_3Pb,	8·291	8·398	186°
Sn_4Pb,	8·173	8·151	189°
Sn_5Pb,	8·028	8·037	194°
Pb,	11·380	—	335°
Sn,	7·291	—	230°

* Sn = 118 : Pb = 207.

The above is also interesting as showing the influence of different proportions on the melting point.

The effect of lead on tin is to harden it, notwithstanding that lead is so soft when alone. The softest alloys of lead and tin are those with excess of lead.

(*b*) With 750 parts lead and 250 parts tin, the alloy has a rough and dull surface. This may be termed common solder. With equal parts of lead and tin, the surface is brighter. This may be termed medium solder. With 250 parts lead and 750 parts tin, the surface is bright, with a dull longitudinal furrow. This is more fusible than the above, and may be termed best solder.

(*c*) Lead-tin alloys are largely used for soft soldering by plumbers and others, the composition varying with the work required to be done. Solders may be roughly classified into fine, medium, and common.

In fine solders the tin is in excess as Sn_3Pb, Sn_4Pb, etc. In medium, the proportions are about equal. In common, the lead is greater than the tin. Plumbers' solder consists of 1 part tin to 2 parts lead. For soldering cast iron the alloy of 1 to 1 is used. For fine metal work the best solders are used, viz., those with excess of tin.

(*d*) In many kinds of work it is necessary to solder a part without over-heating the article, so as not to discolour or fuse it, in which case a very easily melting alloy is required. These are known as "quick" solders or "fusible" alloys, in which bismuth is an important constituent. The alloys in the following table, with their melting points, are those given by Messrs.

Parkes & Martin. The temperatures given are probably too low.

Bismuth,	8 pts.	Lead,	5 pts.	Tin,	3 pts.	Melts at	95°C.
,,	8 ,,	,,	6 ,,	,,	3 ,,	,,	98°
,,	8 ,,	,,	8 ,,	,,	3 ,,	,,	110°
,,	8 ,,	,,	8 ,,	,,	4 ,,	,,	112°
,,	8 ,,	,,	8 ,,	,,	6 ,,	,,	116°
,,	1 ,,	,,	1 ,,	,,	1 ,,	,,	122°

(*e*) *Pewter* is an alloy of lead and tin. Common pewter contains 80 parts tin and 20 parts lead; it is also made with equal parts of the two metals. Other metals, as antimony, zinc, and copper, are sometimes added. The finest pewter consists chiefly of tin with only a little lead and copper. The copper is melted, and twice its weight of tin added; then from ½ lb. to 7 lbs. of this alloy are added to 390 lbs. of block tin. A little zinc is sometimes added to purify the alloy and bring the dross to the surface.

§ 50. *Antimony Alloys.*

The effect of antimony on other metals is to harden them and make them brittle. It is also a volatile metal, therefore the atmosphere should be excluded by means of a covering of charcoal while melting antimony or any of its alloys.

(*a*) 50 parts copper melted in a crucible, then 50 parts of antimony added, produce a very brittle alloy of a violet colour termed "Regulus of Venus."

(*b*) 50 parts lead, 25 parts tin, 25 parts antimony, produce a hard brittle alloy, with a fine crystalline struc-

ture, used for stereotype and type, and known as type metal.

(*c*) 80 parts tin, 10 parts copper, 9 parts antimony, and 1 part lead, is a typical mixture for Britannia metal. It is greyish white in colour, with a tendency in one portion of the alloy to liquate out on cooling, producing a partly crystalline and partly granular fracture. It is brittle when cold. These proportions, as well as the metals, are varied by different makers. The following table illustrates this point :—

	a.	*b.*	*c.*	*d.*	*e.*
Tin, - -	94	90	84	80	75
Antimony, -	5	7	10	10	8·5
Copper, -	1	3	4	9	—
Bismuth, -	—	—	2	—	8
Lead, - -	—	—	—	1	8·5

§ 51. *Silver Alloys.*

(*a*) The most important alloys of silver are those with copper. The two metals can be melted together in almost any proportion, forming for the most part ductile and malleable alloys, with great hardness and elasticity, and are capable of taking a higher polish than pure silver. The specific gravities of silver-copper alloys are less than the mean of the two metals. The colour is white until the copper exceeds one half. The hardest alloy is stated by Guettier to contain one part silver and two parts copper. Prof. Roberts-Austen has determined the melting points, and states that the alloy containing 630·29 of silver per 1000, and represented by the formula AgCu, has a lower melting point than silver, or than any other alloy of silver and copper. His results are given in the following table, but he has since pointed out that

they are too high, as more recent determinations of the melting point of silver make it 940° C., and that of copper 1050° C.

No.	Pure Silver per 1,000.	Approximate Formula.	Melting Point.
1.	1000	Ag	1040°C.
2.	925	Ag_7Cu	931·1°
3.	820·7	Ag_3Cu	886·2°
4.	798	Ag_5Cu_2	887°
5.	773·6	Ag_2Cu	858·3°
6.	750·3	Ag_7Cu_4	850·4°
7.	718·93	Ag_3Cu_2	870·5°
8.	630·29	AgCu	846·8°
9.	600	Ag_7Cu_8	857°
10.	569·6	Ag_7Cu_9	899·9°
11.	561·1	Ag_3Cu_4	917·6°
12.	540·8	$Ag_{20}Cu_{29}$	919·8°
13.	500	Ag_3Cu_5	940·8°
14.	497	$Ag_{25}Cu_{43}$	962·6°
15.	459·4	$AgCu_2$	960·8°
16.	250·5	$AgCu_5$	1114·1°
17.	Pure Copper.	Cu	1330°

No. 7 is Levol's homogeneous alloy, being uniform in composition, while many others undergo liquation on cooling. No. 8 has the simplest atomic relation and the lowest melting point.

(*b*) Silver-copper alloys, when cast into a mould and allowed to cool, have a different composition in different parts, the difference being in many cases much greater when rapidly cooled than when slowly cooled; Levol's

alloy being an exception, as its composition is uniform whether rapidly or slowly cooled.

(*c*) When a silver-copper alloy is heated in a muffle, the latter metal is oxidised in proportion to the amount in the alloy, and affords a rough indication of its composition, by examination of its oxidised surface.

(*d*) In this country there are two standards, known as the Old and New Standards—

Old, 925 parts Ag and 75 parts Cu, which is the proportion in the present silver coinage, also called sterling silver.

New, 959 parts Ag and 41 parts Cu. This was legalised in 1697, but is very seldom used, not being so durable as the 925 alloy. They are expressed per ounce thus :—

	Old Standard.			New Standard.		
	oz.	dwts.	grs.	oz.	dwts.	grs.
Fine silver, - -	0	18	12	0	19	4
Copper, - -	0	1	12	0	0	20
	1	0	0	1	0	0

As standard silver may be Hall-marked, it is important that the full amount of precious metal be present, and as commercial fine silver is not absolutely pure, a little more than the above quantity must be used, thus :—

	Old Standard.			New Standard.		
	oz.	dwts.	grs.	oz.	dwts.	grs.
Fine silver, - -	0	18	14	0	19	6
Copper, - -	0	1	10	0	0	18
	1	0	0	1	0	0

(*e*) The following list shows the composition of various commercial alloys of silver and copper:—

	oz.	dwts.	grs.	Ag per 1000.
1. Ag,	0	18	0	= 900
Cu,	0	2	0	
	1	0	0	
2. Ag,	0	16	0	= 800
Cu,	0	4	0	
	1	0	0	
3. Ag,	0	15	0	= 750
Cu,	0	5	0	
	1	0	0	
4. Ag,	0	14	0	= 700
Cu,	0	6	0	
	1	0	0	
5. Ag,	0	13	12	= 675
Cu,	0	6	12	
	1	0	0	
6. Ag,	0	13	0	= 650
Cu,	0	7	0	
	1	0	0	
7. Ag,	0	12	12	= 625
Cu,	0	7	12	
	1	0	0	
8. Ag,	0	12	0	= 600
Cu,	0	8	0	
	1	0	0	

The alloy No. 8 is as low as it is possible to make without a perceptible change of colour, so that if still inferior compositions are desired, other white metals must be added, such as nickel and zinc.

The French had three standards, viz.: 950, 900, and 800 of silver per thousand.

In Germany there are four standards, viz.: 950, 900, 800, and 750 of silver per thousand.

§ 52. *Silver Solders.*—These are silver alloys used for joining the various parts of articles together by fusion.

The solder must, therefore, have a lower melting point than the body to be soldered with it, yet the fusing point of the solder should approach as near as it conveniently can to that of the article, as a more perfect and more tenacious junction may thus be effected.

The hardest solders consist of copper and silver; the next in point of fusibility are those containing a little zinc in addition to the silver and copper, and the easiest consist of copper, silver, and tin; or brass, silver, and tin.

With regard to the alloys of silver and copper given on the previous page, the lower ones may be used as solders for the higher ones, it does not follow that the fusing point becomes lower, as the silver is diminished; for by reference to the table, § 51A, it will be seen that Nos. 6 and 8 have lower fusing points than No. 9. The following compositions are used as solders :—

	1.	2.	3.	4.	5.	6.	7.
Silver, - -	384	384	360	336	300	300	300
Copper, - -	84	12	96	108	144	—	—
Zinc, - - -	12	—	24	36	36	—	30
Brass ($Cu66\frac{1}{2}$ $Zn33\frac{1}{2}$),	—	84	—	—	—	150	150
Tin, - - -	—	—	—	—	—	30	—
	480	480	480	480	480	480	480

In making the above alloys the copper and silver must be melted first, and the zinc added, using the precautions mentioned in making brass.

§ 53. *Gold Alloys.*

Pure gold is a soft metal, which makes it unfit for many industrial purposes, so that it is usually alloyed with other metals to harden it and yet allow it to retain much of its malleability and ductility. The metals most

generally alloyed with gold are silver and copper. Pure gold is described as 24 carat fine; the pound or 1000 parts being divided into 24 carats; and different alloys are spoken of as being so many carats fine, according to the amount of gold present. The British coinage consists of 22 parts gold and 2 parts copper, hence it is 22 carats fine; this proportion is known as standard gold, although the copper may be replaced partially or wholly by silver. It is of the utmost importance that the alloying metals should be as pure as possible, as the small quantities of arsenic, antimony, lead, etc., which are often present in common copper, would entirely destroy the high malleability and ductility of the alloy. Pure gold has a beautiful yellow colour, but small quantities of other metals alter its peculiar tint, so that different coloured alloys may be formed, thus:—18 parts gold and 6 parts copper form a red, 18 parts gold and 6 silver a green, 18 gold and 6 iron blue, 12 gold and 12 silver, a white alloy. Platinum may be substituted for the silver.

18 carat gold is employed for the manufacture of the best kinds of jewellery, being the second English standard. It is hard, malleable, tenacious, and exceedingly ductile. It is composed of 18 parts gold, 3 parts silver, and 3 parts copper, which proportion is found to work better than with copper alone.

15 carat gold consists of 15 parts gold, 3 parts silver, and 6 parts copper. This is a good alloy to work and very durable.

13 carat gold contains 13 parts gold, 3 parts silver, and 8 parts copper.

12 carat gold—containing 12 parts gold, 3½ parts silver, and 8½ parts copper—is called best bright gold, to distinguish it from the higher alloys which admit of being coloured. It is tolerably soft, malleable, and ductile.

10 carat gold possesses properties very similar to the preceding one. It contains 10 parts gold, 4 parts silver, and 10 parts copper.

9 carat gold consists of 9 parts gold, 4½ parts silver, and 10½ parts copper. This is a good, tough, workable alloy, and is almost the lowest proportion of gold which will withstand the action of nitric acid.

The following table shows the proportion of various jewellers' alloys :—

Carat.	Copper.	Silver.	Gold.
23	½ part	½ part	23 parts
22	1 ,,	1 ,,	22 ,,
20	2 parts	2 parts	20 ,,
18	3 ,,	3 ,,	18 ,,
15	6 ,,	3 ,,	15 ,,
13	8 ,,	3 ,,	13 ,,
12	8½ ,,	3½ ,,	12 ,,
10	10 ,,	4 ,,	10 ,,
9	10½ ,,	4½ ,,	9 ,,
8	10½ ,,	5½ ,,	8 ,,
7	9 ,,	8 ,,	7 ,,

In addition to the above, a little brass is added in some cases to make a hard alloy ; more than this makes the gold brittle and unworkable.

§ 54. *Gold Solders.*

The remarks made with respect to silver solders apply also to gold. Many goldsmiths make the solder from the same gold as that of which the article to be soldered is composed, by adding more copper and silver. The following three qualities may be taken as types :—

	Gold.	Silver.	Copper.
Best,	12½ parts	4½ parts	3 parts
Medium,	10 ,,	6 ,,	4 ,,
Common,	8½ ,,	6½ ,,	5 ,,

§ 55. *Amalgams.*

Gold and mercury readily unite in several proportions, the amalgam being still white when the proportion is 2

parts gold to 1 part mercury. The combination is more rapid when the metals are in a finely divided state and heated. The pasty amalgam of 2 parts gold and 1 part mercury was formerly much used for gilding, the mercury being afterwards volatilised by heat.

(*a*) Silver and mercury easily combine to form amalgams of different proportions in the cold, but they unite much more readily when heated. Native amalgams of the following composition have been found—Hg_2Ag_2; Hg_3Ag_2; Hg_6Ag_2. The character of silver amalgams varies with the composition and mode of formation. They may be soft, granular, or crystalline. The amalgam used in plating consists of 85 per cent. mercury and 15 per cent. silver.

(*b*) Tin and mercury form amalgams in the cold, and more readily by pouring mercury into molten tin. A pasty amalgam of these metals is used for silvering mirrors. A bar of tin rubbed round the middle with mercury becomes exceedingly brittle and may be readily broken.

(*c*) An amalgam of 2 parts tin and 1 part cadmium with excess of mercury is used for stopping teeth. An amalgam made of 1 part gold, 3 parts silver, 2 parts tin, and 6 parts mercury, is used as a cement for teeth.

(*d*) Zinc used in voltaic batteries is amalgamated with mercury to prevent the action of acid when the circuit is open.

(*e*) Sodium amalgam is made by triturating the two metals together in a porcelain mortar fitted with a cover, when combination takes place with violence, with the production of heat, light, and a hissing sound. 30 parts mercury to 1 part sodium is moderately hard, with a

crystalline fracture ; 60 parts mercury and 1 part sodium is pasty ; 128 parts mercury to 1 part sodium is liquid.

Sodium amalgam is very effectual in promoting the amalgamation of gold and silver, in extracting these metals from their ores.

(*f*) Platinum and mercury do not unite when the former metal is in the compact state, but spongy platinum triturated with mercury and heated forms an amalgam.*

FORMATION OF METALLIC OXIDES.

§ 56. (*a*) The most important compounds of metals with non-metals are the oxides. Many valuable ores occur in this form, and in most cases it is the easiest combination from which to isolate the metal. When the oxides contain hydrogen they are said to be hydrated, thus : CuO is copper oxide ; CuH_2O_2, copper hydrate or the hydrated oxide of copper. The effect of oxygen is to entirely destroy the metallic character, to form hard and brittle compounds when in the native state, to lower the specific gravity, to raise the melting point, and to reduce the volatility. A few of the oxides, however, are volatile, such as those of arsenic. Most oxides are powerful bases, neutralising acid substances completely and forming neutral compounds.

(*b*) As a general rule, not without exceptions, the affinity of a metal for oxygen is in inverse ratio to its specific gravity ; sodium and potassium being most easily oxidised, while gold and platinum have no tendency to combine with oxygen.

* For fuller information respecting alloys see the author's work on "Mixed Metals," Macmillan & Co, Ltd.

(*c*) Most metals combine directly with oxygen when heated in air, such as lead, zinc, iron, etc., an operation which is greatly facilitated by a fine state of division; thus when iron is reduced from its oxide by hydrogen gas and the metal brought into contact with air, a spontaneous combustion takes place, reproducing the oxide. Some metals such as sodium have so strong an affinity for oxygen that they require to be preserved in a liquid free from that element. Oxides are often formed by heating in air metallic compounds such as sulphides and arsenides. Many oxides when heated in air take up additional oxygen forming higher oxides; thus litharge (PbO) is converted into red lead (Pb_3O_4). Oxides are also formed from the decomposition of carbonates, most of which are decomposed at a red heat (as in burning limestone to form quicklime), or from the reduction of the nitrate by heat. Many metals decompose steam at a red heat, forming oxides. Lower oxides are sometimes formed from the higher ones, thus the red oxide of copper (Cu_2O) is formed by fusing together the black oxide (CnO) and metallic copper; the tetroxide of manganese (Mn_3O_4) by heating strongly the black oxide (MnO_2). The symbol for oxygen is O, and its atomic weight 16.

(*d*) Some oxides are built up on the H_2O type; as K_2O, Na_2O, Cu_2O, etc. Others contain an equal number of atoms of the element; as CuO, PbO, etc. Others contain double as many atoms of oxygen as the metal; as PbO_2, MnO_2, and SnO_2, generally called peroxides. In some cases the ratio is as 2 : 3; as Fe_2O_3, Al_2O_3, etc., called sesquioxides. In others, as 3 : 4; as Mn_3O_4, Fe_3O_4, Pb_3O_4, etc., called tetroxides. Some have a ratio as 2 : 5; as Sb_2O_5, As_2O_5, Bi_2O_5, etc. In a few cases the ratio is as 1 : 3; as CrO_3.

Exp. 120. Weigh 1000 grains of lead, place in a flat fire-clay vessel known as a roasting dish (Fig. 40), and

heat in a muffle, or over a good Bunsen burner, until melted, keeping the temperature low. A film of oxide soon forms, which may be scraped to one side by means of an iron rod flattened at the end, and turned up at right angles. This process is to be repeated until the whole is oxidised. Then raise the temperature, or push the dish further into the muffle, and press the mass in order to squeeze out any lead mechanically mixed with the oxide, which will soon become oxidised; remove from muffle; allow to cool, and weigh. The following shows the mode of calculation:—

$$\underset{207}{Pb} + \underset{16}{O} = \underset{223}{PbO},$$

taking 207 as the atomic weight of lead, and 16 that of oxygen; then by the equation, 207 parts by weight of lead unite with 16 parts by weight of oxygen to produce 223 parts by weight of lead oxide; therefore 1000 grains of lead will produce $\frac{1000 \times 223}{207}$ grains. $= 1077{\cdot}3$ lead oxide.

$$207 : 1000 : : 223 : 1077{\cdot}3.$$

Great care is required in conducting the above experiment not to work with too high a temperature, or the oxide will fuse and unite with the silicate of which the dish is composed, so that some of the oxide will be lost, while a great part of the remainder will stick to the receptacle, so that it becomes impossible to remove it. In such a case the operation must be commenced again with fresh lead in a new dish. A safer plan, but one taking much longer time, is to heat the dish placed on a tripod stand over a Bunsen burner. The oxide produced in this way, by any one but an experienced workman, is generally much better and freer from lead than when a muffle is used. This oxide should be yellow. The experiment may also be conducted in an iron dish, heated by a circular burner.

Exp. 121. Take 500 grains of tin, place in a roasting dish, and oxidise in a muffle until the whole is converted

into white tin oxide (SnO_2). This operation is much easier than the last and more rapid, because oxide of tin is practically infusible, so that a higher temperature may be employed, and the action completed in half an hour; the lead requiring three or four times as long. Weigh and calculate as before:—$Sn + O_2 = SnO_2$.

Exp. 122. Take 1000 grains of zinc, place in dish, and oxidise as before. A low temperature must be used in this case, as metallic zinc is volatile, although the oxide is not so, neither does it fuse and unite with the fire-clay dish. Zinc oxide is white, very light and bulky, so that a large dish is required. Calculate the possible theoretical quantity from the equation—

$$Zn + O = ZnO.$$

Exp. 123. Take 500 grains of antimony, melt and oxidise as before. This experiment requires the greatest care to obtain anything like an approximate result, the metal being very volatile, and requiring a higher temperature to melt it, so that the temperature must be kept very near the melting point, or very little oxide will be left. The following equation shows the change:—$Sb_2 + 3O = Sb_2O_3$.

This experiment may be performed, in a crucible partly covered with a lid, to show the nature of antimony oxide; it is white in colour, resembling zinc oxide (ZnO).

Exp. 124. Take a strip of copper, place in muffle on a roasting dish, and heat strongly for half an hour; remove, allow to cool, and examine. Notice that it is covered with a black scale; then peel off this film, and notice that it is red underneath on the side which was in contact with the copper. The greater part of the scale is red oxide (Cu_2O), and only the thin outside film which was freely in contact with the atmosphere consists of

black oxide (CuO). Continue the oxidation until the whole strip, when broken, is brittle, and consists entirely of oxide, no trace of copper being left. If the strip of copper be weighed before commencing the experiment, then after its complete oxidation the residue may be taken to be CuO, and its theoretical amount may be computed from the following equation :—

$$Cu + O = CuO.$$

Exp. 125. The red oxide of copper may also be prepared in a crucible thus : Take 200 grains of sheet copper cut up very fine, and add sufficient of the black oxide of copper to give the following reaction :—$CuO + Cu = Cu_2O$.

In conducting this experiment, care must be taken to select a proper crucible, as the red oxide has a great affinity for silicates, especially those in which the silica predominates. Morgan's small "London Round" is very suitable. The crucible, after adding the mixture, should be placed well down in a hot fire, loosely covered with a piece of coke, and the furnace well closed to exclude air as much as possible. In about ten to fifteen minutes the coke should be quickly removed from the top of the crucible, and the finishing stage watched through the space between the two bricks which cover the furnace. As soon as all action ceases, remove from fire, and pour into a round mould. If left after the action is completed, the oxide immediately acts on the crucible, and in a short time will permeate the bottom or sides. The possible quantity obtainable may also be calculated from the above equation.

Exp. 126. Melt 100 grains of bismuth ; keep the temperature low, and scrape the surface as fast as the yellow trioxide forms. Weigh the product when cool. The following equation will indicate the possible amount to be obtained :—

$$Bi_2 + 3O = Bi_2O_3.$$

Melt the oxide in a small crucible; pour into a round mould, and examine the colour and structure.

REDUCTION.

§ 57. (*a*) For metallurgical purposes the only reducing agents which play any conspicuous part are carbon and hydrogen, either alone or in combination; but in some instances the common metals, such as iron, manganese, and lead, as well as sulphides and arsenides, are employed.

Carbon is capable of removing $\frac{4}{3}$rds or $\frac{8}{3}$rds its weight of oxygen respectively, according to the kind of oxide it is mixed with, and the temperature employed for the reduction. In the first case CO is formed, and in the second case CO_2. The former gas is a reducing agent, whilst the latter is oxidising, so that in the case of oxidisable metals like iron, total reduction is impossible, unless the CO is in excess. Thus: suppose the two gases to exist in equal volumes in the presence of Fe_2O_3, this oxide cannot be reduced below FeO, in consequence of the opposing action of the two gases.

(*b*) In all cases where a high temperature is employed to reduce solid matter by carbon, it is most probable that the reduction is effected chiefly by carbonic oxide, which can easily penetrate the pores and fissures to the very centre of each fragment. Moreover, the reduction of oxides, the metals of which have an affinity for carbon, such as iron, nickel, cobalt, etc., is greatly facilitated by the double decomposition which the CO undergoes. The oxide is reduced thus—$FeO + CO = Fe + CO_2$; then the separated iron reacts on more oxide of carbon, thus—$Fe + 2CO = CO_2 + C$; which carbon unites with the iron.

(*c*) When hydrogen acts as a reducing agent for metallic oxides, steam is formed, which is a more powerful oxidiser than CO_2, so that reduction is impossible, unless the hydrogen is present in large excess, and a constant stream of gas maintained to carry away the steam as fast as it is produced.

§ 58. *Reduction of Oxides.*

Exp. 127. Weigh out 500 grains of oxide of lead (litharge) and mix with sufficient carbon to reduce it, calculated from the equation—$2PbO + C = CO_2 + Pb_2$.*
446 12 414

In determining the amount of carbon required to reduce a metallic oxide, it will be necessary to know whether the carbon is completely oxidised, forming carbonic acid, or partially oxidised, forming carbonic oxide, which depends on the temperature at which the reduction is effected. At a low temperature carbonic acid is produced, as in the above case; but at a high temperature the carbonic acid combines with solid carbon, forming carbonic oxide, thus—$CO_2 + C = 2CO$. Now if in the present case carbonic oxide was formed in reducing oxide of lead, double the quantity of carbon would be required thus—$2PbO + 2C = 2CO + Pb_2$.
446 24

That this is not so, will be illustrated by the next experiment. Having calculated the right amount of carbon to add to 500 grains of litharge, either in form of powdered charcoal, coke, or anthracite; thoroughly mix the oxide and reducing agent on a sheet of glazed paper; carefully brush the whole into a clay crucible (Fig. 35*b*); heat at a low temperature for seven to ten minutes, and pour into a round mould as soon as all action ceases, otherwise a silicate will be formed, and the lead button will be short in weight.—As 446 : 500 :: 414 : x = Pb.

* Pb = 207 : O = 16 : C = 12.

Exp. 128. Take 500 grains of litharge and double the quantity of carbon used in the last experiment; place in crucible, and heat as before. Pour the contents into a mould, and observe that a button of lead is formed, but short of the required weight; also, that some carbon remains. This must be ground up fine in an iron mortar, placed in a porcelain basin, and a gentle stream of water run in, when the lighter carbon will rise to the top, and be washed away with the stream, while finely divided particles of lead will remain at the bottom in consequence of their greater specific gravity: these should be dried and weighed with the main portion. The result should then agree with that obtained in Experiment 127.

Exp. 129. Take 500 grains of litharge, and half the requisite amount of carbon; place in crucible and heat as before for seven or eight minutes at a low temperature, then pour into round mould. Observe that the product is lead and unaltered litharge. If the temperature employed be too high, or the operation prolonged after the reduction is completed, a silicate will be formed by the action of the excess of litharge on the crucible.

In speaking of the oxidation of lead, it has been explained that lead unites with oxygen, forming oxide of lead, and that at a certain temperature this oxide melts. Now the oxide formed at the lower temperature is in the amorphous condition and is called massicot, and is of a yellow colour. When this oxide is heated separately at a temperature of about 300° C. it absorbs oxygen and assumes a beautiful red colour; this is called "red lead." The following equation shows the change:—

$$3PbO + O = Pb_3O_4.$$

Exp. 130. Take 300 grains of red lead; place in a small crucible, and raise to a low red heat. The tetroxide is decomposed into protoxide, and oxygen liberated; the

oxide thus reduced melting to a liquid. Pour into a half-round mould and allow to cool. Weigh the button of litharge. The amount possible may be calculated from the following equation :—$Pb_3O_4 = 3PbO + O$.

Now break the button ; notice that it is reddish yellow in colour and exhibits a crystalline structure.

From what has been stated we may assume that if lead could be melted below 300° C., then red lead would be formed by its oxidation ; on raising the temperature to 330°, oxygen would be liberated and yellow massicot formed ; on raising the temperature again to 700° or 800° the massicot would melt and form reddish yellow crystalline litharge.

In the reduction of red lead in the manner explained above, care must be taken not to raise the temperature too high, or the litharge will form a silicate with the clay of the pot.

Exp. 131. Take 500 grains of red lead ; mix with sufficient carbon to reduce it, and heat in a small clay crucible. Calculate the carbon required and the amount of lead obtainable from the following equation :—

$$Pb_3O_4 + C_2 = Pb_3 + 2CO_2.$$

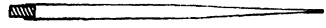
This experiment is carried out precisely as with litharge (Exp. 127).

Exp. 132. Reduce 100 grains of bismuth oxide with carbon, according to the equation—

$$2Bi_2O_3 + 3C = 4Bi + 3CO_2.$$

This metal is similar to lead in some respects ; thus heating metallic bismuth after fusion in a muffle, a yellow oxide forms at first, which becomes darke colour as the temperature is raised, fusing at a red to a glass which is of a deeper tint than the unf oxide. Like fused litharge, it readily corrodes a crucible.

Exp. 133. Weigh out 50 grains of red oxide of mercury and introduce it into a dry glass tube drawn out at one end to a fine point, thus—



Close with a tight-fitting cork and heat with Bunsen burner until the oxide is decomposed. The mercury will condense in the narrowed part of the tube. Cut this off by means of a three-square file; wash out the mercury into a small weighed porcelain crucible; carefully evaporate the water; well dry at 100° C., and weigh the crucible containing the mercury; then deduct weight of crucible, and the remainder gives the amount of metal. This oxide is reduced by heat alone without the addition of a reducing agent, thus—$HgO = Hg + O$.

Exp. 134. Take 200 grains of oxide of zinc, mix with excess of carbon, which may be calculated from the equation—$ZnO + C = CO + Zn$.

Place in a clay crucible; cover with a lid, and heat very intensely for half an hour; remove from fire and examine the crucible when sufficiently cool. Notice that no metal or oxide remains, only the excess of charcoal, zinc being volatile at the temperature required for its reduction.

Exp. 135. Take the same mixture as Exp. 134; place in a small clay retort, the body of which is then to be put into a furnace and strongly heated for half an hour; then remove, cool, and examine the neck, which will contain the metal condensed as a fine powder, mixed with the oxide. Scrape this off and melt it at a low temperature in a crucible, then pour the metal into a half-round mould. Only an approximate result can be obtained in this way, without great care and experience.

p. 136. Weigh out 1000 grains of tin oxide and

mix it with 100 grains of anthracite or coke dust which has been passed through a fine sieve; place the mixture in a plumbago crucible (Fig. 39 *a*, *b*), which must be put well down in the furnace; cover the top with a piece of coke, and heat strongly for twenty minutes; then remove the coke covering, and rub down the inside with a piece of wood to remove any particles of metal or oxide sticking to the sides, and heat for another five minutes. Remove the crucible and impart to it a circular motion to collect all the tin, as far as possible, into a single mass; scrape the anthracite to one side and pour the metal into a long mould; allow to cool, and keep for weighing. The powder must now be ground fine in an iron mortar, taking care that all has been scraped out of the pot, and washed as in Experiment 128, to swill away the lighter particles of carbon, dry the residue, mix it with an equal bulk of carbonate of soda, fuse for ten minutes in a small clay crucible, and pour into a half-round mould. Grind in mortar; pick out any shots of tin and weigh them with the main quantity.

$$SnO_2 + C_2 = Sn + 2CO.$$

To determine the quality of the tin obtained: re-melt, remove from fire, and allow to cool down in the crucible until the surface, on being scraped, remains bright and no more oxide forms; then pour into a dry mould as before, and allow to cool undisturbed. If the metal is pure, the surface will be bright, rounded at the sides, and free from dull-looking spots; moderately soft, malleable, and will emit a peculiar crackling sound when held to the ear and bent. For the effect of impurities, see § 25, Exp. 8.

Exp. 137. Take 100 grains of oxide of tin and mix with 200 grains of potassium cyanide and 30 grains of charcoal; place in a clay pot (Fig. 35 *b*), and fuse for fifteen minutes in a medium fire. Pour into a half-round

mould; allow to cool; break away the slag, and weigh the button of tin.

$$SnO_2 + 2KCy = 2KCyO + Sn.$$
$$2KCyO + C = 2KCy + CO_2.$$

Care must be taken in using potassium cyanide, as both it and the slag are strong poisons; therefore the student should wash his hands after handling them.

Exp. 138. Take 100 grains of antimony oxide, 10 grains of charcoal, and a little carbonate of soda; place in clay crucible, cover with a piece of coke, and fuse at a low temperature until all action ceases. Pour into a half-round mould, carefully detach the slag, and weigh the button of antimony, which should be white and highly crystalline.—$2Sb_2O_3 + 3C = 4Sb + 3CO_2$.

Exp. 139. Take 100 grains of oxide of nickel and place in a crucible lined with charcoal; insert a piece of charcoal to plug up the orifice and lute on a clay lid with clay. Lute the crucible to a piece of brick and place it nearly on the bars of a hot furnace. Now completely fill up with small coke; open damper and door, and continue at the highest temperature for an hour, adding coke as required. Allow the fire to burn down; remove the crucible and break it open when cold to obtain the button of nickel, which will contain carbon in a manner analogous to cast iron. Weigh the metal obtained.—$NiO + C = CO + Ni$.

Exp. 140. Reduce oxide of cobalt in the same way as nickel oxide to obtain metallic cobalt, which very much resembles nickel.

Exp. 141. Take 100 grains of oxide of iron and reduce it in the same way as nickel oxide in a charcoal lined crucible.—$Fe_2O_3 + 3C = 3CO + Fe_2$.

As it is much cheaper, hematite ore is generally used for reduction; but this ore is associated with more or less earthy matter, and a certain amount of flux will be necessary to combine with it, and form a fusible slag.

Take 200 grains of hematite and mix it with 40 grains of China clay, 10 grains of white sand, and 50 grains of lime.

Or, 200 ore, 50 glass, and 60 lime.

The product may be grey, white, or mottled cast iron. The ore and fluxes must be crushed very fine and passed through a sieve with 60 or 80 meshes to the inch, the highest temperature maintained for an hour, and the whole allowed to cool before breaking the pot. The slag must also be crushed to pick out any particles of iron with a magnet, and the whole of the metal weighed.

Exp. 142. Take a lump of hematite weighing about 600 or 700 grains; place it in a crucible and completely cover it with charcoal. Heat the crucible and its contents for an hour at a temperature below the fusing point; allow to cool, and weigh the lump of iron. This experiment is intended to show that oxide of iron may be reduced without melting.

METALLIC SULPHIDES AND ARSENIDES.

§ 59. (*a*) Sulphur combines readily with most metals, producing in many cases compounds of great value in the arts. It is in this form that many ores are found, from which the useful metals are extracted.

(*b*) Sulphur like oxygen often combines with a metal in more than one proportion, as FeS, FeS_2, Cu_2S, CuS, etc. In the native state sulphides are generally dark in colour, crystalline, and possess considerable lustre. They are all solid at the ordinary temperature, most of them fuse

at a red heat, and, when roasted in air below this point, give up a great part of the sulphur forming oxides or sulphates. Some sulphides, such as HgS and As_2S_3, sublime unchanged. At a low temperature sulphates are chiefly formed, and at a higher point oxides are produced. In the case of the sulphides of silver and gold, the sulphur is removed by heat alone, and the pure metal left behind. All sulphides are decomposed when heated in a current of chlorine gas, chlorides being formed.

(*c*) Sulphides may be formed in various ways, as by heating metallic oxides with sulphur; heating the metals with sulphur; reducing a sulphate with carbon; and by wet methods.

(*d*) The combination of a metal with sulphur takes place much more readily when the substances are in a finely divided state, so that the metal should be cut up small, or granulated. In the case of easily fusible metals like lead, they are melted at the lowest possible temperature in a crucible, removed from the fire, allowed to stand until near the point of solidifying, then poured into a rectangular box, the inside of which has been well blackleaded (especially the edges and corners), and the box vigorously shaken. This breaks up the metal into fine grains, which can be separated from the larger lumps by a sieve.

§ 60. *Formation of Sulphides.*

Exp. 143. Weigh 1000 grains of granulated lead, and mix with sufficient flowers of sulphur to give the following reaction:—

$$\underset{207}{Pb} + \underset{32}{S} = \underset{239}{PbS}.$$

Shoot the mixture into a red-hot crucible (Fig. 35, *c*, *d*) placed in a furnace, cover with lid, and heat at a gradually increasing temperature. In about three to five minutes the action should be complete, and the whole mass in tranquil fusion; pour into half-round mould, allow to cool, and weigh. Break to examine its

nature. A good specimen should have a dark bluish grey colour, should be brittle, with a crystalline fracture, and a metallic lustre. If the sample is somewhat malleable with a granular fracture, it is a mixture of lead and lead sulphide. It must then be broken up in an iron mortar and treated over again with some more sulphur. For perfect success with the theoretical quantity, the air must be excluded, the temperature not raised so high as to volatilise the lead sulphide formed, and the quantity operated upon should be small in proportion to the size of the crucible. It is called artificial "galena."

Exp. 144. Take 1000 grains of metallic tin granulated in the shaking box, and add sufficient sulphur to form tin sulphide, conducting the operation precisely as for lead sulphide, thus—$Sn + S = SnS$.

It is a bluish grey crystalline substance, with a metallic lustre, moderately tough, and difficult to pulverise. It will be advisable to break it up and treat again with more sulphur to get a perfect sample.

Exp. 145. Treat a portion of zinc and sulphur together as in the previous experiments, and observe that little or no combination occurs. Zinc sulphide may be formed by mixing finely divided zinc (such as the metal obtained from the condensing tubes in the distillation of zinc), and sulphur together in a copper scoop (Fig. 18), such as is used for charging crucibles, and projecting the mixture into a red hot crucible. The result will be a mixture of zinc and sulphide of zinc.

Zinc sulphide is also formed when a mixture of mercury sulphide and zinc is projected into a red hot crucible, the mercury being volatilised thus—

$$HgS + Zn = ZnS + Hg.$$

At a low temperature the HgS would sublime unchanged. As zinc sulphide is practically infusible, the

resulting sulphide would retain the pulverulent form, or be simply clotted.

Exp. 146. Take 100 grains of either antimony or oxide of antimony and sufficient sulphur to give one of the following reactions :—

$$Sb_2 + S_3 = Sb_2S_3$$
$$2Sb_2O_3 + 9S = 2Sb_2S_3 + 3SO_2.$$

Take the usual precautions to prevent volatilisation of sulphur, and use an excess if necessary. Sulphide of antimony is a dark grey crystalline substance with metallic lustre.

Exp. 147. Take 50 grains of silver and convert it into silver sulphide in the usual manner by fusing with sulphur. $Ag_2 + S = Ag_2S$.

This substance is moderately malleable, of a dark bluish grey colour, with metallic lustre, and a crystalline structure. It is almost as soft as silver.

Exp. 148. Take 1000 grains of hoop iron; place in a crucible, and raise to a white heat; then drop in bit by bit the necessary quantity of roll sulphur calculated from the equation—$Fe + S = FeS$.

When the whole is liquid, pour into a half-round mould and allow to cool. Observe the dark red or bronze-like appearance of the fractured surface, which is often considerably honeycombed, its coarse, granular, stone-like structure, and feeble lustre.

Exp. 149. Raise to a white heat 100 grains of thin sheet nickel, cut into small pieces, and drop in sulphur bit by bit, as in the previous experiment. The combination takes place with some violence with the production of heat and light. This sulphide has a brass-yellow appearance, with a metallic lustre; it is brittle, and has a granular structure. $Ni + S = NiS$.

Exp. 150. Take 1000 grains of thin sheet copper cut up very fine; place in red-hot crucible with a small quantity of flowers of sulphur, and cover with a lid. When the mixture is melted, add more sulphur if necessary, bit by bit as in the former case. The following change occurs, forming cuprous sulphide :—

$$Cu_2 + S = Cu_2S.$$

After weighing, break the button of sulphide and observe its dark bluish grey colour, its finely granular structure, its brittleness and feebly metallic lustre.

Exp. 151. Heat 500 grains of cuprous sulphide with sufficient sulphide of iron to produce the compound (Cu_2S,3FeS). Place the mixture in a crucible, add a little sulphur, cover with a lid, and heat strongly until the whole is melted; pour into a half-round mould, and allow to cool. This substance corresponds to "coarse metal" in copper smelting. It is brittle, coarsely granular, and of a bronze yellow colour, resembling sulphide of iron. When broken hot it assumes a purple or bluish tint.

Exp. 152. Heat 500 grains of cuprous sulphide with the requisite quantity of sulphide of iron to form ($2Cu_2S$,FeS). Proceed as above, and pour into half-round mould. Break a portion when hot. Notice that it is brittle, finely granular, with a deep purplish blue colour. Allow to cool and break; it is then more bronze-like in colour, with a semi-metallic lustre. It corresponds to the "blue metal" of the copper smelter.

Exp. 153. Place 200 grains of mercury in a porcelain mortar, and add sufficient flowers of sulphur to form HgS, thus—$Hg + S = HgS$.

Rub the two substances together by means of the pestle for some time, when they will combine, forming a black powder. Collect the powder, and introduce it into

a hard glass tube closed at one end. Heat strongly with a Bunsen burner, when the sulphide will volatilise and condense on the cooler part of the tube in the form of a crystalline sublimate of a red colour, which is artificial "cinnabar."

Or melt sulphur in excess in a crucible just sufficiently hot to keep the sulphur melted, and add 200 grains of mercury drop by drop, when a mixture of HgS and Hg_2S will be formed. Now add more sulphur; allow it to combine, and pour into a dry mould, or on to an iron plate if it is desired to sublime it as above to form vermillion.

Exp. 154. Melt 10 to 20 grains of gold in a small crucible; add sulphur, allow to cool, break pot, and remove the gold. Examine to prove that no combination has occurred.

§ 61. *Reduction of Sulphides.*

Sulphides may be reduced in various ways. Some, such as silver, by heat alone; others, such as lead, by heat and air; some, by iron and other metals which have a great affinity for sulphur. In many cases, sulphides are employed to reduce oxides, and, vice versa, oxides to reduce sulphides. Common salt and other chlorides are occasionally used to effect the reduction. Carbon and carbon compounds in many cases separate sulphur from its state of combination, with isolation of the metal.

Exp. 155. Crush up a quantity of sulphide of lead, and pass it through a 60 sieve. Take 500 grains, place in a clay crucible (Fig. 35 *d*), and add a strip of iron in just sufficient quantity to give the reaction :—

$$PbS + Fe = FeS + Pb.$$

Heat for about fifteen to twenty minutes, or until all action ceases, and pour into a half-round mould; allow to cool, and remove the layer of sulphide of iron by

hammering the button on its edge, so as to squeeze off the brittle sulphide. Care must be taken not to hit the top or bottom side, or else some of the sulphide will be forced into the soft lead, and increase its weight. When perfectly clean, weigh the lead, and compare with the possible theoretical amount.

Exp. 156. Reduce 500 grains of lead sulphide by heating in an iron crucible; pour into mould; detach slag, and weigh the button of lead.

Lead sulphide is only partially reduced by carbon, as may be proved by heating these substances together, when a mixture of lead and lead sulphide is obtained, the button being hard, granular and brittle.

Exp. 157. Heat 200 grains of cuprous sulphide with metallic iron to give reaction:—

$$Cu_2S + Fe = FeS + Cu_2.$$

Pour into mould when complete; allow to cool, and examine the product, which is an alloy of copper and iron, with a double sulphide of iron and copper on the top, showing that the reduction is imperfect by this method.

When sulphide of copper is heated with carbon, zinc, or lead at a high temperature, only partial reduction occurs.

Exp. 158. Take 50 grains of silver sulphide, and heat with iron as in case of lead sulphide, when complete reduction occurs. The weight of silver may be calculated thus—$Ag_2S + Fe = FeS + Ag_2$.

Exp. 159. Take 300 grains of sulphide of antimony, and calculate the requisite quantity of iron filings required for its reduction.

$$Sb_2S_3 + 3Fe = 3FeS + Sb_2.$$

Care must be taken not to have the temperature too

high, or some of the antimony and unreduced antimony sulphide will volatilise. If excess of iron is used, it will form an alloy with the reduced antimony, part of which passes into the regulus. The sulphide of iron has a density very nearly equal to that of antimony, so that, unless the mass is kept fused for some time, the metal cannot be separated.

Exp. 160. Repeat the last experiment with the addition of 100 grains of carbonate of soda, and 20 grains of charcoal. In this case less iron will be required, so that there will be no danger of the metal being contaminated with iron; the slag will be lighter and more liquid, so that loss of antimony from keeping the mass in fusion for some time after complete reduction, as in former experiment, will be avoided.

Exp. 161. Take 200 grains of tin sulphide, mix with 200 grains of common potassium cyanide and 30 grains of charcoal. Heat in a clay crucible for fifteen minutes, and pour into a half-round mould; allow to cool and detach the slag. The following change occurs :—

$$SnS + KCy = KSCy + Sn.$$

Exp. 162. Take 200 grains of tin sulphide, and reduce with iron in just the requisite quantity.

$$SnS + Fe = FeS + Sn.$$

Exp. 163. Take 50 grains of mercury sulphide, and reduce with lime in a glass tube closed at one end. (See § 31.)

First add a portion of perfectly dry sodium bicarbonate, then the 50 grains of mercury sulphide mixed with an equal bulk of quick-lime, then some more lime, and lastly a plug of asbestos to keep the whole in its place. Now draw out the open end to a fine point, and bend it downwards, so that it may just dip beneath the surface

of water in a dish; place it in a tube furnace. Raise the portion near the neck to a red heat, and gradually heat the tube to the middle where the sulphide is placed, until the whole is decomposed. Now heat the sodium bicarbonate, which liberates carbonic acid; this sweeps the last remnants of mercury forwards to the neck. The greater portion of the metal may be in the water. Cut off the bent part, swill the residue into the water, pour off the water, and remove the last portions with blotting paper; then carefully dry the mercury, and weigh.

$$4HgS + 4CaO = 4Hg + 3CaS + CaSO_4.$$

In the above process, it is necessary that all the materials should be dry or the moisture will crack the hot glass.

CONVERSION OF SULPHIDES INTO OXIDES AND SULPHATES.

§ 62. The formation of oxide or sulphate in roasting metallic sulphides depends to a great extent on the temperature employed. At a low temperature sulphates are produced, and at a higher temperature these are decomposed with the formation of oxides; so that in many roasting operations the product is a mixture of oxide and sulphate. Some sulphides, such as silver sulphide, cannot be roasted alone to sulphate or oxide, because they are decomposed below the temperature at which this change is effected; but if other sulphides are present, the conversion is brought about by the products of their oxidation and decomposition.

Exp. 164. Crush up very finely 200 grains of lead sulphide; place in a roasting dish (Fig. 40), and heat in a muffle at a low temperature for half an hour, with frequent stirring; then remove and allow to cool. Observe

that the surface has become white, due to the presence of lead sulphate. Remove a portion, and boil in a test-tube with strong hydrochloric acid; dilute with distilled water, allow to settle, pour off the clear liquid, and add a solution of barium nitrate, when a white precipitate of barium sulphate will be formed, which remains insoluble on boiling, proving the presence of sulphuric acid.

$$H_2SO_4 + Ba2NO_3 = BaSO_4 + 2HNO_3.$$

Continue the roasting, gradually increasing the temperature, but not sufficiently to fuse the substance, stir occasionally, and proceed until no odour of sulphurous acid can be perceived when the dish is removed, and a current wafted to the nose by the hand. The whole should now be in the form of oxide, and no sulphate. Prove this by testing as before, when no precipitate should be produced by barium nitrate.

Exp. 165. Take 200 grains of iron sulphide, and treat in a similar way to the lead sulphide, proving the presence and absence of sulphuric acid at the different stages.

Exp. 166. Take 50 grains of silver sulphide, crushed very fine, and roast at a low temperature for some time. Boil with water, and test for sulphuric acid as in Exp. 164, and prove its absence.

Exp. 166A. Mix with the silver sulphide 50 grains of iron sulphide and 200 grains of copper sulphide. Roast at a low temperature for half an hour, then at a cherry-red heat for an hour with frequent stirring. The sulphides of iron and copper are first oxidised to sulphates, then these sulphates are decomposed with liberation of sulphuric acid, which unites with the silver to form silver sulphate. Now prove the presence of silver sulphate by boiling with water, and adding hydrochloric acid, which precipitates the silver in the soluble sulphate,

as silver chloride. This is the basis of the Ziervogel method of extracting silver from its ores.

Exp. 167. Take 200 grains of finely crushed copper sulphide, and roast as before with frequent stirring. Prove the presence of copper sulphate after roasting at a low temperature, by dissolving a portion of the copper sulphate in water, and observing the blue colour. Add a little powdered anthracite, and continue the roasting until all the sulphur is expelled, and then prove the absence of copper sulphate by treatment with barium nitrate as in Exp. 164.

Exp. 168. Take 100 grains of antimony sulphide, and roast to oxide. This operation requires great care, as antimony sulphide is volatile when strongly heated, and in any case some loss will be experienced.

Exp. 169. Roast 200 grains of tin sulphide to oxide in the usual way.

Exp. 170. Roast 100 grains of zinc blende till "sweet"; that is, until the whole of the sulphur is removed. This is a tedious operation, as a portion of the sulphur clings tenaciously to the zinc; but zinc sulphide has the advantage of being practically infusible, and is only volatile at a high temperature, so that a higher temperature may be employed at the commencement without fear of clotting than with many sulphides. After roasting for half an hour, the temperature may be considerably raised to decompose any sulphate, and oxidise the last remnants of sulphur.

Exp. 171. Place 20 grains of mercury sulphide in a glass tube, and heat it with a Bunsen burner, when the sulphide will volatilise unchanged, and condense on the colder part of the tube. (See Exp. 133.)

Exp. 172. Treat 100 grains of nickel sulphide in the same way as lead sulphide so as to form sulphate and oxide. (See Exp. 164.)

ACTION OF SULPHIDES ON OXIDES AND SULPHATES.

§ 63. (*a*) In some cases when a metallic oxide is heated with a sulphide, double decomposition occurs with exchange of elements, thus: oxide of iron gives up its oxygen to sulphide of zinc, while the sulphur of the zinc unites with the iron.—$ZnS + FeO = ZnO + FeS$.

(*b*) Litharge is an energetic oxidiser for some sulphides; thus, when sulphide and oxide of lead are heated together the sulphur is oxidised and the lead isolated.

(*c*) Oxide of copper, by means of the great affinity of copper for sulphur, decomposes other sulphides, such as sulphide of iron, forming iron oxide and copper sulphide. When oxide of copper is heated with sulphide of copper in the right proportion the whole of the copper is reduced, and sulphur takes the oxygen, forming sulphur dioxide.

(*d*) Blende sometimes furnishes sulphur by exchange; it acts on oxide of copper in the same way as sulphide of iron does.

(*e*) Sulphates also act on metallic oxides, forming sulphur dioxide and metal, or metallic sulphide. The sulphates of barium and calcium when heated with oxide of copper or iron, in presence of silica, form sulphides of iron and copper, and silicates of barium and calcium.

Exp. 173. Take 500 grains of lead sulphide and sufficient litharge to give the following reaction:—

$$\underset{446}{*\,2PbO} + \underset{239}{PbS} = \underset{621}{SO_2} + 3Pb.$$

* Atomic weight of lead is taken as 207.

Both substances must be in a finely divided state and intimately mixed. Place in clay crucible (Fig. 35 *b*), cover with lid, and heat moderately for about ten minutes until the action is complete. Pour into half-round mould and weigh the button of lead, which must be free from slag. This experiment requires great care, or the litharge will melt and unite with the clay to form a silicate, before the action on the sulphide is commenced. A plumbago crucible is preferable.

Another plan is to melt the sulphide first, then drop the oxide (screwed up in a bit of tissue paper, or placed in a copper scoop) into the molten sulphide.

Exp. 174. Take 500 grains of lead sulphide and sufficient lead sulphate to reduce the whole of the lead; thus—$PbS + PbSO_4 = 2SO_2 + 2Pb$.

The operation is conducted precisely the same as in Experiment 173. Weigh the button of lead.

Exp. 175. Break up some sulphide of lead into pieces about the size of peas, or a little less; weigh out 500 grains and roast at moderate temperature for an hour. The product will consist of oxide, sulphate, and unaltered sulphide. Place the whole in a crucible, and fuse till all action ceases, taking care to exclude the air as much as possible, then pour into mould and, when cold, weigh the button obtained. Then break it and observe whether the button is malleable or brittle, also observe the nature of the fractured surface. As no reliable guide can be given to indicate when sufficient of the sulphide has been oxidised and sufficient sulphide left to react, as in the two previous experiments, the time of roasting must be left to the judgment of the operator.

When a sulphide is roasted in pieces in this way, instead of in powder, there will always be left a nucleus of sulphide, while the outer portions will be oxidised in proportion to the time they are exposed to heat and air.

Exp. 176. Take 200 grains of coarsely powdered copper sulphide and roast for fifteen minutes at a low temperature with constant stirring or the material will clot together; then raise the temperature and continue for another fifteen minutes. Treat the product as in Experiment 175, and weigh the button of copper obtained. After a few trials, with careful observation, the right amount of roasting may be ascertained. The following equation may be used for calculating the copper:—

$$Cu_2S = Cu_2 + S.$$

Exp. 177. Take 200 grains of copper sulphide and sufficient oxide to give the following reaction:—

$$Cu_2S + 2CuO = SO_2 + 4Cu.$$

Place in crucible and heat with exclusion of air until all action ceases; pour into mould, allow to cool, and weigh the button of copper, which, if the experiment has been successful, will be free from slag.

Percy states that when cuprous sulphide is heated with the oxide or sulphate in such proportions that the sulphur and oxygen exist in the ratio in which they are combined in sulphur dioxide (SO_2), and the mixture is heated to the melting point of copper, the whole of the copper will be reduced, and the sulphur oxidised, so that sulphide of copper, like lead, may be reduced by the action of heat and air alone. When the oxygen exceeds this ratio, a quantity of cuprous or cupric oxide will remain in the product. Conversely, when the sulphur exceeds this ratio, sulphide of copper will be in excess.

Exp. 178. Verify the correctness of the preceding remarks by the following series of experiments; taking 200 grains of cuprous sulphide in each case, and calculating the amount of oxide or sulphate required from the respective equations:—

1. $Cu_2S + 2Cu_2O = 6Cu + SO_2$.
2. $Cu_2S + 2CuO = 4Cu + SO_2$.
3. $Cu_2S + 3CuO = 3Cu + SO_2 + Cu_2O$.
4. $Cu_2S + 6CuO = SO_2 + 4Cu_2O$.
5. $Cu_2S + CuSO_4 = 3Cu + 2SO_2$.
6. $Cu_2S + 2CuSO_4 = 3SO_2 + 2Cu_2O$.
7. $Cu_2S + 4CuSO_4 = 5SO_2 + 6CuO$.
8. $2Cu_2S + 2CuO = 2Cu + SO_2 + Cu_2S$.
9. $2Cu_2S + 2Cu_2O = 6Cu + SO_2 + Cu_2S$.

EXAMPLE.

In No. 1 the molecular weight of Cu_2S is 158,* and the weight of two molecules of Cu_2O is 284; then the amount of oxide required for 200 grains of sulphide is calculated by simple proportion,

As 158 : 200 : : 284 : x.

The amount of copper is computed in the same way,

As 158 : 200 : : 378 : x.

Exp. 179. Reduce sulphide of antimony by fusing it with the oxide according to the following equation:—

$$Sb_2S_3 + 2Sb_2O_3 = 3SO_2 + 6Sb.$$

Exp. 180. Reduce 100 grains of sulphide of bismuth by reaction with the oxide as in the following equation:—

$$Bi_2S_3 + 2Bi_2O_3 = 3SO_2 + 6Bi.$$

ARSENIC AS A METALLURGICAL AGENT.

§ 64. (*a*) Arsenic plays a very important part in some metallurgical operations, being often found associated with the ores of nickel, cobalt, iron, copper, silver, tin, and antimony, as well as existing in ores of arsenic proper.

(*b*) Some metals, such as nickel and cobalt for instance, may be separated from other substances with which they are united by taking advantage of their affinities for

* Atomic weight of copper is taken as 63.

arsenic and the formation of a speise. In this way nickel and cobalt, in presence of arsenic, may be separated from earthy matter, by fluxing the latter with silica; and from copper and iron by taking advantage of the superior affinities of the iron and copper for sulphur. Three distinct products are thus obtained; speise being the heaviest, at the bottom, then regulus, then slag.

Exp. 181. Weigh 25 grains of nickel oxide, 15 grains of cobalt oxide, 10 grains of copper oxide, 10 grains of iron wire, 70 grains of arsenic, 20 grains of lime, 20 grains of silica, and fuse the whole together; then drop in 20 grains of sulphur and 20 grains more arsenic. Pour into mould (Fig. 17 *a*) and examine the product when cold.

Exp. 182. Take 45 grains of nickel oxide, 5 of cobalt oxide, 10 of iron wire, and 60 of metallic arsenic. Fuse at a low temperature for fifteen minutes in a clay crucible, and pour. Crush up and mix with—10 grains of arsenic, 100 of sodium carbonate, 80 of tartar, and 30 of borax. Replace in crucible and heat at a bright red heat till tranquil (about fifteen minutes); pour into half-round mould, allow to cool, detach the button of speise, and weigh the result.

Exp. 183. To make speise containing copper. Take 10 grains of the black oxide of copper, 25 grains of nickel oxide, 15 grains of cobalt oxide, 10 grains of iron, and 70 grains of arsenic. Fuse as before, then mix with 100 grains of carbonate of soda, 30 grains of borax, 80 grains of tartar, and 20 grains of arsenic. Fuse and pour into half-round mould. Weigh and examine the button of speise.

Exp. 184. To make cobalt speise. Take 45 grains of cobalt oxide, 5 grains of nickel oxide, 10 grains of iron, and 60 grains of arsenic. Heat as before, then mix with 10 grains of arsenic, 100 grains of carbonate of soda, 80

grains of tartar, and 30 grains of borax. Fuse, pour, weigh, and examine the speise obtained.

CUPELLATION AND SCORIFICATION.

§ 65. Cupellation has for its object the removal, by the aid of fused litharge, of every constituent of a substance, except gold and silver, which are unoxidisable metals, and therefore cannot be dissolved by molten litharge. The same remarks apply to platinum and some rare metals of a similar character. The vessel in which the operation is performed is called a cupel, and is generally made of bone ash, although other substances may be employed, such as apatite, wood ashes, and marl (which is a mixture of carbonate of lime and clay), or mixtures of the above substances. In this country, bone ash is almost invariably used. A description of the mode of making cupels is given in § 22.

Exp. 185. Make two dozen large cupels (Fig. 43 *b*). By large is meant a vessel capable of cupelling 500 grains of lead. Also make three dozen small cupels capable of treating 200 grains of lead (Fig. 43 *a*). After making, they should be allowed to stand for twenty-four hours in a warm place to dry. Care must be taken not to use too much water and too great a pressure in moulding, or the cupels will be too dense and compact; on the other hand, if insufficient water and pressure be used, they will be tender and friable. It may be taken as a general rule that a cupel will absorb an amount of lead equal to its own weight.

Exp. 186. Place three small cupels (Fig. 42 *a*) in a hot muffle, and keep the temperature at a bright red heat for ten minutes. In the meantime weigh out 50 grains of lead, 30 grains of copper, and 10 grains of silver. Place each in separate cupels by means of the cupel tongs, without removing from the muffle, nearly close the

opening with the brick door, and watch the changes which occur. The lead should melt in a minute, then the surface becomes covered with greasy-looking drops of oxide of lead, which are rapidly absorbed by the porous cupel and replaced by others which pass slowly over the surface. As the operation proceeds, the motion is quickened, and in about ten to fifteen minutes the last traces of lead are oxidised, and disappear. The temperature should not be high enough to melt the silver. Close the muffle, and leave for another fifteen minutes, then remove and allow to cool. Observe that the cupel which contained the lead is coloured yellow or orange; that the silver is unaltered in colour and weight; that the copper is oxidised, black on the surface, and red in the interior, that it has increased in weight, and produced a dark brown stain on the cupel.

Exp. 187. Place two small cupels in a red hot muffle; weigh two lots of silver about 10 grains each; wrap them separately in 50 grains of sheet lead and introduce them into the cupels. Close the front of the muffle for a few minutes, then watch for the conclusion, which should take place in about ten minutes, with a proper heat. Just before the finish, the metallic bead appears uniformly dull and glowing; this is succeeded by a beautiful display of colours due to extremely thin films of liquid litharge; these soon disappear, leaving the liquid globule bright; this is called "brightening." Remove one of the cupels and allow the silver to solidify while exposed to the air. Observe that protuberances are thrown up on the surface, or one large bubble may be formed. This is called "spitting" or "vegetating." Close up the front of the muffle containing the other cupel, and allow it to cool gradually, which can be very conveniently done in a gas muffle, by turning off the gas. Observe that no "spitting" has taken place, and that the button is smooth on the surface This phenomenon of spitting is due to

the expulsion of mechanically absorbed oxygen during cooling, which takes place violently when the cooling is rapidly effected.

Exp. 188. This experiment is intended to show that one part of copper requires sixteen times its weight of lead to carry it into the cupel, when the former metal is submitted to cupellation.

Heat two large cupels, and place in one 20 grains of copper wrapped in 160 grains of lead; in the other 20 grains of copper with 320 grains of lead. Conduct the operation as before until no further action occurs: allow to cool and examine the cupels. The former will be found to contain a little oxidised copper unabsorbed; the latter will contain no residue, all having been taken up by the cupel. When the copper is alloyed with silver or gold it is less readily oxidised than when alone, consequently a much larger proportion of lead relatively to the copper must be used, as shown by the following table:—

Silver.	Copper.	Quantity of Lead for one part of Alloy.	Lead.		Copper.
90	10	7	70	:	1
80	20	10	50	:	1
70	30	12	40	:	1
60	40	14	35	:	1
50	50		32	:	1
40	60		27	:	1
30	70	16-17	23	:	1
20	80		20	:	1
10	90		18	:	1

When the copper amounts to more than one half of the alloy, the same proportion of lead is required for cupellation in each case.

Exp. 189. Experiment to show that antimony and tin cannot be cupelled except when present in very small quantities. Place four large cupels in a hot muffle and weigh out the following quantities :—(*a*) 20 grains of antimony and 320 grains of lead; (*b*) 20 grains of tin and 320 grains of lead; (*c*) 10 grains of antimony, 10 grains of silver, and 320 grains of lead; (*d*) 10 grains of tin, 10 grains of silver, and 320 grains of lead. Charge each into one of the cupels; continue the operation until all the lead is absorbed; allow to cool, and examine the results. Weigh the buttons of silver from (*c*) and (*d*). Observe that in (*a*) a brownish red crust is formed round the edge of the cupel, which is badly cracked; that in (*b*) a grey crust of oxide of tin has formed; that (*c*) and (*d*) are similar to (*a*) and (*b*), and that the silver is probably short of its proper weight in consequence of some being entangled in the scoria.

Dr. Percy gives the following table to show the effect of different metals on the cupel :—

Metal.	Appearance of Cupel.
Antimony,	Pale yellow to brownish red scoria, which sometimes cracks the cupel.
Arsenic,	White or pale yellow scoria.
Chromium,	Dark brick-red stain.
Cobalt,	Dark green scoria and greenish stain.
Copper,	Dark brown or green colour.
Iron,	Dark red stain at commencement of operation, leaving a dark ring on cupel, which is corroded.
Lead,	Straw or orange yellow colour.
Manganese,	Dark bluish black stain and corrosion of the cupel.
Nickel,	Dark green scoria and greenish stain.
Palladium, Platinum,	Greenish stain and very crystalline buttons.
Tin,	Forms a grey scoria.
Zinc,	Yellow ring on cupel; the metal burns with a brilliant flame, gives out copious vapours, and corrodes the cupel.

Exp. 190. Experiment to show that commercial lead contains silver. Make a large cupel red hot as usual, add 500 grains of lead, and continue until the whole is oxidised and absorbed. The process requires careful watching towards the conclusion, so as to remove the cupel the moment the last traces of oxide disappear and the speck of silver brightens. Allow the cupel to cool; detach the small globule with the point of a penknife; flatten on an anvil, and weigh the silver if sufficient has been obtained. In exact assays of silver the amount present in the lead employed has to be allowed for.

Exp. 191. Make three different alloys of silver and lead by melting the two metals together in a small clay crucible Weigh out (*a*) 500 grains lead and 25 grains silver, (*b*) 500 grains lead and 15 grains silver, (*c*) 500 grains lead and 10 grains silver. Cut up the two metals into small pieces in each case, place in crucible, add a little charcoal, cover with a clay lid, and heat in furnace for about ten minutes at a moderate temperature. Remove from fire, slowly revolve crucible to well mix the contents, and pour into a round mould; allow to cool, weigh, and roll out each alloy in a thin sheet. The loss in each case should be within 5 grains.

Exp. 192. Place five small cupels together in the middle of a hot muffle, thus—

o o
o
o o

Weigh out five pieces of the alloy (*a*), each weighing 50 grains; roll into a packet; charge into the cupels, and allow to remain until the silver in each brightens; then cover up the front of muffle, and allow to cool slowly. When cold, detach the buttons with a pair of round-nosed pliers; squeeze off any adhering bone ash, and clean with a hard tooth brush; then weigh the silver obtained to find whether they all agree in weight.

Exp. 192A. Repeat the last experiment with the alloys (*b*) and (*c*).

Exp. 193. Heat four small cupels. Weigh four pieces of pure silver of 10 grains each, and wrap them separately in 50 grains of lead, previously made into a small envelope, and charge into the cupels. When finished, cool down the muffle; detach and clean the silver buttons, and weigh. The loss indicates the amount volatilised, and that absorbed by the cupel.

Exp. 194. Clean a shilling and roll out to a thin strip without annealing. Heat five small cupels. Weigh four pieces of 10 grains each, wrap them separately in 60 grains of lead. Also weigh 9·25 grains of pure silver and ·75 grain of copper, and wrap them in 60 grains of lead: this is used as a "check," and assayed in the middle cupel. Charge into the cupels; operate as before, and weigh the resulting silver. The weight of the check piece is accurately noted, and the known loss of pure silver is added to the weight of each of the other four beads, by which means the true quantity of silver in the shilling is ascertained, all having been assayed at the same time, and under identical conditions.

Exp. 195. Repeat the last experiment with a "5 Franc" piece, or with a prepared alloy containing 90 per cent. silver and 10 per cent. copper.

Exp. 196. Make an alloy of 91·666 grains gold and 8·334 grains copper (standard gold). Roll out thin; weigh four pieces of 10 grains each, and wrap each in 60 grains of lead. Also a check containing 9·166 grains of gold and ·833 grain of copper. Charge into five cupels and conduct the operation as with silver in Experiment 194; but the temperature must be higher, especially at the finish, as the melting point of pure gold

is higher than that of silver. A gold coin may be used instead of making the above alloy.

Exp. 197. Make an alloy of 90 grains gold, 5 grains silver, and 5 grains copper. Roll out; weigh four pieces of 10 grains each, and cupel with 60 grains of lead as before. Remove from muffle as soon as finished, and notice that no spitting occurs. Clean as before when cold, and weigh. The weight denotes the gold and silver present.

(*a*) To part the silver from the gold, add 25 grains of silver to each button; wrap in 60 grains of lead and cupel, so as to obtain the alloy in one bead in each case; clean, place on a bright anvil, and flatten somewhat with a smooth and polished hammer, so that it may be more easily rolled out to a strip about 2 inches long. Anneal the strip, and coil it into the form of a spiral, called a "cornet." Place this in a conical beaker, or parting flask (Fig. 62 *a*); well cover with dilute nitric acid containing 1 of acid to 3 of water, and boil gently until all brown fumes cease. In boiling, the acid is liable to bump and break up the cornet, which may be prevented by adding a ball of baked clay about the size of a pea. Pour off the liquid which contains the greater part of the silver, add stronger acid of the proportion 1 to 1, and boil for about fifteen minutes to dissolve the last traces of silver. Pour off the liquid; well wash the gold with distilled water; then fill up the flask with distilled water. The cornet now consists of pure gold, and still retains its original shape, but is porous in structure, and of a brown colour. The gold is now transferred to a small crucible nearly full of water by inverting the flask, when the metal falls by gravity to the bottom of the crucible; the water is then poured off, the gold dried, and then exposed to a bright red heat, when it acquires the usual yellow colour of gold and shrinks in bulk. After allowing

to cool, it is weighed, and the difference between this and former weight gives the amount of silver.

Exp. 198. Alloys of gold and silver containing notable quantities of metals, such as antimony and tin, cannot be cupelled so as to dissolve their oxides and cause them to pass into the cupel without an enormous quantity of lead. In such a case a preliminary process is resorted to, known as scorification.

Make alloys of (*a*) 950 grains lead, 25 grains silver, and 25 grains antimony, (*b*) 950 grains lead, 25 grains silver, and 25 grains tin, by melting together in a clay crucible.

Heat two scorifiers (Fig. 41) to a bright red heat in a muffle; remove and add the above alloys; then replace and allow the oxidation and formation of silicates with the clay of the scorifier to proceed, until the scoria just covers the surface of the remaining molten lead; then pour each into a separate mould; allow to cool, break away the brittle slag with a hammer, and cupel the buttons of lead, which contain practically the whole of the silver.

In cases where great accuracy is required, the scoria is cleaned to recover any silver it may contain, thus:—Grind the scoria in an iron mortar, and fuse it in a clay crucible with a mixture consisting of 300 grains of red lead, 15 grains of charcoal, and 20 grains of carbonate of soda. Pour into round mould, allow to cool, tap away the slag and cupel the button of lead. The amount of silver in the red lead employed must be deducted from the weight of silver obtained.

Scorification depends on the fact that molten oxide of lead has the property of uniting with infusible silicates such as fire-clay, dissolving oxides of other base metals which may be present, and forming a fusible slag, leaving unoxidisable metals such as silver and gold in combination with the metallic lead present in excess.

LIQUATION.

§ 66. When a mixture of two or more bodies of different fusibilities is raised a little above the melting point of the most fusible one, the latter flows away, or, as it is termed, "liquates" out, leaving the residue in a more or less porous condition. Such a separation is always imperfect, even with bodies having little affinity for each other, and with widely different melting points, because of the adhesion between them. By this process crude sulphur is separated from earthy matter in sulphur minerals; likewise sulphide of antimony, bismuth, etc., from their ores.

Many metals which are mixed when in the liquid state separate or re-arrange themselves on cooling. In fact, a cooling mass of mixed metals, or metals with non-metals, often behaves much as water containing suspended matter does in freezing, when the ice first formed rejects the foreign matter. In like manner the portion of certain alloys which first solidifies rejects certain other portions of the constituent metals. This action is also termed liquation (See § 51A).

Exp. 199. Weigh 100 grains of stibnite (native sulphide of antimony) and place in a small crucible *a* (Fig. 47), the bottom of which is perforated with a number of small holes, cover with a lid, and lute it on with clay. Place this in another crucible *b*, leaving sufficient space between the two to receive the liquated sulphide, and lute the two crucibles together. Now raise the upper crucible to a red heat with a large gas blow-pipe such as Fletcher's; when the molten regulus will run through the perforations into the bottom crucible, which should be kept as cool as possible. Allow to cool, and weigh the liquated sulphide.

Fig. 47.

Exp. 200. Make an alloy of 400 grains of lead and 20 grains of zinc, pour into a rectangular mould, and when solid, place on an inverted crucible lid, arranged in an inclined position on a tripod stand over a crucible, and heat with a large Bunsen burner; the greater part of the lead will flow away, leaving a very porous mass behind, consisting of the zinc with a little lead. The liquated lead will also be contaminated with zinc.

Exp. 201. Make an alloy of 400 grains lead, 50 grains copper, and 10 grains silver, by melting together in a crucible, then pour into a rectangular or a plate mould (Fig. 17); allow to set, place on crucible lid, and liquate the lead from the copper as in last experiment. The lead contains the silver, which may be separated by cupellation. As some of the silver remains in the copper, it may be separated by alloying with more lead, repeating the liquation, and cupelling the lead obtained.

Exp. 202. Melt together 500 grains of tin and 15 grains of sheet iron cut into small pieces, then add 40 grains of arsenic and pour into a rectangular or a plate mould. Allow to cool. Observe its brittleness, and the crystalline structure of the fractured surface. Then liquate out the tin; re-melt, and repeat the liquation. Then pour into mould, fracture, and observe that the crystalline character has disappeared in the liquated portion. Melt and cast the residue on the lid, and notice that it is highly crystalline; it contains most of the iron and arsenic. In tin smelting it is known as "hard head."

Exp. 203. Weigh 200 grains of "tap cinder" obtained from a puddling furnace, place in crucible arranged as in Experiment 199. In this case the crucibles may be placed in a furnace and strongly heated, when a fusible silicate will liquate out, leaving behind an infusible mass con-

sisting chiefly of Fe_3O_4, and known as "bull-dog." The liquated portion is bull-dog slag, and contains most of the impurities.

Exp. 203*a*. Melt 400 grains of copper in a crucible, and add 400 grains of antimony and 400 grains of lead, well stir with a stick and pour into a cylindrical mould. Allow to cool; break across the middle, and observe that the lead is in the centre, and some on the outside of the ingot, whilst a purple coloured alloy of antimony and copper surrounds the central core of lead.

WET METHODS.

§ 67. The following experiments are given to illustrate wet methods of extraction :—

Exp. 204. Dissolve 10 grains of silver in boiling sulphuric acid, add water, then place a strip of clean copper in the liquid, and allow to stand for a few hours in a warm place, when the whole of the silver will be precipitated.—$Ag_2SO_4 + Cu = CuSO_4 + Ag_2$.

Exp. 205. Mix 100 grains of finely powdered copper pyrites with an equal quantity of common salt also in powder. Place the mixture in a roasting dish and roast at a moderate temperature for an hour in a muffle, with frequent stirring. Transfer to a glass beaker, and heat with water containing a little hydrochloric acid. Filter the solution and place a strip of clean iron in it; allow to stand in a warm place for a few hours to precipitate the copper.—$CuCl_2 + Fe = FeCl_2 + Cu$

Exp. 206. Take 100 grains of copper pyrites, 100 grains of common salt and 10 grains of silver sulphide, all finely powdered. Roast as in previous experiment,

and dissolve the soluble matter with boiling water containing hydrochloric acid. Filter, and add a solution of potassium iodide which precipitates the silver thus—

$$AgCl + KI = AgI + KCl.$$

This forms the basis of the Claudet process of extracting silver from its ores.

Filter again to remove the silver iodide, and precipitate the copper with iron as before.

Exp. 206*a*. Mix pyrites, salt, and silver sulphide, and roast as before. Warm the residual mass with a 10 per cent. solution of sodium thiosulphate ($Na_2S_2O_3$). Filter and wash. To the filtrate add ammonium sulphide, allow to settle, dry the precipitate, cupel it with lead and weigh the silver. This forms the basis of the Von Patera process of extracting silver from its ores.

Exp. 207. Take 5 grains of gold, dissolve in two parts hydrochloric acid and one part nitric acid; evaporate to dryness, re-dissolve in a pint of boiling water, and add a clear solution of sulphate of iron, which precipitates the gold as a brown powder. Allow the gold to settle; pour off the liquid; wash two or three times; then transfer to a small crucible, heat in muffle to produce the ordinary yellow colour, and weigh the gold.

Exp. 208. Weigh out 5 grains of the precipitated gold from the last experiment, mix it with 10 grains of sand, and put the mixture into a flask and cover with water. Pass into the water a current of chlorine gas, cork up the flask and allow to stand for fifteen minutes. Then pass in some more gas and repeat the operation at intervals for an hour, keeping the flask full of gas. Filter off the insoluble residue, and precipitate the gold from the filtrate as in last experiment. Weigh the gold obtained.

AMALGAMATION.

§ 67A. The following experiments will illustrate the extraction of metals by amalgamation.

Exp. 209. Weigh out 10 grains of silver which has been prepared in the manner described in Exp. 204, place it in a mortar, and add about 100 grains of mercury. Grind the metals together by means of a pestle until the mercury has dissolved all the silver. Squeeze the whole in a piece of chamois leather until the excess of mercury has run through it, then transfer the pasty amalgam to a small porcelain crucible, and heat in a fume chamber until the mercury has all volatilised. Cool and weigh the silver.

Exp. 210. Weigh out 10 grains of precipitated silver and mix it with 90 grains of sand. It will now represent an ore containing 10 per cent. of silver. Grind the mixture as in last experiment with 100 grains of mercury until the silver is all dissolved. Place the mixture in an evaporating basin, and allow a stream of water to flow into it until the sand has been washed away. Squeeze the residue as before through chamois leather, heat and expel the mercury, cool and weigh the residual silver.

Exp. 211. Weigh out 10 grains of silver, place in a beaker, and dissolve it in dilute nitric acid. Then add a solution of hydrochloric acid, a little at a time, well stir the contents of the beaker with a glass rod, and continue the addition of acid until no further precipitate is formed.

$$AgNO_3 + HCl = AgCl + HNO_3.$$

Filter off and wash the silver chloride formed. Transfer the precipitate to a mortar, add 100 grains of mercury,

and grind with a pestle as before until the silver chloride is dissolved. Squeeze off excess of mercury, heat the amalgam, cool, and weigh the silver.

Exp. 212. Dissolve 10 grains of silver in dilute nitric acid, using as little acid as possible, dilute largely with hot distilled water, then add a solution of sulphuretted hydrogen, or pass the gas, until the whole of the silver is precipitated as black silver sulphide.

$$AgNO_3 + H_2S = Ag_2S + HNO_3$$

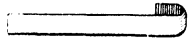
Filter and wash the precipitate, then amalgamate with mercury, and proceed as in the last experiment.

ELECTRO-METALLURGY.

The following exercises form a suitable basis for a course of instruction in practical electro-metallurgy.

§ 68. *The Voltaic Cell.*

Exp. 213. Cut a strip of sheet zinc about 3 inches long and $\frac{1}{4}$ inch wide, scour it with emery cloth and bend one end thus—



Suspend it by its crook in a test-tube containing one part of sulphuric acid to ten parts of water. Observe that bubbles of hydrogen gas are evolved from the surface of the zinc. Now take a bit of clean copper wire, also 3 inches long, and suspend it opposite the zinc, but so as not to touch it. Notice that no additional effect is produced. Now let the two metals touch each other either inside or outside the liquid, and observe that hydrogen gas is given off from the copper as well as from the zinc.

Now remove the zinc, and rub a globule of mercury over its surface until it is uniformly bright. The zinc is then said to be "amalgamated." Replace the zinc in the liquid and observe that no gas is given off, which shows that amalgamated zinc does not dissolve in dilute sulphuric acid. Next let the two metals touch each other, or connect their free ends with a bit of clean wire. Observe that the gas bubbles arise from the copper only, and that they cease to be evolved the moment the two metals are disconnected.

(*a*) These experiments teach : (i.) That commercial zinc dissolves in dilute sulphuric acid whether in contact with another metal or not. (ii.) If such zinc be amalgamated it will not dissolve in the acid liquid except whilst in contact directly or indirectly with another metal, such as copper or some conducting substance like graphite. (iii.) That in order to prevent waste of zinc and acid, all zinc plates should be kept well amalgamated.

(*b*) Zinc plates may be conveniently amalgamated by immersing them for a few minutes in a mixture of one measure of sulphuric acid and three measures of water. Remove each from the acid, and while still wet, hold it over a dish and pour mercury over its entire surface. If any patches refuse to amalgamate, scrape them with an old knife, re-dip in the acid, and add mercury again to the uncovered parts. When complete, rinse the amalga-

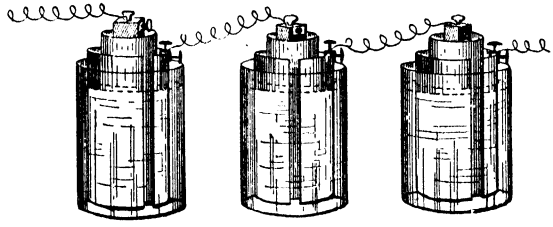


Fig. 48.

mated plates in clean water, place them upright in an earthenware dish until the excess of mercury has drained

off; this should be returned to the bottle for use at another time. The trouble taken in this process will be amply repaid by increased efficiency and economy in working.

§ 69. In an electro-metallurgical laboratory each student should be supplied with a pint size Bunsen cell, and if it is necessary to work a brassing solution with a battery current, two or three students may unite their cells in series as in Fig. 48 and work together.

Exp. 214. Charge the battery cell as follows :—After well amalgamating the zinc cylinder, clear out the holes of the binding screws with the point of a file. Build up the cell, fill the porous pot with aqua-fortis, and the outer cell containing the zinc with a mixture of one measure sulphuric acid and nine measures of water. If any effervescence occurs in pouring in this mixture, either the zinc is imperfectly amalgamated or nitric acid has accidentally fallen in. This must be remedied at once before proceeding. Connect a stout insulated copper wire to each pole and the cell is ready for use.

§ 70. Another instrument which is indispensable in studying the principles of electro deposition is a galvanometer. Figures 49 and 50 represent one specially devised for this purpose by Mr. T. J. Baker, which may be made as follows :—

Exp. 215. (*a*) Cut a straight strip of stout sheet brass, 8 inches long and $\frac{3}{8}$ inch wide ; bend it into a semi-circle; fasten it vertically upon a circular board $5\frac{1}{2}$ inches diameter and $\frac{3}{4}$ inch thick. Describe a circle $4\frac{1}{2}$ inches in diameter upon a card, and divide the circle into quadrants, and each quadrant into 90° ; then fix card on the board.

Fasten a binding screw (*a*, Fig. 49) adjacent to one extremity of the arch, then to the binding screw solder

one end of a stout insulated copper wire, bend it over the arch, pass it through a small brass staple at the other extremity of the arch, then pass the wire round a groove turned in the edge of the base board to the starting point, carry it again over the arch and round the edge as before, but in the opposite direction; then repeat so that the wire passes four times over the arch. Fasten the free end of the coil to the binding screw (*b*).

Anneal a bit of watch spring $\frac{1}{2}$ inch long, punch a hole through its centre, cut it into a lozenge shape, then

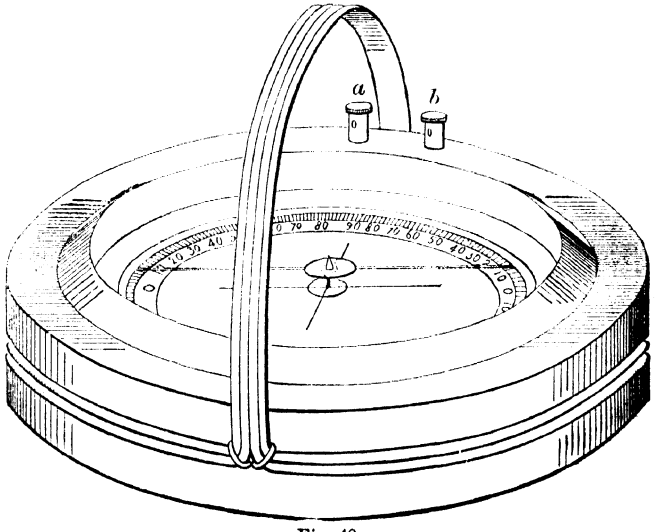


Fig. 40.

harden and magnetise it. Draw off a piece of narrow glass tubing to a point, cut off a small portion to form a cap, and cement it into the hole of the magnet. Cut a small circle of stiff paper $\frac{5}{8}$ inch diameter, perforate centre, insert glass cap into the orifice, and secure the magnet to it with slips of gummed paper. Select two straight and slender fibres of hay, and fasten each on opposite

sides of card, and perpendicular to the axis of the magnet.

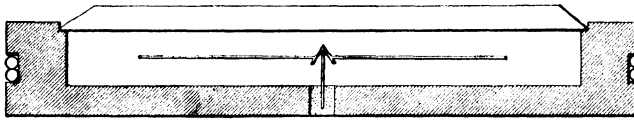


Fig. 50.

The centre of the base must have a hole bored through it, into which a cork is fitted, and through this cork is passed a needle, on the point of which the magnet is balanced. (Fig. 50.)

The needle and card are then covered with a plate of glass to protect the needle from currents of air. If this instrument is made to the dimensions stated, the numbers expressing the values of the tangents of the angles of deflection will also approximately express the strengths of the corresponding currents in ampères. (See table of tangents, in Appendix.)

(*b*) With this apparatus the student will be able to study the effect of altering the resistances in the circuit, while he is learning to control the current with which he is working.

Exp. 216. Arrange the galvanometer with the pointer at zero, then connect the galvanometer wires to a battery cell, one wire to the zinc, and the other to the carbon, and observe that the pointer turns away from 0°. Note the amount of deflection. Now slowly raise the carbon plug out of the cell, and notice that the needle slowly returns to its original position, which it reaches when the carbon is completely out of contact with the acid, and the current has therefore ceased to flow. The same remarks apply to the zinc plate. The current may be diminished in amount by only partly immersing either of the battery plates in the acid. Replace the carbon plug in the cell, and substitute a yard of thin German

silver wire for one of the galvanometer wires. Observe that the deflection of the needle is much less than before.

§ 71. *Resistance of depositing Solution.*

Dissolve 8 ounces of powdered copper sulphate in hot water, and when cold add 1 fluid ounce of sulphuric acid, and sufficient water to make the bulk of the solution up to 1 quart.

Exp. 217. Connect one pole of the battery to one of the terminals of the galvanometer. Take two strips of clean copper, and fasten each strip to a separate copper wire, connect the free ends of the wires to the remaining terminal of the battery and galvanometer respectively. Now see that the pointer of the galvanometer points to zero, then immerse the copper strips 2 inches apart in the copper sulphate solution, and note the deflection of the needle. Observe that the deflection is diminished on increasing the distance between the strips, and that the deflection is increased when the distance between them is diminished. The strip connected with the carbon or positive pole of the battery is called the "Anode." It is the plate by which the current enters the solution. The other strip which is connected with the zinc or negative pole of the battery is called the "Cathode." It is the plate which receives the deposit, and the one by which the current leaves the liquid. This plate gradually increases in weight, because copper is being constantly deposited upon it while the current is passing. The anode plate loses weight because it dissolves into the solution to supply the copper gained by its neighbour.

Re-immerse the two plates in the solution 1 inch apart, and note the galvanometer reading; then raise the anode partly out of the solution, and observe that the deflection of the needle is diminished. By the above and similar experiments the student learns how to control the strength of the current.

(*a*) To reduce the current, either :—

(i) Substitute a German silver wire for one of the copper wires ; (ii) place the anode and the work farther apart in the solution ; or (iii) raise the anode partly out of the depositing vessel, or substitute a smaller one.

(*b*) To increase the current, either :—

(i) Shorten the German silver wire, or replace it by a copper one ; (ii) place the anode nearer to the work ; or (iii) immerse the anode further in the solution, or substitute a larger one.

When a suitable strength of current has been found for working a particular solution, read off the indication of the galvanometer, and record it. In future work, regulate the current, so as to obtain the same deflection.

COPPER.

§ 72. Symbol Cu. Atomic weight 63·2. Chemical equivalent $\frac{63\cdot2}{2}$ = 31·6. Electro-chemical equivalent = ·00506 grains. One ampère of current deposits 18·216 grains of copper per hour in an acid bath of copper sulphate. Pressure required = ·5 to 1·5 volts. Current density (for parcel coppering) = 2 to 6 ampères per square foot of cathode surface. Current density (for electrotyping) = 6 to 15 ampères per square foot of cathode surface.

For preparation of copper sulphate solution, see § 71.

(*a*) *Parcel Coppering on Brass and similar Copper Alloys.* This is done by first thoroughly cleaning the work, and drying out in hot sawdust. The parts not to be coppered must then be neatly painted over (stopped off) with asphaltum varnish. When the varnish is dry, the work should be dipped for an instant in dilute aqua-fortis, rinsed in water, then suspended in the above depositing solution,

and connected with the negative pole of the battery or dynamo. The lower the current density the smoother will be the deposit, but the longer the work will have to remain in the solution to receive a given deposit. The work when taken out is rinsed in water, dried, and brushed over with turpentine to remove the varnish, and expose the uncovered brass. The turpentine is then washed off with hot potash solution, and the metal scratch-brushed, polished and lacquered.

An artistic effect can easily be produced on parcel coppered work by immersing it in a hot saturated solution of copper nitrate, and after rinsing in water, drying out in sawdust and lacquering.

(*b*) *Copper Cyanide Solution.* This is a double cyanide of copper and potassium. One ampère deposits 18·216 grains of copper per hour, provided that no hydrogen is deposited with the copper. Pressure required = 3 to 5 volts. Current density = 3 to $4\frac{1}{2}$ ampères per square foot of cathode surface.

To prepare the solution proceed exactly as in preparing the brassing solution, § 86, but use 800 grains of powdered copper sulphate instead of the mixed sulphates of copper and zinc. The preparation of the work to receive a deposit varies with the nature of the metal. Iron and zinc are pickled in dilute sulphuric acid. Britannia metal and pewter *are* immersed in hot potash solution and transferred without rinsing into the coppering solution.

§ 72A. *Electrotyping.* Begin by making a copy of a coin.

Exp. 218. (*a*) Soften a piece of gutta-percha, about four times the bulk of the coin, in hot water, well knead it, and roll into a ball between the hands until its surface is free from seams or fissures. Place the coin upon a flat and smooth piece of wood, which must be wetted to prevent the gutta-percha from sticking to it. Bring the latter down upon the centre of the coin, and press it

outwards so as to obtain an impression free from air bubbles. Wet another similar flat piece of wood, and press it upon the top, where it should be allowed to remain with a heavy weight upon it, until the mould is cold and hard; then remove the coin, and examine the mould obtained. It should be an exact reverse of the coin, every line and feature being sharply defined; if this is not the case, the process should be repeated until success is achieved. Gutta-percha will not conduct an electric current, therefore the face of the mould must be coated with some conducting material. Brush finely-powdered blacklead over the surface with a camel hair brush, breathing upon it from time to time, and continue the process until every crevice has been reached, and the whole impression shines like a newly-polished grate. Now heat one end of a copper wire, and embed it in the front of the mould, so that its extremity very nearly touches the edge of the impression. Carefully blacklead the portion of the mould between the impression and the wire so that they may be electrically in contact, or the current will not pass; the mould is then ready to receive a deposit.

(*b*) *Deposition.* Use the solution, § 71. Connect a clean strip of copper to the carbon pole of a Bunsen's cell by means of a copper wire, and place the copper plate upright in the solution; this forms the anode. Connect also the mould with the zinc cylinder of the battery by means of a similar wire, and suspend it in the solution opposite the anode. The mould thus forms the cathode or negative plate. A few minutes after immersion, lift the mould out of the solution, and examine it. If a little pink patch of

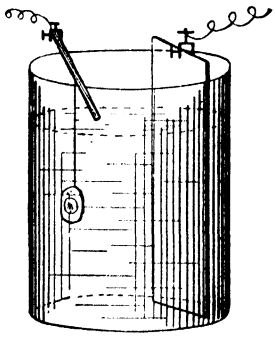


Fig. 51.

copper has appeared at the extremity of the wire, replace it in the solution, and inspect it from time to time until the deposit has extended completely over the surface. If on examination no change has occurred even on the wire, it indicates that no current has passed. In such a case, see that the mould is connected with the zinc (–) pole of the battery, and that all the connections are clean; then try again.

(*c*) If a dark brown powder is deposited on the wire, but the deposit does not extend to the mould, then the mould has been imperfectly blackleaded. Dry the mould, and repeat the blackleading, paying particular attention to the junction of the wire with the mould.

(*d*) If now the deposit extends to the mould, but is still powdery or dark coloured, the current is too strong and must be reduced by one of the methods given in § 71.

(*e*) If the deposit has the characteristic salmon-pink colour of pure copper, but one or two little patches remain uncovered, the blackleading is still imperfect. Dry as before, and pay special attention to covering these parts with the conducting powder, then return the mould to the solution, and continue the deposition until a sufficient thickness is obtained. The electrotype may then be separated from the mould, made red hot on a piece of wire gauze over a Bunsen burner, cleaned in dilute sulphuric acid (1 to 10), its edges trimmed and filed. It may then be finally bronzed, silvered, or gilt.

Exp. 219. (*f*) Having succeeded with the coin, the student may attempt a larger object. In this case, it is well to provide a frame of stout sheet brass or hoop iron about $\frac{1}{4}$-inch deeper than the object, and fitting it loosely. Proceed as follows:—Surround the object with its frame, and apply the gutta-percha as before, giving it a final squeeze in a letter press, under which it may be

left until cold. The metal frame will prevent the object being injured.

(*g*) Having obtained a good mould, blacklead it, taking the above mentioned precautions. If it contains any deep depressions, the deposition in those parts may be much facilitated by twisting a few thin copper wires upon the mould wire, and placing them so that their free ends lightly touch the surface of the mould at those points. Make a loop in the wire, so that it will overhang the back of the mould, and from this loop suspend a sufficient mass of lead by means of string to sink the mould in the solution, and retain it in the vertical position. If the electrotype does not readily separate from the mould, immerse in warm water for a few minutes, and try again.

§ 73. Moulds may also be made in white wax or in bee's-wax as follows :—Cut a strip of gummed paper, and fasten it round the edge of the coin to be copied. Melt the wax in any suitable vessel, place the coin in an inclined position, and pour in the wax at the lowest point, allowing it to flow gradually over the surface, so as to prevent the entanglement of air bubbles. Cover it over, so that it may cool slowly, and be less liable to crack. When cold, remove the paper, coil a thin copper wire round the edge of the mould, blacklead it as before, but with greater care, as the wax surface is more easily injured than gutta-percha. Remove all blacklead from back of mould by wiping it with a bit of rag wetted with alcohol, or by scraping it with a knife. This precaution will prevent a deposit of copper on the back.

Exp. 220. Larger objects may be copied in wax, thus :—Suppose the object to be a terra-cotta tablet ; cut a strip of tin plate about half an inch wider than the maximum thickness of the tablet, bend it around the

edge of the latter and secure it with soft solder, or by means of binding wire. Place the whole in a shallow dish and pour warm water into the latter until it reaches half-way up the edge of the tablet, and allow it to remain until a delicate film of moisture appears on the surface. Pour the water away, lute the outside of the metal rim with clay, pour in the wax at a temperature but little above its melting point, and observe the same precautions as before. If the separation is difficult, immerse the tablet only in slightly warm water for a few minutes.

Exp. 220A. Excellent moulds may be made in wax as follows :—Melt in a glue-pot $\frac{1}{2}$ lb. each of bee's-wax and white wax, and stir into the mixture $\frac{1}{2}$ ounce black lead and 1 ounce Venice turpentine. Turn up the edges of a stout sheet of brass or copper, so as to make a tray a little longer, wider, and deeper than the object to be copied. Set the tray upon a level surface and fill it with the molten composition. Allow it to completely solidify, and whilst it is still warm blacklead its surface thoroughly with a very soft brush. The object should also be blackleaded and then pressed into the warm solid wax composition by hand pressure. A flat piece of wood may then be placed upon the object and a final squeeze in a letter press will finish the moulding operation.

The excess of wax will be squeezed out of the tray and should be neatly cut off, and the face of the mou again well blackleaded.

The back of the tray should be stopped off asphaltum varnish, or better still, with the fluid composition. The tray containing the mould is suspended with copper wires and made the cat the depositing solution as in the preceding met

§ 74. Exp. 221. Beautifully sharp impres may be obtained in fusible alloy, which m and used as follows :—Melt together in a

over a gas flame or slow fire, eight parts by weight of bismuth, and four parts each of lead and tin. Pour the alloy in a thin stream into water, collect the granulated particles, and repeat the operation two or three times so as to ensure a perfect alloy.

To make a mould of a coin, put sufficient alloy in an iron spoon and hold it considerably above a gas flame until it just melts; then pour it gently into the rim of an inverted teacup which has been heated by being filled with hot water previously to inversion. If the surface is bright, the coin may be immediately dropped upon it and allowed to remain undisturbed until cold. If the surface of the molten alloy is dull, the film of oxide must first be removed by promptly but gently sweeping the edge of a card over it.

The clean cathode wire may be connected with the mould by gently heating it and pressing it flat on the back of the latter, which melts and behaves like solder. A little resin facilitates the adhesion. The back of the mould and the wire must be coated with copal varnish or smeared with melted paraffin to prevent deposition of copper thereon.

§ 75. *Elastic Moulds.*

Exp. 222. (*a*) When the object to be copied is undercut, the mould is prepared as follows:—Take four parts by eight of the best glue and let it remain in an excess of old" water for several hours. Then put the swollen which has absorbed much water, into a clean tin l and place this in a second larger vessel containing so that it may be heated like a glue pot. When has melted, pour in one part by weight of treacle oughly stir the mixture until the whole is of mposition. Surround the object to be copied luted outside with clay and oiled to make face uniformly greasy, avoiding excess of he hot fluid composition with the same

precautions observed in making a wax mould, and let it stand undisturbed for twenty-four hours. Moulds made in this material may be stretched without injury, and little difficulty arises in separating them from the object. They swell and become distorted in an ordinary depositing solution, so that a saturated solution of copper sulphate must be used, and the mould covered with a layer of copper as quickly as possible.

(*b*) Instead of depositing on such a mould, it may be used to obtain a cast in plaster of Paris. In this case, it must be well oiled, and the plaster, of about the consistence of cream, poured on the mould which has been surrounded with a luted frame as before. It should not be disturbed for several hours, when it may be separated from the mould and set aside for a few days to dry. (The mould may be used several times.) When dry, the cast may be moulded in wax or gutta-percha and electrotyped. In this way works of art may be copied directly without risk of being injured in the process.

If the student weighs his mould before and after deposition of copper he will be able to judge of the progress of the operation. An increase in weight of 4 grains per square foot of electrotype surface will be sufficient for a good stout deposit.

§ 76. *Refining Crude Copper.*

Exp. 223. In the copper sulphate solution suspend two stout copper anodes and connect them with the positive pole of the battery. Suspend a thin copper cathode of the same dimensions between the anodes, and join it with the negative pole of the battery. Interpose the galvanometer (Fig. 49), and adjust the resistance so that a deflection of 45° is obtained. Stir the anodes from time to time, and observe that they become black and ultimately shed a powder. Copper is deposited upon the cathode is bet-

fine salmon-red colour. Let the current pass for several hours.

The copper transferred from the anodes to the solution, and from the latter to the cathodes, has been deprived of its impurities, part of which remains upon the anodes and constitutes the slime, part has fallen to the bottom of the depositing vessel, and part has dissolved in the solution. Such residues have been frequently analysed and found to contain copper, iron, arsenic, antimony, lead, tin, nickel, gold, silver, sulphur, and oxygen. The gold and silver have in some instances occurred in such quantity as to pay the expenses of working, and leave a good margin of profit besides.

Exp. 224. Dip the two anodes in aqua-fortis and rinse in water. Make one of them the cathode, use the other as an anode, and for the second anode substitute a piece of refined copper deposited in the last experiment. Compare the appearance of the refined and unrefined anodes from time to time.

The above experiments illustrate the manner of refining copper by electricity on the large scale, dynamo machines being employed instead of batteries.

SILVER.

Ag. Atomic weight 107·6. Chemical equivalent 107·6. Electro-chemical equivalent ·017243 grain. One ampère will deposit 62·0747 grains per hour. Electro-motive force = ·5 to 1 volt. Current density = 1·5 ampère per square foot of cathode.

PRELIMINARY EXERCISES.

Water free from chloride must be used, unless otherwise stated, and all vessels must be carefully washed in water previous to use.

Exp. 225. Take a fragment of fine silver; place in a test tube, and cover with pure nitric acid diluted with an equal bulk of water. Heat gently; red fumes appear, and the silver dissolves; then evaporate to dryness. The white residue obtained is silver nitrate ($AgNO_3$). If the residue is coloured green, the silver contained copper. Add water; well shake, and warm if necessary, until the silver salt dissolves and the solution becomes colourless. Divide the solution into three equal portions—*a*, *b*, and *c*.

Exp. 226. To (*a*) add dilute hydrochloric acid in excess; to (*b*) add a solution of common salt; pour (*c*) into a tumbler of ordinary water, and stir with a glass rod. Observe that in (*a*) and (*b*) a white curdy precipitate of silver chloride is formed, and that with (*c*) the common water has become milky from the same cause. This exercise teaches that hydrochloric acid, or a soluble chloride, added to a solution of silver nitrate, precipitates silver as chloride, and shows why distilled water is requisite in diluting the above liquids, and in swilling out the vessels employed.

Exp. 227. Decant the clear liquid from the precipitates (*a*) and (*b*), Exp. 226, and well wash them with distilled water; pour off the wash waters, and add to each precipitate a few drops of a solution of ammonia; the silver chloride dissolves. Add to solution (*a*) dilute hydrochloric acid in excess, and to solution (*b*) nitric acid in excess of that required to neutralise the ammoniacal solution; silver chloride is re-precipitated in each case This exercise shows that silver chloride is insoluble in water and dilute acids, but soluble in ammonia.

Exp. 228. Add precipitates (*a*) and (*b*), Exp. 227, together; wash several times, until the wash water ceases to redden blue litmus paper; then add drop by drop with shaking, a dilute solution of potassium cyanide (KCy). The precip-

itate dissolves, and the solution contains the double cyanide of silver and potassium (AgCy,KCy). This reaction is sometimes used in preparing a plating solution.

Exp. 229. To the previous solution add dilute hydrochloric acid as long as a precipitate forms, or until the solution after shaking is acid to test paper, when the whole of the silver is precipitated as chloride. This reaction is frequently used in recovering silver from old plating solutions, but care must be taken to avoid inhaling the hydrocyanic acid gas evolved, as it is a powerful poison.

Exp. 230. Wash the silver chloride precipitated in the last experiment; add a few drops of dilute hydrochloric acid, and a scrap of zinc, and set aside for a few hours. The zinc reduces the silver chloride to metallic silver, and forms zinc chloride, which, being soluble, may be removed by hot water. The residue is silver.

Exp. 231.—Take a portion of silver nitrate solution, and add to it drop by drop with shaking, a solution of potassium cyanide as long as a cloud is formed in the clear liquid. (If more than this is added the precipitate will be re-dissolved.) The precipitate is silver cyanide (AgCy). Observe that it is exactly similar in appearance to silver chloride, from which it cannot be distinguished, except by a special test.

Exp. 232. Decant the liquid from the silver cyanide obtained in the last experiment; wash the precipitate, and add to it a solution of potassium cyanide drop by drop, until the precipitate exactly dissolves. The solution obtained is the double cyanide of silver and potassium.

The two last experiments illustrate the method of preparing one of the best silver plating solutions.

Exp. 233. Divide the solution obtained in the last experiment into two equal portions (*a*) and (*b*). To (*a*) add hydrochloric acid in excess, and to (*b*) add nitric acid in excess. The former precipitates silver chloride (AgCl), and the latter silver cyanide (AgCy). Wash and dry both precipitates; transfer each to a separate porcelain crucible, and heat to low redness over a gas flame. The silver chloride fuses but is otherwise unaltered. The silver cyanide is decomposed, and the residue consists of finely divided silver and a dark-coloured substance called paracyanogen. The silver chloride may be removed from the crucible by ammonia. (See Exp. 227.) The metallic silver may be dissolved in nitric acid. (See Exp. 225.)

This exercise shows (*a*) that the double cyanide of silver and potassium (AgCy,KCy) is decomposed and converted into silver chloride (AgCl) by the action of dilute hydrochloric acid; (*b*) that dilute nitric acid decomposes it also, but leaves silver cyanide (AgCy); (*c*) that silver chloride simply fuses when ignited, but silver cyanide is decomposed. If too high a temperature be employed, silver chloride is also decomposed. By this means the one salt may be distinguished from the other.

Exp. 234. Make a little silver nitrate (Exp. 225); evaporate to dryness, re-dissolve in distilled water, and add a solution of potassium cyanide drop by drop with brisk shaking until the precipitate formed just re-dissolves.

$$AgNO_3 + 2KCy = AgCy,KCy + KNO_3.$$

This reaction is employed in estimating the percentage of pure potassium cyanide in a sample of the commercial salt.

Exp. 235. Divide the solution obtained in the last experiment into two portions. To one add a solution of

silver nitrate exactly as long as it produces a precipitate.

$$AgCy,KCy + AgNO_3 = 2AgCy + KNO_3.$$

To the other add dilute nitric acid in excess.

$$AgCy,KCy + HNO_3 = AgCy + KNO_3 + HCy.$$

Either of these reactions may be employed to recover silver cyanide when that salt has been re-dissolved by excess of potassium cyanide. (See Exp. 231.)

§ 78. Exp. 236. To estimate the percentage of pure potassium cyanide in a sample of the commercial salt. Weigh out 100 grains of the sample; transfer to a 100 c.c. measuring flask; add water, and shake or stir with a glass rod till dissolved; then fill up to the mark with water, and well shake. Each c.c. of the solution will contain 1 grain of the sample. Fill a 50 c.c. burette with this solution, and carefully adjust until the upper surface of the liquid stands at 0°.

Weigh out 17 grains of pure crystallised silver nitrate, and dissolve in about 50 c.c. of distilled water in a glass beaker. Place the beaker under the burette, and run in the cyanide solution until the whole of the silver cyanide which is first precipitated is exactly re-dissolved (converted into the double cyanide of silver and potassium AgCy,KCy). The solution must be well stirred during the whole operation, and the latter portions of cyanide added drop by drop. (See Exp. 232.) Care must be taken not to add a single drop more than is necessary to complete the reaction, or the estimation will be too high.

The calculation is based on the following equation:—

$$\underset{(170)}{AgNO_3} + \underset{(130)}{2KCy} = AgCy,KCy + KNO_3,$$

which shows that 17 grains of silver nitrate demands 13 grains of potassium cyanide to convert it into AgCy,KCy. In an estimation made by the author 18·9 c.c. of solu-

tion containing 18·9 grains of the sample were used; therefore, 18·9 grains contained 13 grains of KCy.

1 grain contained $\frac{13}{18{\cdot}9}$

100 grains „ $\frac{100 \times 13}{18{\cdot}9} = 68{\cdot}78$ per cent.

PREPARATION OF SILVER PLATING SOLUTION.

§ 79. The preparation of a silver plating solution comprises three distinct operations, viz.:—

(*a*) The conversion of silver into silver nitrate.

(*b*) The precipitation of the whole of the silver from the above solution as silver cyanide or chloride.

(*c*) The conversion of the insoluble cyanide or chloride into the soluble double cyanide of silver and potassium.

Note.—Distilled water or filtered rain water should always be used.

It is assumed that the potassium cyanide used in making the following solution contains 75 per cent. of KCy.

Exp. 237. To prepare one quart of solution, proceed as follows:—Put 240 grains of fine silver in an evaporating dish; cover with nitric acid diluted with an equal bulk of water, and heat gently on a sand bath until dissolved. If the action becomes violent, add a little cold water, and remove the source of the heat. Any excess of acid should be avoided. Evaporate cautiously to dryness to expel the free acid, and dissolve the residue (which is silver nitrate) in water, and make up the solution to a quart with distilled water.

Make a solution of potassium cyanide by dissolving

200 grains in about 4 ounces of water, and add it in successive small portions to the silver nitrate solution with brisk stirring until a precipitate ceases to form in the clear liquid. (See Exp. 231.) If too much cyanide is added, some of the precipitated silver cyanide will be dissolved, but this error may be corrected by the reactions given in Experiment 235. Allow to stand till clear, then decant the clear liquid, and well wash the precipitate (AgCy) several times with water.

Dissolve 400 grains of potassium cyanide in 4 ounces of water, and transfer the solution to a tall glass jar. Make a paper scale, divided into inches and eighths, paste it upon the jar, and note the level of the solution. Add this solution to the precipitated silver cyanide, with brisk stirring, until a very small portion remains undissolved. The solution is the double cyanide of silver and potassium. Observe by reference to the paper scale the proportion of potassium cyanide solution used, then add an equal quantity to supply the necessary amount of "free cyanide"; add sufficient water to make the solution up to 1 quart, and filter. It is then ready for use. This forms one of the best silver plating solutions.

When deposited silver is required to have a dead pearly white appearance, a solution prepared as follows should be used:—

Exp. 238. Prepare a solution of silver nitrate as before, and precipitate the silver as AgCl, with hydrochloric acid in excess (Exp. 226). Well wash with hot water until the wash waters cease to redden blue litmus paper. Dissolve 600 grains of potassium cyanide in 6 ounces of water, and transfer to the glass jar containing paper scale mentioned in the previous experiment. Add the solution gradually to the silver chloride precipitate, stirring the whole time until it is almost completely dissolved. The reaction is as follows:—

$$AgCl + 2KCy = AgCy,KCy, + KCl.$$

Read off the proportion of cyanide used, and add one-half more for "free cyanide." Make up to 1 quart with water, and filter for use.

When the percentage of potassium cyanide in the commercial article is known, much time may be saved by adding the exact quantity required to precipitate the silver as cyanide (AgCy). This quantity is found by multiplying the weight of silver by 0·6 and by the reciprocal of the percentage.

§ 80. *Battery Method of Making a Silver Plating Solution.*

Exp. 239. Dissolve 2 ounces of potassium cyanide in 1 quart of water; place in this liquid a silver plate to form the anode, and a much smaller silver plate for the cathode. Pass a current through the solution until a piece of bright German silver the same size as the anode receives a good deposit when made the cathode in place of the small silver plate. Or pass the current until $\frac{1}{2}$ ounce of silver is dissolved from the anode. The following equations show the action which takes place:

$$KCy + Ag = AgCy + K.$$
$$K + H_2O = KHO + H.$$
$$KCy + AgCy = KCy,AgCy.$$

§ 80A. Copper brass and German silver work should be "quicked" immediately before plating. The quicking solution may be prepared as follows:—

Dissolve $\frac{1}{4}$ ounce of mercuric oxide in a strong solution of potassium cyanide. Note how much of the potassium cyanide solution was used to dissolve the red powder, and then add one half of that quantity for free potassium cyanide, and make up the bulk of the solution with water to 1 quart.

The work should be dipped in this solution until it becomes uniformly white. It should then be rinsed in

water and immersed in the plating solution to receive a deposit of silver.

Work that has been quicked before plating is less liable to strip in undergoing the subsequent processes of scratch-brushing and burnishing.

Iron, steel and zinc should be coppered in the cyanide bath (page 155) before silvering.

Pewter, Britannia metal, etc., is usually steeped in a hot potash solution, and transferred without rinsing to a "plating solution" containing a large excess of potassium cyanide, in which it is "struck," with a current dense enough to give evidence of incipient burning of the deposit. When struck the work is scratch-brushed and transferred to an ordinary plating solution to receive its final deposit. A beginner would no doubt find it easier to treat these metals as he would iron and zinc by first giving them a coat of copper in the cyanide bath.

GOLD.

Symbol Au. Atomic weight 196·2. Chemical equivalent $\frac{196·2}{3} = 65·4$. Electro-chemical equivalent ·0104679 grain. One ampère deposits 37·716 grains per hour. Pressure required = ·5 to 4 volts. Current density = ·75 to 1·5 ampères per square foot of cathode.

§ 81. Gold is dissolved in aqua-regia in the same way that silver is dissolved in nitric acid. The solution of gold chloride ($AuCl_3$) is evaporated over a water bath nearly to dryness to expel excess of acid, and the residue is dissolved in a small quantity of water. To the concentrated solution, add a solution of good potassium cyanide as long as a precipitate of gold cyanide (AuCy) is formed. Well wash the precipitate, and then add just sufficient potassium cyanide (KCy) solution to dissolve

it. Afterwards add, say one fourth of the quantity of potassium cyanide used in dissolving the precipitate to give the requisite amount of "free cyanide."

(*a*) Another method of preparing a gilding solution, is to precipitate the gold as fulminate by adding ammonium hydrate to a dilute solution of chloride of gold until the precipitate ceases to form. Thoroughly wash the precipitate, and whilst it is still wet add a solution of potassium cyanide until it exactly re-dissolves. Add free potassium cyanide as in the former method.

Notes.—Fulminating gold is very explosive when dry. The precipitate must therefore be dissolved in potassium cyanide immediately after washing.

This solution is more easily prepared than the preceding one, and works well.

(*b*) Gold plating solutions may be also prepared by the battery method in a similar manner to that described for silver (Exp. 239), but it is necessary to use 2 ounces of potassium cyanide per pint of water, and to substitute gold anode and cathode for the silver ones. This is the best method for non-chemical students.

All these solutions should be worked at about 150° F, with a gold anode, and with a current from two Bunsen cells arranged in series.

A good gilding solution should contain 1 ounce of gold per gallon, but a solution containing less than half that amount will work fairly well.

§ 82. *Recovery of Gold from Old Solutions.*

1st Method. Add hydrochloric acid in excess to the solution, in the open air or in a fume chamber, so as to avoid inhaling the fumes of hydrocyanic acid; syphon off the clear liquid, and collect the cyanide of gold. Dissolve it in aqua regia; evaporate nearly to dryness; add water, and precipitate the gold with ferrous sulphate.

2nd Method. Evaporate the solution to dryness; fuse the residue at a red heat; dissolve the saline mass in

water, and finely-divided gold remains. Dissolve this gold in aqua regia, and recover it, as in the first method, by precipitating it with ferrous sulphate.

§ 83. *Recovery of Silver from Old Solutions.*

Add hydrochloric acid in excess, syphon off the clear liquid, collect the precipitated silver chloride, dry and fuse in a clay crucible with twice its amount of sodium carbonate and a little nitre; pour into mould, allow to cool, and detach the slag by striking it with a hammer. Or the solution may be evaporated to dryness, the residue fused at a red heat, the soluble matter dissolved in water, and the finely-divided silver fused with carbonate of soda as before.

NICKEL.

Symbol Ni. Atomic weight 58·6. Chemical equivalent $\frac{58·6}{2} = 29·3$. Electro-chemical equivalent ·0046944 grains. One ampère deposits 16·899 grains per hour. Pressure required = 5 volts, and when struck reduce to 2 volts. Current density—strike with 15 ampères per square foot of cathode surface and then reduce to 3 ampères per square foot of cathode.

§ 84. Dissolve 3 ounces of the double sulphate of nickel and ammonium in 1 quart of water, and test the solution with blue litmus paper; if acid, ammonia must be cautiously added until the solution is slightly alkaline.

The above double salt may be made by the battery method thus:—

Suspend a large plate of nickel in sulphuric acid, and connect it with the carbon pole of the battery. Place a small nickel plate in connection with the zinc. Pass the current until sufficient nickel has been dissolved from the anode, which is determined by weighing it before and

after the experiment. The solution is then neutralised with ammonia. To each ounce of nickel sulphate in solution, add 1 ounce of ammonium sulphate, and test with litmus paper as described above.

All articles to be nickel plated, must be clean and polished very bright.

§ 84A. A dry process of preparing work for receiving a deposit of nickel is in successful operation. After the work has been well polished, it is thoroughly rubbed over with dry whitening, which is afterwards rubbed off, and the article suspended in the nickeling solution. A strong current is used at first so that the work may be struck as quickly as possible.

Iron and steel articles are first coppered, then polished with a mop or "dolly" as it is sometimes termed, wiped quite clean with dry whitening and quickly covered with a deposit of nickel in the nickel vat. The work is then taken out, polished, wiped with whitening, and again put in the plating vat for the complete deposit.

Britannia metal articles are first brassed (see § 86), then treated as mentioned above for articles of iron and steel.

Tin-plate work is treated like Britannia metal, except that it is put through the brassing solution twice before being plated.

The advantages claimed for the above methods are—that they are much cleaner and healthier; that, the work being less liable to receive scratches, has a better finish. The objections are—that the nickel is liable to crack and strip off if left too long in the vat; that the work is liable to tarnish and the deposit to strip if allowed to stand too long after wiping before being put into the vat. This method is only suitable for large work. Small work is better prepared in the wet way.

As nickel solutions are used in the concentrated state, the nickel salt begins to crystallise after a time, especially in a warm place; in which case water must be added.

It should also be borne in mind that the anode does not maintain the strength of the solution, so that it is necessary to add crystals of the double salt from time to time to replenish the weakened solution.

PREPARATION OF SOLUTIONS FOR DEPOSITING ALLOYS.

BRASSING SOLUTION—PRELIMINARY EXERCISES.

§ 85. Exp. 240. Crush a crystal of copper sulphate about the size of a pea, in a porcelain or wedgwood ware mortar; transfer to a clean test tube; add water, and heat until dissolved. Filter if not clear. Allow to cool, and to the cold solution add a single drop of ammonia; the solution becomes turbid. Add more ammonia drop by drop, occasionally shaking the tube, until the turbidity disappears, and the solution assumes a beautiful blue colour.

Exp. 241. Take a lump of potassium cyanide about the size of a horse bean, dissolve it in a test tube half full of water, and filter if necessary. Add this solution drop by drop to the blue copper solution obtained in Experiment 240; shaking after every addition until the blue colour is resolved into a faint violet tint; then a few drops more will render the solution colourless. From such a solution copper alone could be deposited.

Exp. 242. Dissolve a small portion of sulphate of zinc in water placed in a test tube, and add a portion of ammonia solution drop by drop until the white precipitate which forms at first re-dissolves, and a clear, colourless solution results. Then, add to this ammoniacal zinc solution, the potassium cyanide solution obtained in Experiment 241, and observe that no visible change

occurs, so that there is no indication when sufficient of the cyanide has been added. From this solution, if the proper amount of potassium cyanide has been added, zinc alone could be deposited.

Exp. 243. Mix together the colourless cyanide solution of copper and the cyanide solution containing zinc, in about equal quantities of each, then such a combination would constitute a solution from which brass, which is an alloy of copper and zinc, could be deposited.

§ 86. Exp. 244. To prepare 1 quart of good brassing solution, proceed as follows :—

(*a*) Weigh out 400 grains each of copper sulphate and zinc sulphate. Dissolve both together in 12 ounces of hot water; allow to cool and decant the clear liquid; or pass it through a large filter paper fixed in a glass funnel into a quart bottle, then add liquid ammonia cautiously, shaking after each addition until the precipitate which forms at first re-dissolves, then add more liquid ammonia until the clear blue solution smells strongly of the gas.

(*b*) Dissolve 2000 grains of good commercial potassium cyanide in 16 ounces of water; allow to cool, filter, and transfer to a pint bottle.

Make a paper scale, divided into inches and eighths, paste it on the bottle, and note the level of the solution. Pour the cyanide solution very gradually and with constant stirring or shaking into the ammoniacal zinc-copper solution until the colour is reduced to a very faint violet tint. Read off from the scale the quantity of cyanide solution used, and add one-sixth of that quantity to completely destroy the colour and to furnish the requisite quantity of "free" cyanide. Then fill up the bottle with water. This solution is a mixture of the potassio-cyanides of copper, zinc, and ammonium, to-

gether with a small proportion of free potassium cyanide and free ammonia.

It should be worked at a temperature of about 55° C., using a good brass anode and a current equal to that produced by three or four Bunsen's cells, each 1 pint size. The student is enjoined to pay strict attention to the directions given in preparing the solution, especially with respect to the amount of potassium cyanide used. The writer has found that the first solution of this kind prepared by the majority of students fails to give a deposit on account of too much potassium cyanide having been used. It is more difficult to deposit copper and zinc simultaneously so as to constitute brass, than to deposit either metal separately, and a brass of good colour can only be obtained by nicely adjusting the strength of the current. If the current is too strong, either zinc alone will be deposited or the brass may be too pale in colour, whilst if the current be too weak, either copper only will appear, or a red brass will deposited.

The first defect may be remedied by lifting the anode partly out of the solution, or by increasing the distance between the anode and the receiving surface. The latter defect, by immersing more of the anode, or by placing the anode and the work nearer together in the solution.

§ 87. *General Method of preparing Solutions of Alloys, as Brass, German Silver, etc.*

To make 1 quart of solution, dissolve ¼ oz. of the alloy in a mixture of two measures of strong nitric acid with one measure of water. The acid mixture should be added to the alloy in successive small quantities, and heat applied until red fumes cease to come off, and just a small fragment of the metal is left undissolved. In this way all injurious excess of acid will be avoided. The solution thus obtained should be diluted with sufficient water to make up its bulk to 12 fluid ounces. Decant the clear solution into a quart bottle, add strong ammonia

until the precipitate formed at first re-dissolves, and then potassium cyanide solution until the blue colour is just removed. Finally add one-sixth more cyanide, then fill up the bottle with water.

In making an alloy solution in this way, observe the same precautions, and proceed exactly as prescribed for preparing the brassing solution. Use a strip of the same alloy for the anode, and work the solution hot, using a current strong enough to evolve hydrogen from the cathode.

§ 88. *Pickles, Dips, etc.*

To remove grease,	½ lb. of common potash per gallon of water. Used hot.
To remove mere films of oxide from surface of work,	½ lb. of potassium cyanide per gallon of water. Very useful for preparing work for nickel plating.
Pickle for cast iron,	½ lb. oil of vitriol per gallon of water.
For brass (dead),	Nitric acid, 2 measures; oil of vitriol, 1 measure; and a little common salt.
For brass (bright),	Nitric acid, 1 measure; oil of vitriol, 2 measures; water, 2 measures.
For zinc,	Oil of vitriol, 1 measure; water, 20 measures.

§ 89. *Stripping Liquids.*

For nickel,	Nitric acid, 4 lbs.; sulphuric acid, 16 lbs.; water, 5 lbs. Used cold.

For silver, - - -	Cover the work with sulphuric acid, and add nitre from time to time in small quantities Used hot.
Do., - -	Sulphuric acid, 10 measures; nitric acid, 1 measure. Used cold Work must be dry before being dipped in this liquid.

All deposits may be stripped from work by making the articles the anode in a suitable liquid.

PART II.

ASSAYING BY DRY METHODS.

§ 90. Assaying (Fr. *essayer*; Lat. *exigo*, to examine, to weigh) was a term originally used to denote the estimation of a particular metal in an ore, alloy or other metallic compound by the dry way. At the present time the word has a far more extended signification, and assaying has become so identified with chemical analysis that the two terms are often used synonymously, and it is not unusual to call the determination of an *organic* constituent of a mixture 'an assay.' It should further be borne in mind, that analysis contemplates the determination of every constituent, while an assay only involves the estimation of one or more.

§ 91. Practical assaying may be conveniently classified under two heads, viz.—"Dry" and "Wet."

In the former, the operator effects the isolation of the metal by the agency of heat, generally following the methods, and even the sequence of the methods carried out on the large scale in the works, by which means he considers he will be able to discover the amount of metal a given ore will yield when treated in quantity. But the amount of metal obtained will often differ according to the plan pursued and the kind of apparatus used. Improvements now follow each other so rapidly that a larger yield is obtained from the same compound than formerly, so that many *dry* methods of assaying have been superseded by the more accurate although often tedious *wet* processes.

In the latter, advantage is taken of the strong chemical affinities of those liquids which easily dissolve metals and their compounds (sometimes at the ordinary temperature), and of those re-agents which form insoluble compounds with different elements by which means they are precipitated and separated in a weighable form. In some cases, minerals are first acted on by gaseous agents such as chlorine and sulphurous acid, the metal being afterwards separated by solution and precipitation. In others, a metal in solution is displaced by the addition of another metal whose chemical affinities are greater, such as copper by iron, silver by copper, etc.

Under the head of *wet* methods may be included those operations in which a component is isolated by the agency of electricity, although in some cases solution is not necessary, the compound being simply melted and maintained in a state of fusion while the current passes through it.

§ 92. Wet assays may very conveniently be divided into two classes—

1. *Gravimetric*, which aims at transforming the known components of a body into their elementary state, or some combinations which will admit of exact determinations by weight, and of which the composition is accurately known.

2. *Volumetric*, or analysis by volume. This admits of a more rapid estimation than by weighing, and consists of the determination of that volume of a re-agent of definite strength which is required to effect a certain change in the liquid to be analysed. For example, if we wish to know the amount of copper in a solution of its nitrate which has been rendered blue by ammonia, it may be ascertained by running into that liquid from a graduated burette a sufficient quantity of potassium

cyanide to exactly decolourise such solution; the potassium cyanide having been previously standardised by observing how much of it is required to decolourise a solution containing a known quantity of pure copper. The standard solution having been accurately determined, the balance will only be required to weigh out the samples to be tested.

PRELIMINARY OPERATIONS.

§ 93. *Sampling.* In determining the quantity of any constituent of an ore or metallurgical product, it is absolutely essential that the portion of the substance taken for assay corresponds to the average quality of the ore or product. This is best done by taking a large quantity, thoroughly mixing, and removing small portions, about $\frac{1}{20}$th of the whole, from different parts of the heap, which must also be thoroughly mixed together. This is again repeated on the reduced quantity till a sample of about $\frac{1}{2}$ lb. is obtained.

If the sample is a liquid it is sufficient to shake up the bottle containing it, and take a measured quantity. If the liquid contain solid matter in suspension, measure the whole, filter, well wash the residue, make up to original bulk, and assay the liquid and solid portions separately.

If the sample is a metal or alloy, it should be cleaned and a hole drilled through it, the borings being used for the assay. Soft metals may be cut with a knife instead of boring.

§ 94. *Drying.* If the returns are required on a dried sample, the substance must first be crushed to a fine powder, and carefully dried at a temperature of 100° C., so as to remove all the moisture which has been mechanically absorbed. This can only be done when the body

under examination does not yield its combined water or otherwise decompose at that temperature. When it is unsafe to heat at 100°, a lower temperature may be obtained by immersing the vessel containing the powder in a liquid which has a lower boiling point than water; or the drying may be partly effected by pressing between blotting paper; or placing in a dish in a desiccator, which latter is kept dry by means of sulphuric acid, or chloride of calcium. If the substance persistently retains water at 100°, then the air bath (Fig. 52) may be employed, the temperature of which is regulated with the aid of a thermometer.

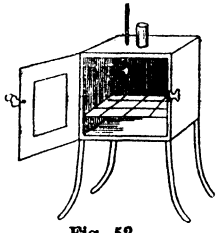


Fig. 52.

§ 95. *Mechanical subdivision.* The facility with which a body may be dissolved or acted on by fluxes is largely influenced by the state of division of the particles; the finer these are, the more perfect and more rapid will be the action. The crushing and grinding is performed in small quantities at a time, in mortars of various kinds made of cast iron, steel, gun-metal, porcelain, or agate. For moderately soft bodies porcelain is used, for ordinary ores and products the iron mortar. When it is necessary to avoid loss and the mineral is very hard, the steel mortar is indispensable. In cases where the substance requires to be reduced to an impalpable powder, it is effected by pulverising in small portions at a time in the agate mortar.

It sometimes happens as in the case of gold and silver ores that particles of metal are present, which, on account of their malleability, cannot be crushed to powder, and passed through the sieve. These "metallics" as they are termed are assayed separately, and the amount relative to the portion examined added to the final result.

After crushing and drying a given quantity, it should be put in a dry stoppered bottle for further use.

§ 96. *Weighing.*

See § 17. No exact rule can be given for the amount to be taken for analysis, which will differ according to the amount of the body present in the substance to be examined. In a sample of brass for example, 1 gramme or 15 grains would be a suitable amount; but in iron, containing a minute quantity of phosphorus or manganese, five to ten times this amount would be best to determine the amount of these elements. The greater the quantity taken the more accurate is the result likely to be, but the smaller the quantity the sooner will the assay be finished, so that if the operator avoids both extremes he will best combine accuracy with economy of time.

In weighing, the knife edges must not be allowed to fall suddenly on the agate planes. During the addition or removal of weights or other matter, the balance must be lifted off the agate planes. The pans must not swing during the weighing. The balance must be perfectly horizontal. The weights should not be lifted with the fingers, but manipulated with forceps. Both weights and pans should be scrupulously clean and a camel hair brush kept at hand for removal of dust, etc.

Bodies should never be weighed while hot, but first allowed to cool in a desiccator. Solid substances are generally weighed in watch glasses, or, if the substance be hygroscopic, it may be weighed in a stoppered bottle, then a portion turned out for analysis, and the bottle and its contents again weighed; the loss indicating the amount taken.

Sometimes a precipitate is decomposed by ignition; it then becomes necessary to weigh it on a tared filter paper, previously dried at 100°. This drying of the paper is repeated until the weight is constant. But as paper rapidly absorbs moisture on cooling, it must be

cooled and weighed in a stoppered bottle which has been accurately counterpoised. A pair of watch glasses with carefully ground edges, and a clip, may be substituted for the weighing bottle.

Liquids should always be weighed in stoppered bottles, as loss by evaporation is very likely to occur from open ones.

As the ashes of burnt filters are usually mixed with the ignited precipitates, the average weight of the ash, previously determined, must be subtracted from the weight obtained. This is assumed to be done in the following examples. The average weight is determined by burning a number of similar papers (say ten) until all carbonaceous matter is removed, in a weighed platinum crucible, cooling in a desiccator, carefully weighing and dividing by the number used.

§ 97. *Estimation of Moisture.*

In some cases it is desirable to estimate the amount of moisture in a given substance, as in fuel, for example. A portion, say 30 grains, is first weighed in a counterpoised pair of dry watch glasses. The top-glass having been removed, the whole is put into a water oven (Fig. 53), and maintained at 100° C. for an hour. The cover is then put on, being held in position by a clip, the whole is cooled in a desiccator, and weighed. The operation is repeated until the weight is constant.

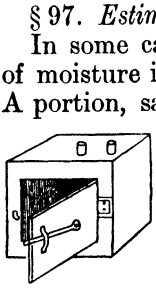


Fig. 53.

The mode of estimating combined water depends on the nature of the substance. When the body may be ignited, so as to remove the water, a platinum or porcelain crucible would be most convenient. When the body is decomposed at a red heat, but the water not removed at 100°, then the air bath (Fig. 52) may be employed.

§ 98. *Solution.*

Substances are generally dissolved in flasks, beakers,

or dishes; the solution being promoted, in most cases, by the agency of heat.

The most suitable beakers, especially where ebullition is necessary, are of a conical form, which may be conveniently closed with a small funnel. In cases where liquids require to be evaporated, the ordinary cylindrical shape is most suitable, as a greater surface is exposed, and solid matter readily washed out. The top should be covered with a clock glass, having a hole at one side for escape of vapours and for the introduction of a glass rod to stir the liquid, as bumping is to a large extent prevented, and solution or evaporation accelerated when continuous stirring is possible. Glass rods should be carefully rounded at the ends, and never left in a liquid when the latter is liable to bump. In cases where long continued ebullition is necessary, a flask with a long neck is commonly used, the liquid being less liable to loss, as the fluid which is spurted up is stopped by the sides and flows back again to the main liquid. These vessels however, are more difficult to clean than beakers. If alkalies have to be treated, glass is unsuitable, being acted upon by these bodies.

§ 99. *Evaporation.*

The simplest case is where the fluid merely requires to be concentrated, and is most rapidly performed in a large dish, generally of porcelain, which should never be more than two-thirds full, and the top loosely covered with a clock glass. The vessel should be heated on a sand or water bath (Fig. 54); and the operation will be much more safely performed if the liquid is kept just on the point of ebullition.

Fig. 54.

A convenient water bath may be made by placing the evaporating dish on the top of a beaker in which water

is kept boiling. When it is desirable to evaporate a liquid to dryness the action must be closely watched towards the conclusion, as small particles are projected upwards by the vapour. This may be avoided by supporting the dish or other vessel on an iron ring, 2 inches from the bottom plate, under which the burner is placed, the vessel being also surrounded by a case of sheet iron; in this way a uniform heat will be communicated to all the parts.

Some bodies have a tendency to creep up the sides and over the edge of a vessel during evaporation; in such cases, the inside edge should be slightly greased with tallow. Residues which are thick or gelatinous are dried more quickly, and spurting avoided, if agitated with a glass rod.

§ 100. *Ignition.*

This is generally effected in dishes and crucibles of platinum and porcelain, the greatest care being required to prevent loss by spurting and decrepitation. In all cases where platinum may be used, vessels of this metal are preferable on account of lightness, infrangibility, and the readiness with which they may be heated to redness. Sometimes patches of carbonaceous matter adhere tenaciously to the cover and sides of the crucible. These parts must be very strongly ignited to remove such stains before weighing. A gas muffle will be found exceedingly convenient for igniting precipitates, as the temperature is uniform and may be easily regulated. With regard to this subject, Fresenius lays stress on the following four points:—

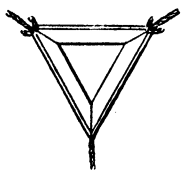


Fig. 55.

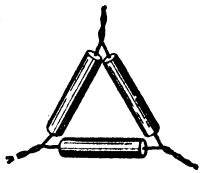


Fig. 56.

(1) No loss of substance must be incurred.

(2) The ignited precipitates must really be the bodies

they are represented to be in the calculation of the results. (3) The incineration of the paper must be complete. (4) The crucibles must not be attacked.

Crucibles are usually supported on triangles of platinum or pipe-clay (Figs. 55 and 56).

§ 101. *Precipitation.* Cylindrical glass beakers, in all cases where glass is admissible, are preferred on account of the facility with which the precipitate may be washed on to the filter, and the last traces removed. Sometimes the precipitation is effected by means of a gas such as sulphuretted hydrogen; in that case the beaker should be covered with a glass plate having a hole through which the glass tube conveying the gas may pass. That portion of the tube inside the beaker should be detachable, so that any precipitate may be removed from the inside. A large tube drawn out thus

will be found very convenient for cleaning. Precipitation is generally hastened by warming the solution, and by much stirring.

§ 102. *Filtration.* This operation is in the vast majority of cases performed by means of paper, which should be sufficiently close in texture to prevent the finest precipitate passing through; such paper should filter rapidly and be as free as possible from ash. The amount of ash is found by igniting a given number of papers of equal size in a platinum crucible till a perfectly white ash is left, cooling in a desiccator, weighing, and deducing the amount for each one.

(*a*) The funnels used should incline at an angle of 60°, the ribbed form being preferred for rapidity. The paper should never protrude beyond the funnel, and should, in fact, be a little less. The funnel is supported either in the mouth of a beaker or flask, or on a suitable wooden

stand. The stem of the funnel should be allowed to touch the side of the beaker, so that the liquid may run quietly down the side and not splash. Whenever possible, a liquid should be filtered hot, as it runs through much more quickly, and for the same reason the precipitate should be washed with hot water. A liquid should never be poured directly into the centre of the filter, but poured cautiously down a glass rod, so as to run on to the sides. In order to prevent a liquid creeping over the edge of a beaker and running down the outside after pouring on to a filter, the edge may be greased with a little tallow smeared on the outer edge at the part where the pouring is effected.

(*b*) In cases where a precipitate or insoluble residue is not required for weighing, a plug of cotton wool may be inserted into the neck of the funnel and used as a filter. Sometimes asbestos is substituted for paper where strong acids would attack paper, being especially useful where a precipitate has to be dried at a certain temperature and weighed. For this purpose a glass tube is drawn out at one end, and the asbestos loosely plugged into the narrowed part.

(*c*) To remove the last traces of a precipitate from the containing vessel, a glass rod having one end covered with a bit of India-rubber tubing is employed to rub the sides of the beaker, or a caoutchouc finger stall may be used. If the precipitate has been filtered from a flask, then a long feather, from which all the plumules have been stripped except a tuft at the end, is used.

(*d*) It is generally advisable to allow a precipitate to completely settle before filtering, so that the supernatant liquid may be poured through the paper first, and the precipitate washed two or three times before the main body is swilled on to the filter by a jet of water projected from a wash bottle. To ascertain whether a precipitate is properly washed, the last few drops may be evaporated on platinum foil, when no residue should be left.

RE-AGENTS.

By the term re-agents is meant substances used by the chemist to ascertain the nature of the body being examined. One class is used to separate the bodies into different groups, another to recognise the special members of a group.

§ 103. (*a*) *General Re-agents.*

Acetic Acid, - - -	$HC_2H_3O_2$	1 part water to 1 acid.
Ammonium oxalate, - -	$Am_2C_2O_4$	20 parts ,, ,, 1 salt.
,, chloride, - -	AmCl	Saturated solution.
,, carbonate, -	Am_2CO_3	4 parts water, 1 part salt, and 1 part ammonia.
,, sulphide, - -	Am_2S	Saturate 3 parts of ammonia with sulphuretted hydrogen, and add 2 parts of ammonia.
Ammonia solution, - -	AmHO	Used strong and dilute.
Ammonium sulphate, - -	Am_2SO_4	Saturated solution.
Silver nitrate, - - -	$AgNO_3$	20 parts water to 1 of salt.
Barium chloride, - -	$BaCl_2$	10 ,, ,, ,, 1 ,, ,,
,, nitrate, - - -	$Ba2NO_3$	15 ,, ,, ,, 1 ,, ,,
Calcium chloride, - -	$CaCl_2$	5 ,, ,, ,, 1 ,, ,,
Cobalt nitrate, - - -	$Co2NO_3$	10 ,, ,, ,, 1 ,, ,,
Calcium hydrate, - -	CaH_2O_2	Saturated solution.
Ferric chloride, - - -	Fe_2Cl_6	2 of water to 1 of salt.
Hydrochloric acid, - -	HCl	3 ,, ,, ,, 1 ,, acid.
Nitric acid, - - -	HNO_3	2 ,, ,, ,, 1 ,, ,,
Lead acetate, - - -	$PbH_6C_4O_4$	10 ,, ,, ,, 1 ,, salt.
Sodium hydrate, - -	NaHO	10 ,, ,, ,, 1 ,, hydrate.
,, phosphate, - -	Na_2HPO_4	10 of water to 1 of salt.
,, carbonate, - -	Na_2CO_3	Saturated solution.
Potassium cyanide, - -	KCy	6 of water to 1 of salt.
,, ferrocyanide, -	K_4FeCy_6	12 ,, ,, ,, 1 ,, ,,
Sulphuretted hydrogen, -	H_2S	Saturated solution.
Sulphuric acid, - - -	H_2SO_4	5 of water to 1 of acid.

(*b*) The following re-agents are used in the dry state:—

Borax, $Na_2B_4O_7$. Fusion Mixture, $K_2CO_3 + Na_2CO_3$. Nitre, KNO_3. Potassic cyanide, KCy. Lime, CaO. Sodium carbonate, Na_2CO_3.

(*c*) *Special Re-agents.*

Ammonium sulpho-cyanide,	AmSCy	10 parts water to 1 salt.
,, acetate - -	$AmC_2H_3O_2$	10 ,, ,, ,, 1 ,,
,, molybdate, -	Am_2MO_4	
Alcohol, - - - -	C_2H_6O	
Barium hydrate, . -	BaH_2O_2	
Barium carbonate, - -	$BaCO_3$	In suspension in water.
Carbon disulphide, - -	CS_2	
Copper sulphate, - -	$CuSO_4$	10 of water to 1 salt.
Chlorine water, - - -		
Calcium sulphate, - -	$CaSO_4$	Saturated solution.
Ether, - - - -	$C_4H_{10}O$	
Hydrochloric acid, - -	HCl	Concentrated.
Hydrofluosilicic acid, - -	$2HF,SiF_4$	
Mercuric chloride, - -	$HgCl_2$	20 of water to 1 salt.
Indigo solution, - - -		
Magnesium sulphate, -	$MgSO_4$	10 ,, ,, ,, 1 ,,
Methylated spirit, - -		
Magnesia mixture, - -		
Nitric acid, - - -	HNO_3	Concentrated.
Platinum chloride, - -	$PtCl_4$	10 of water to 1 salt.
Potassium ferricyanide, -	$K_6Fe_2Cy_{12}$	12 ,, ,, ,, 1 ,,
,, chromate, - -	K_2CrO_4	10 ,, ,, ,, 1 ,,
,, iodide, - -	KI	10 ,, ,, ,, 1 ,,
Sodium acetate, - -	$NaC_2H_3O_2$	10 ,, ,, ,, 1 ,,
,, hypochlorite, -	NaClO	By passing Cl gas into dilute solution of soda.
Hydrogen sodium sulphate,	$NaHSO_4$	5 of water to 1 salt.
Sodium thiosulphate, -	$Na_2S_2O_3$	30 ,, ,, ,, 1 ,,

(*d*) *Solids.*

Oxalic acid, $H_2C_2O_4$; Hydrogen potassium sulphate, $HKSO_4$; Potassium chlorate, $KClO_3$; Microcosmic salt, $HNaAmPO_4$; Barium hydrate, BaH_2O_2; Calcium chloride, $CaCl_2$; Calcium carbonate, $CaCO_3$; Ferrous sulphate, $FeSO_4$; Manganese dioxide, MnO_2; Starch; Sulphur; Iron Sulphide, FeS; Iodine; Bromine; Sodium Chloride, NaCl; Zinc; and copper.

CHARACTER AND USES OF RE-AGENTS WITH THEIR COMMON IMPURITIES.

§ 104. (*a*) *Acids.*

Sulphuric Acid is most likely to be contaminated with nitric acid, sulphate of lead, and arsenious acid. It is used as a solvent for liberating sulphuretted hydrogen, and for precipitating lead, barium, etc.

Hydrochloric Acid should be colourless and free from arsenic, sulphurous acid, chloride of iron, and free chlorine. It should leave no residue when evaporated on platinum foil. It is largely used as a solvent, being especially useful where it is not desirable to form insoluble compounds or to oxidise the body acted upon. It cannot be used in presence of silver, lead, or mercurous salts.

Nitric Acid is a good oxidising agent, and largely used as a solvent for metals and metallurgical products. Its commonest impurities are oxides of nitrogen, potassium and sodium sulphates, and chlorine.

Acetic Acid, if impure, is liable to contain sulphuric acid, hydrochloric acid, copper, lead, iron and calcium. It is employed in cases where a mineral acid is not admissible.

Tartaric Acid is used as a saturated solution, and also as a dilute solution. It may contain calcium and sulphuric acid.

Sulphuretted Hydrogen forms a most useful group re-agent as well as for special cases. It is decomposed by contact with air and should be prepared every two or

three days and kept in a black stoppered bottle. It is frequently used in the gaseous form.

(*b*) *Alkalies.*

Potash and Soda are most likely to be contaminated with silica, alumina, carbonic, sulphuric and hydrochloric acids, and oxide of lead. They are seldom perfectly pure, but good potash and soda should effervesce but slightly with acids, and their solutions should be kept in bottles of German glass which contain no lead. They are chiefly used for dissolving certain oxides, and thus separating them from insoluble ones.

Ammonia.—The solution is used both concentrated and dilute. It should be colourless, and leave no residue when evaporated on platinum foil. It may contain sulphate, chloride, and carbonate. This is one of the most frequently used re-agents, being employed to precipitate many oxides and to neutralise acids.

Barium Hydrate.—The crystals of this re-agent are dissolved in water and the insoluble matter filtered off. It is used to precipitate magnesia; also carbonic, sulphuric and phosphoric acids.

Calcium Hydrate Solution or lime water is used to separate magnesia, etc., from the alkalies, and for the detection of carbonic acid. It must be kept excluded from the air.

(*c*) *Salts of the Alkalies.*

Sodium Hydrogen Sulphite is a powerful reducing agent and used to reduce arsenic to arsenious acid, chromic acid to the sesquioxide, and ferric oxide to ferrous oxide, etc. Also used to separate sulphide of arsenic, in which it is soluble, from the sulphides of antimony and tin.

Hydrogen Sodium Phosphate, when in solution, must be kept in German glass bottles since it acts on glass containing lead. It precipitates the alkaline earths and all heavy metallic oxides. It is a special test for magnesia. The commercial salt may be purified by re-crystallisation.

Sodium Thiosulphate is used for precipitating many metals as sulphides, chiefly in separations, such as copper from zinc.

Sodium Acetate is employed principally to precipitate phosphate of iron, and to separate oxide of iron from alumina. Its chief impurities are sulphates.

Sodium Carbonate.—The impurities of this salt are likely to be chlorides, phosphates, and silicates; it may be largely purified by re-crystallisation. It precipitates most metals as basic carbonates, and decomposes certain insoluble salts. It is frequently used for neutralising acid solutions where ammonia could not be employed.

Ammonium Carbonate acts in much the same way as carbonate of soda, being generally preferred because of its volatile character. It is chiefly used to precipitate barium, strontium, and calcium, so as to separate them from magnesia. If impure, it may contain lead, iron, sulphates, and chlorides.

Ammonium Chloride serves principally to retain certain oxides or salts in solution, when others are precipitated by ammonia or other re-agents. It should leave no residue when evaporated on platinum foil. Its most common impurity is iron.

Ammonium Molybdate.—This salt is used in the estimation of phosphorus, and prepared for that purpose by dissolving it in ammonia, and decanting the clear fluid

into strong nitric acid till the precipitate re-dissolves. The following proportions may be taken :—

60 grams. of ammonium molybdate.
500 c.c. of nitric acid (specific gravity 1·4).
400 c.c. of ammonia (specific gravity ·96).
400 c.c. of water.

Ammonium Sulphide is a valuable group re-agent, as it effects the precipitation of several metals which are not thrown down by sulphuretted hydrogen. It also dissolves the sulphides of tin, antimony, arsenic, etc., and thus separates them from lead, bismuth, etc.

Sodium Sulphide.—This re-agent is substituted for ammonium sulphide to dissolve sulphides of antimony, tin, etc., in separating them from sulphide of copper.

Potassium Sulphate is used to separate baryta and strontia ; it is used in many cases in preference to sulphuric acid.

Potassium Nitrite is used in the separation of nickel and cobalt, and to liberate iodine from its compounds in the presence of free acid.

Potassium Bichromate is a valuable re-agent in the volumetric estimation of iron. Also a good test for lead.

Potassium Cyanide is of great importance in the separation of nickel and cobalt, and of copper sulphide from cadmium sulphide, the latter being insoluble in potassium cyanide.

(*d*) *Salts of Alkaline Earths.*

Barium Chloride serves to precipitate sulphuric acid

by which means the acid may be estimated, and thus, indirectly, the estimation of sulphur also.

Barium Nitrate is used for the same purpose as the chloride in cases where insoluble chlorides, such as silver, would be formed by barium chloride.

Barium Carbonate is useful in separating the sesquioxides of iron and alumina from zinc, manganese, etc., when sulphuric acid is absent.

Calcium Sulphate is chiefly employed in distinguishing between barium, strontium, and calcium. Also for the detection of oxalic acid.

Magnesium Sulphate is employed in the detection of phosphoric acid. The following mixture is used in quantitative estimations :—

Magnesia Mixture.—The preparation of this re-agent is described by Fresenius as follows :—

Dissolve 83 grammes of crystallised sulphate of magnesia in boiling water, add 5 c.c. of hydrochloric acid, then 82 grammes of crystallised barium chloride, previously dissolved in water ; boil, decant, filter, and test whether dilute sulphuric acid gives any precipitate in the filtrate ; if it does, add a little more sulphate of magnesia. Mix the filtrate and washings ; concentrate by evaporation ; allow to cool ; transfer to a litre flask ; add 165 grammes of pure ammonium chloride, 260 c.c. of ammonia, and then add water to the mark. Allow to stand a few days and filter, if necessary.

(*e*) *Salts of Heavy Metals.*

Ferrous Sulphate furnishes a most delicate test for nitric acid in virtue of its reducing character. It is also used to precipitate gold from its solutions.

Ferric Chloride serves to effect the decomposition of phosphates of the alkaline earths, and for the detection of hydroferrocyanic acid, with which it forms Prussian blue.

Copper Sulphate is used for the detection of arsenic, ferrocyanides, and in the estimation of hydriodic acid.

Stannous Chloride is a good test for mercury and gold.

Platinum Chloride is the best re-agent for estimating ammonium and potassium.

Silver Nitrate serves for the separation and detection of some acids.

ASSAYING BY DRY METHODS.

IRON ORES AND RICH IRON SLAGS.

§ 105. First roughly crush half a pound of the ore and dry it at a low temperature to expel the mechanically absorbed water, taking care that the portion selected is typical of the whole mass of ore. Then crush to a fine powder in a clean iron mortar, until the whole can be passed through a sieve with twenty meshes to the linear inch. Now take from this 1000 grains and reduce sufficiently to pass through a sieve of sixty to eighty meshes to the linear inch and place in a dry corked bottle for use. It sometimes happens with hard quartzose ores, that triturating or grinding rubs off portions of iron from the mortar and pestle, so that such ores should be powdered by a percussive action of the pestle. Soft ores, such as limonite, may be pulverised in Wedgwood-ware mortars.

The object of the dry assay is to obtain the iron as a compact button of cast iron, by reducing its oxide with carbon, and separating the earthy matter as slag by the agency of suitable fluxes, which will vary with the nature of the ore. This is often ascertained by inspection, or by repute. Thus hematites, both red and brown, are usually associated with silica, and require both lime and alumina. Spathic and calcareous ores, not containing clay, require sand, or an acid silicate such as glass, besides lime and alumina ; while clay ironstones may be fluxed with lime alone.

§ 106. Iron ores may be conveniently arranged for assaying in the dry way, into five classes :—

1. Ores containing silica, lime, and another base, which are fusible, *per se*.

2. Ores in which silica predominates.
3. „ „ lime „
4. „ „ alumina „
5. Ores containing a large amount of magnesia; these are most difficult to liquefy.

§ 107. In case the nature of the ore is unknown, and cannot be ascertained by inspection, the following preliminary investigation, devised by Berthier, will be found useful.

(*a*) Weigh out 100 grains of the ore; heat to redness in a porcelain crucible; cool and weigh. The loss represents the amount of carbonic acid, water, and other volatile matters; except when the ore contains ferrous oxide, which is thus oxidised to the ferric condition with a proportionate increase in weight.

(*b*) Weigh out another 100 grains, and heat with very dilute nitric acid, which dissolves out the calcium and magnesium carbonates; filter, wash the residue, dry and weigh. This insoluble portion consists of oxide of iron, quartz, and clay; the difference gives the amount of earthy carbonates.

(*c*) Weigh out another 100 grains, and digest with strong hydrochloric acid, which dissolves both the earthy carbonates and the oxide of iron, while the clay and silica remain insoluble; these are weighed, and the difference gives the amount of the carbonates of lime, magnesia, and oxide of iron. Now, the amount of these earthy carbonates having been previously determined, the quantity of oxide of iron present is easily computed.

§ 108. Having thus roughly ascertained the composition

of the ore, the nature and proportion of the fluxes can be calculated so as to produce a fusible slag. The following are suitable slags to aim for :—

$$6(2CaO.SiO_2) + 2Al_2O_3.3SiO_2, \text{ and}$$
$$3(CaO.SiO_2) + Al_2O_3.3SiO_2.$$

—the former consists of 38 silica, 15 alumina, and 47 lime; while the latter contains 30 lime, 14 alumina, and 56 silica. But the temperature of an ordinary assay furnace is barely sufficient to melt the second of these slags, without the addition of a little borax and fluor-spar. Borax, however, is not desirable when it may be dispensed with, as it takes up a portion of the iron oxide, which would then escape reduction, causing a loss on the assay. Good blast furnace slag, obtained from a furnace producing grey iron, if carefully freed from shots of metal, may be used as a flux for rich ores containing but little foreign matter.

§ 109. The readiest way of determining the proper amount and kind of flux for a given ore is to make three trial assays, which may be all done at the same time, by using the small brasqued crucibles (Fig. 34). The best proportion will yield the highest result. See § 111.

The following mixtures of fluxes will be found suitable for 100 grains of the ordinary ores of iron :—

a	*b*	*c*
White Sand, 10 China Clay, 20 Lime, - - 25	Lime, - - 25 Glass, - - 25	Fireclay, - 30 Lime, - - 25

The weight of fluxes in most cases is about one half that of the ore used.

	Lime.	Fluor Spar.	Clay.
PLATNER recommends :—			
For magnetic ore, - - - - - - - - -	10	25	—
For specular ore, - - - - - - - - -	5	25	—
For earthy and siliceous hematites, clay ironstone, and limonite, - - -	25	25	—
For forge cinders, - - - - - - - - -	20	20	—
For spathic ores, - - - - - - - - -	—	20	10

With the above proportions 100 grains of ore would be used.

§ 110. (*a*) The assay may be conducted in a clay or blacklead crucible, or the former lined with charcoal paste; the author has always found the lined crucible to give the best results. In naked crucibles 25 per cent. of charcoal must be added to the charge, so as to reduce the oxide of iron. Moreover, the assayer gains valuable information from the character of the slag, which, in a naked pot, clings so tenaciously to it, that the slag cannot be detached with any degree of accuracy; the slag, moreover, dissolves a quantity of argillaceous matter from the clay of the crucible, which alters its character, and increases its weight. Lined crucibles withstand the fire better than plain ones, because the lining supports the sides when they soften; they require no carbon to be added for reduction; the button of slag and iron can be readily removed, and each of these may be weighed, if desired.

(*b*) When the assay mixture has been introduced into the cavity, the hole is stopped with a charcoal plug, the lid of crucible luted on with clay, and the pot fixed on a piece of a brick, so as to retain it in an upright position

in the furnace. The brick is then placed on the bars of a hot furnace; small coke, packed carefully round the sides and top so as to fill up the furnace to the level of the draught hole, and the fire urged to its full extent by opening the damper. In about half an hour a fresh charge of fuel should be added, and the fire allowed to burn down, when the crucible may be removed, broken open, and the assay extracted. If the operation has been successful, the iron will be found as a rounded button covered with a mass of well melted slag, which can be easily separated. Sometimes the slag will contain small shots of metal; it must then be crushed to powder, the metal extracted with a magnet and weighed with the main button.

(*c*) The character of the slag may be judged according to the following considerations:—If perfectly transparent and of a green tint, silica is in excess; if a light grey or bluish enamel or translucent glass be found, then the earthy bases, lime and alumina, are in proper proportion; if stony and rough, or crystalline and dull in lustre, it is too basic. If the materials have only fritted and not melted, containing the iron as a grey powder, silica and alumina are deficient, lime and magnesia in excess. A vesicular slag with the iron interspersed in malleable scales indicates the presence in the ore of iron and manganese silicates, or an excess of silica which react on the carbide of iron, producing malleable iron and carbonic acid, which latter escaping, produces the spongy texture. This may be corrected by adding more lime to the fluxes used.

Manganese in small quantity imparts an amethystine tint; but in larger quantity a yellow green or brown colour. Titanium produces either a black scoria, sometimes much wrinkled on the outside, or a vitreous scoria of a blue tint. On the surface there may be particles of the red cyano-nitride of titanium. Chromium produces

a black resinous slag, sometimes surrounded by a thin metallic covering.

(*d*) After weighing the button it should be broken, which is usually done by wrapping it in paper and striking it with a hammer on an anvil. The appearance of its fractured surface will afford indications of any foreign bodies which may be present. Thus, a hard, white, "cold-short" metal indicates the presence of phosphorus. A somewhat fine grained mottled metal, fairly malleable when cold, but "hot-short," indicates sulphur, dark patches often existing on the surface and partially so on the fractured part. Manganese in quantity produces a bright crystalline structure, but in smaller proportion the iron may be strongly mottled. Titanium produces a button smooth on the outside, with a deep grey fracture which is sometimes crystalline. It adheres tenaciously to the slag, and is sometimes covered with red cyano-nitride of titanium. Chromium yields sometimes a well-fused button with a white crystalline fracture ; sometimes a half-fused mass of a white or grey colour, according to the amount of chromium present. This alloy is often very hard. A dark grey graphitic iron indicates an easily reducible ore, or that a very high temperature has been employed in the furnace. The weight of metal obtained may be more than the iron contained in the ore, as the reduced metal absorbs a little carbon and other bodies. But a little iron is generally taken up in the slag, and the cast iron obtained will therefore very nearly represent the true amount of iron in the ore.

§ 111. The most convenient and rapid method of conducting a number of assays is that introduced into this country from Sweden. The weight of ore taken in each case is 10 grains, and the total fluxes 5 to 5½ grains. The small brasqued crucibles (Fig. 34), the making of which is described in § 18, are used. After introducing the ore

mixture into the charcoal cavity the hole is plugged with a bit of charcoal, shaped with a penknife to fit the same, and as four crucibles are fixed to the same piece of brick, it is advisable to mark each plug so that each assay may be recognised afterwards, especially in a preliminary trial. A convenient way of doing this is to mark the under side of the plug with a small cavity scooped out, or by a line filed across, or a double line, and so on, taking care to enter these marks opposite the corresponding assay in a note book. The lids are then to be luted on, the crucibles attached to the brick with clay, and placed in the fire. When finished and cool, the crucibles are detached, broken open, and the iron weighed and examined as in § 110 (*d*).

ASSAY OF COPPER ORES AND PRODUCTS.

§ 112. Ores of copper for the dry assay may be very conveniently divided into three classes, viz :—

(1) Rich oxidised ores and products, which may be fused direct for coarse copper, or after a preliminary roasting.

(2) Pyritic ores, commonly called "yellow" ores, which require a preliminary roasting, or the addition of nitre when fusing for regulus.

(3) Grey ores, which contain sulphide of copper and a little iron, and require the addition of iron pyrites to form a proper regulus.

§ 113. The fluxes and re-agents required are :—

(*a*) *Calcined Borax* to form a fusible compound with bases, such as lime and oxide of iron.

(*b*) *Glass* free from lead, which forms readily fusible

double silicates with metallic oxides. It may be easily reduced to powder by heating in a muffle, plunging into water and finally pounding in a clean mortar.

(*c*) *Lime*—to flux off silica and silicates.

(*d*) *Fluor-spar* (free from galena, blende, and copper pyrites), which acts as a flux for gypsum, heavy spar, phosphate of lime, and silica. It induces fluidity in a slag and causes it to disintegrate on cooling.

(*e*) *Nitre.*—This salt in the fused state is known as "sal prunella." It forms a powerful oxidising substance for sulphur and metals.

(*f*) *Common Salt*, which should be free from sulphate, is best used in the previously fused state to prevent decrepitation. It is employed to impart fluidity to the slag, and acts advantageously in forming volatile chlorides with antimony and arsenic, although a little copper is carried off with the vapours. Berthier found that by heating equal weights of sodium chloride and copper until the former was volatilised, 3 per cent. of the latter was lost. It also moderates the action of those bodies which produce violent ebullition. (See also § 23, No. 22.)

(*g*) *Carbonate of Soda* forms very fusible compounds with silica, etc., being basic in character. It should be used in the dried state. If mixed with carbonate of potash the action is much more powerful, and the combination melts at a lower temperature.

(*h*) *Tartar* (Hydrogen-potassium tartrate).—The common variety known as "argol" (containing tartrate of lime and other impurities) is preferred on account of its greater reducing power.

(*i*) *Sulphur.*—Both roll and flowers of sulphur are used

(*j*) *Carbon.*—Used in the form of powdered charcoal and anthracite.

(*k*) *Iron Pyrites.*—This agent must be free from copper pyrites; the variety obtained from the coal measures is preferred for this reason.

(*l*) *Ferrous Sulphide* may be substituted for iron pyrites.

(*m*) *Refining Flux.*—This is prepared by inserting a red hot iron rod into a mixture of—nitre, 3 parts; tartar, 2 parts; and common salt, 1 part; all by measure. The operation is very conveniently performed thus:—Put the mixture into a large crucible; place the pot in a cold assay furnace; then plunge the hot iron in and remove it as soon as deflagration commences; cover the furnace with the bricks and leave until all action ceases. When cold, the brownish white mass can be detached and put into a bottle for use. The product consists of potassium carbonate, undecomposed nitrate, potassium tartrate, and the impurities present in the tartar and common salt. Carbonate of potash and a little nitre may be used for refining instead of the above, but experienced assayers prefer the deflagrated compound.

§ 114. In dealing with copper ores, an experienced assayer will generally determine by inspection to which category a given sample belongs, and treat it accordingly. If the nature of the ore cannot be ascertained from its appearance, a portion is ground fine and washed by vanning on a shovel, or in a copper ladle designed for the purpose (Fig. 24), by which means the different constituents will separate according to their specific gravities, or into ore and earthy matter. If this is insufficient, a preliminary rough assay should be made by fusion in a pot, or by the blowpipe.

ASSAY OF OXIDISED ORES OR PRODUCTS SUFFICIENTLY RICH TO BE FUSED FOR COARSE COPPER DIRECT.

§ 115. (*a*) *Fusion for Coarse Copper, with Oxidation and Scorification of Iron, etc.*

Take for this purpose, 200 grains of ore.

160	,,	tartar.
300	,,	carbonate of soda.
60	,,	borax.
60	,,	lime.

These proportions are only intended as a general guide, and will vary with the quantity and quality of the foreign matters to be slagged off. Thus if the ore contains lime, that body need not be added. Too much borax tends to cause copper to be retained in the slag. 15 to 20 grains of charcoal may be substituted for the tartar; the tartar must be regulated according to the quantity of copper present, as great excess would reduce the other oxides present, and produce an impure coarse copper. The crucibles known as "Cornish" are invariably used for copper assaying, being sold in nests of two; the larger size is called No. 1.

For 200 grains of ore and proportionate fluxes, No. 2 is sufficient (Fig. 36 *a*). Introduce the materials into the pot, and place in a moderately hot fire so surrounded with hot coke that all parts shall be uniformly heated to the same temperature: exclude the air as much as possible. When the surface remains tranquil, pour immediately into a dry and blackened half-round mould (Fig. 17 *a*). If the temperature be too high, and the operation prolonged after the copper oxide is reduced, iron and other oxides will be also reduced, and will become alloyed with

the copper: it will be impossible in refining to remove these impurities without loss of copper. However, iron in less quantity than 1 per cent. tends to free the accompanying slag from copper, and easily passes out in refining. When in much larger quantity, an irregularly shaped button with projecting points is obtained, and occasionally an imperfectly fused mass in consequence of the higher melting point of the iron-copper alloy. When the slag has set, it may be cooled by dipping into water (but must not be left in the water to cool), by which it is made brittle, and readily crushed to powder. After picking out any small shots of copper with a pair of brass forceps, the slag is cleaned by fusion to remove any copper remaining. If the assay be properly performed, the slag should be dark coloured, glassy, and free from red scales.

(*b*) *Cleaning the Slag by Reduction of the contained Copper.*
Mix the slag with 30 grains of carbonate of soda, 50 grains of tartar, and 5 grains of charcoal. Melt as before in the same crucible; pour into mould; cool; grind the slag in mortar, and pick out any shots of copper.

(*c*) *Refining the crude Copper by Oxidation and Scorification of Foreign Matter.*
The crucible used in the previous operations should be employed. Place it well down in the centre of the fire, so that the copper may be seen through the space between the two bricks which cover the furnace, and when a bright red heat has been attained, drop in the copper button and shots. The copper first melts, and is covered with a dull skin due to impurities; in a little time this coating of oxides clears off, leaving the metal bright, and emitting a bluish green light from its centre, termed the "eye." Now add about 100 grains of refining flux, close the furnace for a minute or two, then pour the contents of the crucible into a half-round mould. When set, partially cool as

before by dipping in water, so that the slag may be readily detached when cold. The refined button should be flat or only slightly depressed on its upper surface, with a thin film of an orange red colour; it should be soft, malleable, and tough; should break with difficulty and have a fine silky fracture. If impure, it has more or less the character of coarse copper.

(*c*) *Cleaning Refinery Slag to extract the Copper.*

Fuse the slag with 20 grains carbonate of lime, 30 of tartar and 10 of charcoal, and weigh the button of copper obtained with the refined button.

Refinery slag is either grey, flesh-coloured, pink, pale red, blue, or bluish green, from the presence of copper oxide, or deep red from the presence of cuprous oxide, which is probably due to the refining flux being too "sharp," *i.e.*, containing too much nitre.

The effect produced on copper by the presence of other metals may be seen by reference to § 26.

ASSAY OF YELLOW ORES OF COPPER.

§ 116. Pyritic ores are the most abundant ores of copper, and when pure may be represented by the formula (Cu_2S,Fe_2S_3) containing 34·81 per cent. of copper.

The dry assay of copper ores by the Cornish method is intended to give the purchaser an idea of the quality and quantity of metal that can be obtained by smelting, but the loss is greater in the assay than in the smelting on the large scale. The loss of copper in the dry assay is shown by the table on the following page.

The Cornish assay comprises the following operations:—1. Fusion for regulus. 2. Roasting the regulus obtained. 3. Fusion for coarse copper. 4. Cleaning the slag from No. 3. 5. Refining the coarse copper. 6. Cleaning the refining slag.

Assuming the ore to contain from 10 to 20 per cent. of copper, the following fluxes may be taken as a general guide :—400 grains of ore, 300 borax, 300 glass, 400 lime, 400 fluor-spar, and 100 nitre.

Borax may be used alone in many cases, taking about 1200 grains instead of the above mixture. If the ore be a very poor one, then 500 to 600 grains should be taken; if rich, 200 grains will suffice.

Copper Present.	Dry Assay.	Margin.
35	33·25	1·75
30	28·5	1·5
25	23·5	1·5
20	18·5	1·5
18	16·5	1·5
16	14·5	1·5
14	12·75	1·25
12	10·75	1·25
10	8·75	1·25
8	7·0	1·0
6	5·0	1·0
5	4·0	1·0
4	3·0	1·0
3·5	2·6	·9
3	2·1	·9
2	1·3	·7

(*a*) *Fusion for Regulus.*

Use the copper assay pot (Fig. 36 *b*) which has been previously annealed by placing over a hot furnace in an inverted position. The ore and fluxes must be ground to a fine powder, and sifted if necessary, as a fine state of division greatly assists in the chemical reactions which occur between the components of the mixture. The ingredients should be well incorporated, placed in the pot, and the whole covered with about 50 grains of borax. Then place in a hot fire, using same precautions as given in § 115. Only a moderate draught should be

allowed at first, which may be regulated by partly closing the damper, and drawing the back brick slightly forward, so as to allow a little air to enter without passing over the crucible; as the operation proceeds, the brick is pushed back so as to close the furnace and the damper opened. After a few minutes, effervescence occurs, producing large bubbles which may cause some of the ingredients to overflow the sides; these bubbles may be broken by touching with an iron rod. In about fifteen minutes all action ceases, and the mass settles down into tranquil fusion. The pot must then be removed from the fire by tongs, and a rotatory motion imparted to dissolve any particles from the sides, and cause the whole of the regulus to collect into one button; then pour the whole contents into a half-round mould. When the slag on the top has set, it should be slightly squeezed with the tongs in the centre to form a lip, so that it may be removed from the mould and dipped in water to make the slag brittle, and facilitate its separation from the regulus when cold. The mass should not on any account be left in the water till cold, otherwise the dampness will prevent perfect separation. Any slag adhering to the regulus should be carefully scraped off with a knife. Generally one or two small shots of regulus will be found round the edge of the slag, and must be detached and added to the main button. If the regulus cannot be easily detached from the slag, the latter should be re-melted with a little sulphur or iron sulphide to obtain another small button of regulus.

The slag from yellow ores is generally glassy and dark green or black in colour, due to oxide of iron. A good slag should be uniform throughout in colour and constitution, and not variegated or streaked; should be frangible and readily detached from the regulus. The addition of fluor-spar in the fusion facilitates the separation. Too much of the latter, however, produces a thick stony-looking slag which corrodes the crucible.

If the regulus is coarse and dull in appearance resembling sulphide of iron and if it is more or less flat, hard, and crystalline, with a brassy yellow colour, the slag will be free from copper, and may be thrown away.

When the regulus is very fine grained, smooth, bright, and round on the external surface, with a dark colour, its fractured surface presenting a fine bluish-black colour with a glassy or compact structure, the slag is then liable to contain copper, and must be re-melted with a little sulphide of iron to obtain the copper as regulus.

A good regulus should be reddish brown in colour, moderately fine grained, convex on upper surface, readily frangible, and should contain from 50 to 60 per cent. of copper, which corresponds to the "blue metal" of the copper smelter.

A coarse regulus shows that more nitre was required for the fusion. A very fine regulus, that the sulphur was insufficient.

(*b*) *Roasting the Regulus.*

Reduce the regulus to fine powder in an iron mortar, preferably one with a lid having a hole in the centre through which the upper part of the pestle can pass to prevent particles being lost (Fig. 57), or the mortar may be covered with a duster, part of which is wrapped round the pestle. Then carefully brush the powder on to a sheet of glazed paper, remove any residue from mortar by rubbing in 5 grains of anthracite, and add this to the former. Introduce the powder into a clean No. 2 crucible and calcine till sweet. For this purpose the hot furnace is filled up with small coke and the crucibles (generally two assays are worked at one time) placed in an inclined position in the fire with the open end towards the operator. An iron rod (Fig. 15 *l*) flattened and smooth

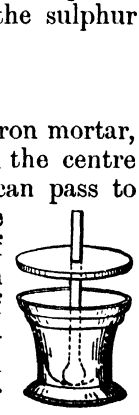


Fig. 57.

at the end is put in each pot, being used for occasional stirring during the process. The operation should be commenced at a low red heat, and the temperature gradually increased to a clear red. For the first twenty minutes frequent stirring is necessary to prevent clotting, afterwards only occasional stirring will be required. If the temperature is too low at first, sulphate of copper is formed; if too high, the mass will frit together and prevent perfect oxidation. The completion of the roasting may be determined by removing the crucible from the fire and wafting a current of air across it with the hand, when no odour of sulphur dioxide will be perceived if the oxidation is complete. In order to decompose any sulphate which may have formed, 20 grains of finely-powdered anthracite is added, and the roasting continued with stirring for ten or fifteen minutes at a bright red heat. With a successful operation the powder should remain free from lumps to the end. If any lumps are formed by clotting, the regulus must be ground in the mortar again with a little anthracite, transferred to crucible, and again roasted. Any particles adhering to the stirring rods must be completely scraped off. Instead of a crucible, the roasting may be performed in a scorifier, previously rubbed with hematite powder, and heated in a muffle: this method requires less attention than the former.

(*c*) *Fusion for Coarse Copper.*

The roasted regulus is mixed with—

50 grains of carbonate of soda, 80 grains of tartar, and 30 grains of borax. Or, 80 grains of tartar, 30 of borax, and 20 of nitre, in the same crucible employed for roasting, which avoids any liability to loss as is the case when it has to be transferred from a scorifier. Put into a hot fire and proceed as described in § 115 (*a*).

(*d*) Clean the slag according to directions given in § 115 (*b*).

(*e*) Refine and clean refinery slag as in § 115 (*c*).

It should be observed that roasted regulus is a similar substance to a rich oxidised ore, and may be treated in the same way.

GREY ORES.

§ 117. Under this category are included all those ores which contain little or no iron, and require the addition of sulphur, sulphide of iron, or iron pyrites, to yield a proper regulus; such as copper glance (Cu_2S) (containing, when pure, 79·7 per cent. of copper, also known as "vitreous" or grey sulphide of copper) and Fahlerz, or true grey copper ore, containing antimony, arsenic, iron, zinc, lead, silver, etc. The following analyses collected by Dr. Percy show the composition of Fahlerz:—

	1	2	3	4	5	6
Copper, - -	38·42	37·98	39·18	40·57	38·63	30·73
Antimony, - -	25·27	23·94	23·66	21·47	16·52	17·76
Arsenic, - -	2·26	2·88	4·4	2·42	7·21	11·55
Silver, - - -	·83	·62	—	·56	2·37	10·53
Iron, - - -	1·52	·86	6·99	2·92	4·89	1·42
Zinc, - - -	6·85	7·29	—	5·07	2·76	2·53
Sulphur, - -	25·03	25·77	25·64	26·10	26·33	25·48
	100·18	99·34	99·87	99·11	98·71	100·0

Take 100 grains of ore, 100 grains sulphide of iron, 20 grains tartar, 200 grains lime, 200 grains fluor-spar, 150 grains glass, and 150 grains borax. Fuse for regulus and proceed as with yellow ores. The regulus from rich ores is very fine grained and rich in copper, with a great tendency to clot, so that great care is required in roasting, especially during the first fifteen minutes. When the ore contains lead the regulus is very liable to fuse, and it becomes extremely difficult to moderate the heat so as

to expel arsenic and sulphur, and at the same time prevent agglomeration of the powder.

GERMAN COPPER ASSAY.

§ 118. This operation differs from the Cornish method in several particulars; and the results obtained, as a general rule, are said to be a little higher.

The fluxes and re-agents employed are borax, glass, salt, charcoal, graphite, and black flux (obtained by deflagrating two parts of tartar and one of nitre), which is used as a reducing agent.

The method comprises the following operations :—

1st. Roasting to oxidise and remove volatile impurities.

2nd. Melting for coarse copper.

3rd. Refining the crude copper obtained from No. 2.

(*a*) *Roasting.*

About 60 grains of the finely-powdered ore is placed in a roasting dish or scorifier, which has been previously rubbed with an unctuous variety of hematite to prevent the ore sticking to the vessel, introduced into a red-hot muffle, and stirred for about fifteen minutes, or until no odour of sulphurous acid is perceived, using all the precautions mentioned in the English method. The dish is then removed from muffle, the powder brushed into an iron or bronze mortar, and mixed with 15 grains of graphite, and thoroughly incorporated by grinding with pestle. This mixture is then introduced into a peculiar egg-shaped crucible (Fig. 58), which is laid sideways in the hot muffle, with its open end to the front, and roasted till sweet, which generally takes ten to fifteen minutes. When lead and antimony are present, a low temperature, with careful stirring, is required to prevent clotting.

Fig. 58.

The temperature is then gradually raised, during which the contents become liquid, giving off quantities of gas. In ten to fifteen minutes the sides of the pot should be scraped with an iron rod to detach any particles of metal which may adhere to it. The crucible is again covered and left in the closed furnace another five minutes, then removed, and the contents poured into a half-round mould. The sides are then scraped with an iron rod to obtain any particles of lead remaining, which particles are cleaned from slag, and added to the main bulk of metal, and the whole weighed.

(*c*) As wrought-iron crucibles are expensive, pots made of malleable cast-iron may be substituted, but the temperature must not be allowed to get too high, or the crucible itself will melt.

For fusion in an iron pot with fluxes, the following proportions may be used :—

I.		II.	
Ore, - -	500 grs.	Ore, - -	500 grs.
Sodic carbonate,	500 ,,	Sodic carbonate,	450 ,,
Tartar, -	50 ,,	Tartar, -	50 ,,
		Borax, -	50 ,,

With the first proportions, about 50 grains of carbonate of soda are left to cover the mixture after placing in the pot. In the second case the 50 grains of borax serve this purpose.

As before, the crucible is made red hot, removed from the fire to introduce the assay mixture and then replaced. The operation is conducted in precisely the same way as when the iron crucible alone is used.

Operating on the same ore as mentioned in § 121*a*, the following results were obtained from two assays :—

78·60 per cent. and 78·88 per cent.

(*d*) *Assay of Pyromorphite, known as Green Linnet.*

Phosphate of lead ores are treated with the following proportions of fluxes, and assayed in an earthen crucible. Either of the two following proportions may be used:—

I.		II.	
Ore, - -	300	Ore, - -	300
Carb. of soda, -	350	Carb. of soda, -	400
Tartar, - -	100	Charcoal, -	25
Borax, - -	30	Borax, - -	30

The first three substances are well mixed together, placed in clay crucible, and covered with the 30 grains of borax. The temperature should be gradually raised, and care should be taken to obtain a uniform heat in all parts of the pot, as a somewhat violent reaction occurs, and the substance is liable to boil over, when the assay would be vitiated.

The general temperature should be higher than with galena, and a good bright red heat obtained to finish with. The lead is detached from slag as before, and weighed. The following results were obtained with the above mixtures:—

1st mixture, 62·23 per cent.	2nd mixture, 61·96 per cent.
„ „ 62·16 „	„ „ 61·66 „

METHOD EMPLOYED IN THE UPPER HARTZ.

§ 122. 5·7 grammes of the finely powdered ore is mixed with three or four times its weight of dry carbonate of potash, placed in a clay crucible of the Hessian shape, and the mixture covered with a layer of common salt about ¼ inch thick. The lid is then put on, and the pot put into a hot muffle, which is then raised to its highest heat. To prevent undue accession of air, the mouth of the

muffle is surrounded with glowing coals. In from twenty to thirty minutes the mass will be perfectly fused; the damper is then partly closed, and the muffle opened until the temperature has fallen to a low red heat, and the vapours have disappeared. The temperature must all the while be maintained sufficiently high to keep the mass in perfect fusion. The assay is left at this point, for another fifteen minutes, then removed, allowed to cool, the crucible broken, the slag detached, and the button of lead weighed.

If the assay has been successful, the button of metal has the characteristic colour, malleability, and softness of pure lead. If the slag shows on the surface of separation from the metal lead-grey spots with a metallic lustre, there will generally be glistening lead sulphide undecomposed on the surface of the button of metal, which then has a dark colour and high metallic lustre. If the button is laminated, brittle, and white in fracture, there has been an insufficiency of flux, or the metal contains antimony and arsenic. When successful, the lead should have a bluish appearance, rather dull than brilliant. The slag should be homogeneous and well settled down towards the bottom of crucible, showing that there has been proper fusion. The sodium chloride covering forms a thick light-coloured slag overlying the thick dark coloured slag which contains the metallic oxides. A porous slag containing metallic globules indicates too small a quantity of flux or too low a temperature; a brilliant vitreous slag, too high a temperature and scorification of lead.

§ 122A. Lead Matt (PbS) and Lead Fume are smelted with the addition of borax and coal dust to the potassium carbonate, and the first heat continued longer than when assaying ores. The potash of the carbonate is reduced to potassium, while it yields its oxygen to the sulphur of the matt forming sulphuric acid; the liber-

ated potassium takes up sulphur from another portion of the matt forming potassium sulphide. The matt would in this way soon lose all its sulphur if a combination—a sulphur salt—of potassium sulphide with lead sulphide did not form, and resist all further action of the potassium carbonate thus :—

$$4K_2CO_3 + 7PbS = 4Pb + 3(K_2S,PbS) + K_2SO_4 + 4CO_2.$$

SECOND METHOD.

§ 123. The assay of oxidised ores and products free from sulphur, arsenic, and phosphorus, is a simple operation, if care be taken that sufficient carbon or carbonaceous matter is added, to reduce the oxide to the metallic state. The metalliferous matter must be ground and passed through a fine sieve.

(*a*) Take 400 grains of ore, mix with 600 grains of dry carbonate of soda, and 15 to 20 grains of charcoal, place in a clay crucible, which should not be more than half full, and cover with a layer of common salt. The crucible should be placed well down in the fire, and must be kept at a moderate temperature, carefully watched through the space between the two bricks to see if any portion through swelling up of the fluxes passes over the sides. In such a case, the draught should be checked and the bubbles broken as they form, by means of an iron rod ; but if the crucible is placed well down in the fire, and all parts at the same temperature, this nuisance will be avoided. In a few minutes the boiling will cease, and gas will no longer be given off ; then raise the temperature for a few minutes, when the mass will soon settle down into tranquil fusion. Remove from fire, impart to crucible a rotatory motion to shake down all particles of lead, so as to form a single button at the bottom, and pour into a dry mould, which has been

blackened to prevent the metal sticking. When the operation has been successfully performed, the cooled slag will present a smooth concave surface with a vitreous lustre. A safer plan is to allow the contents to cool in the pot, and break the latter to obtain the lead. The button, with its adhering slag, is then hammered on an anvil to squeeze off the slag; some small portions cannot always be separated by mechanical means. They may be removed by boiling in water containing sulphuric acid, and brushing the metal with a hard brush.

(*b*) Instead of the assay mixture given above, equally correct results may be obtained by either of the following:—

I.	II.
400 grains ore.	400 grains ore.
500 ,, carbonate of soda.	800 ,, black flux.
200 ,, tartar.	

Each of the above mixed and covered with borax.

ESTIMATION OF SILVER IN LEAD.

§ 124. As many ores of lead contain silver, this metal is always tested for, and its amount estimated in a sample whose character is unknown. This information is ascertained by subjecting the lead obtained to the process of cupellation. This method is based on the fact that lead heated in a current of air is oxidised, while silver remains unaltered (except that it absorbs some of the oxygen mechanically), and when this is effected in a porous receptacle, the oxide of lead is completely absorbed, leaving the silver on the surface in the unalloyed state, or alloyed only with gold and members of the platinum group.

(*a*) The assay for silver is conducted in shallow vessels made of bone ash called cupels, a description of the manufacture of which is given in § 22. The cupels are placed in a hot muffle, and left for a few minutes to attain the same temperature, which should be of such a degree that the lead may melt in a minute or two after its introduction. The lumps of metal are weighed and then charged into the cupels. When melted, the muffle door is closed until the operation is completed. If the temperature is too low, the lead will oxidise instead of melting, forming a thick crust on its surface, then when the temperature is raised, the lead is spirted up through this crust causing loss. If the temperature is too high, dense fumes will arise from the volatilisation of lead carrying with them particles of the molten metal, hence causing a loss of silver. When the right degree of heat is secured, the lead will have a bright and convex appearance, the vapours arise gently, and be promptly carried away by the draught, but there will be no violent projection of liquid particles, and the film of oxide as it forms will be carried from the top to the base of the liquid button, there being absorbed by the bone ash. Towards the completion of the process, the film of oxide becomes much thinner, producing a display of iridescent colours. In a short time these disappear, and the silver remains bright. During this stage the temperature should be raised by opening the damper, so as to remove the last traces of lead from the silver. The phenomenon of "flashing," which is quite distinct from brightening, then takes place. The button cools down below its solidifying point without actually becoming solid, and then suddenly emits a bright light or "flashes," and then becomes solid.

(*b*) Success also depends on the quantity of air passing through the muffle in the draught. When the air current is too rapid, the cupel is cooled, and the lead

being oxidised faster than the oxide can be absorbed by the cupel, the oxide may completely cover the metal and protect it from further oxidation. When the current is too feeble, the completion of the assay is unnecessarily delayed.

(*c*) When properly conducted, the assay button should be round, bright, and smooth on its upper surface, and when cold, easily removed from the cupel by a pair of pliers. Any matter adhering to the bottom may be removed by squeezing the button with the pliers, or tapping on the edge with a hammer, and brushing with a hard tooth brush.

Silver contained in lead or ores is reported in this country in troy ounces, dwts., and grains, per ton of 2240 lbs.

(*d*) The following are the results from two buttons of lead obtained from the assay of 400 grains of galena in earthen crucibles mentioned in § 121.

Lead obtained	-	312·0		313·8			
Silver „	-	·202		·204			
Wt. of Pb. in grains.	:	No. of grains in 1 lb.	::	W. of Ag obtained.	:	x.	
312	:	7000	::	·202	:	4·532.	
		lbs. in 1 ton.					
1 lb.	:	2240	::	4·532	:	10152.	

One ton of the above lead therefore contains 10152 grains Ag, and this is reduced to oz. and dwts. thus :—

$$24 = \begin{cases} 6 \mid 10152 \\ 4 \mid 1692 \\ 2{,}0 \mid 42{,}3 \\ \underline{21{\cdot}3{\cdot}0.} \end{cases}$$

The lead contains 21 oz. 3 dwts. of silver per ton. The amount of silver per ton of ore is calculated in same way, substituting 400 in the first proportion for 312, and both results shown as follows :—

			Per Ton of Lead.			Per Ton of Ore.		
		grs.	oz.	dwts	grs.	oz.	dwts	grs.
1. Wt. of ore 400 } ,, lead 312 }	Wt. of Ag	·202	21	3	0	16	9	22
2. Wt. of ore 400 } ,, lead 313·8 }	,,	·204	21	4	16	16	13	5

§ 125. Table showing amount of silver contained in one ton of ore corresponding to the weight obtained from 400 grains :—

If 400 Grains of Ore yield fine Metal	One Ton of Ore will give			If 400 Grains of Ore yield fine Metal	One Ton of Ore will yield		
gr.	oz.	dwts.	gr.	gr.	oz.	dwts.	gr.
·001	0	1	15	·200	16	6	16
·002	0	3	6	·300	24	10	0
·003	0	4	21	·400	32	13	8
·004	0	6	12	·500	40	16	16
·005	0	8	4	·600	49	0	0
·006	0	9	19	·700	57	3	8
·007	0	11	10	·800	65	6	16
·008	0	13	1	·900	73	10	0
·009	0	14	16	1·000	81	13	8
·010	0	16	8	2·000	163	6	16
·020	1	12	16	3·000	245	0	0
·030	2	9	0	4·000	326	13	8
·040	3	5	8	5·000	408	6	16
·050	4	1	16	6·000	490	0	0
·060	4	18	0	7·000	571	13	8
·070	5	14	8	8·000	653	6	16
·080	6	10	16	9·000	735	0	0
·090	7	7	0	10·000	816	13	8
·100	8	3	8				

When the silver obtained in the above processes contains gold, it is separated by dissolving out the silver in nitric acid, and the weight of the gold is deducted before computing the amount of silver present.

ASSAY OF SILVER ORES, PRODUCTS, AND ALLOYS.

This assay may be conveniently studied under three heads, viz. :—

I. Treatment of bullion, coin, and plate.

II. Ores of all kinds containing silver.

III. Various products and waste matters containing silver, such as litharge, slags, sweep, etc.

First Method. BULLION, COIN, AND PLATE.

§ 126. This assay is effected by means of cupellation which has been partly explained under the assay of argentiferous lead. Care must be taken that the sample employed represents the whole mass from which it is obtained, as alloys of silver and copper are liable to undergo liquation, so that different parts of the same ingot will give discordant results.

(*a*) Professor Roberts-Austen has made a special study of this subject. He cast the alloys in cubical fire-brick moulds, in which they could be cooled either rapidly or slowly. His results are embodied in the following table :—

No.	Name of Alloy.	Parts of Silver in 1000 of Alloy.	Rate of Cooling.	Maximum Variation of Silver in different parts.
I. *a*	British standard coin	925	rapid	12·8 per 1000
I. *b*			slow	1·4 ,,
II. *a*	Old French standard coin	900	rapid	10·1 ,,
II. *b*			slow	1·3 ,,
III.	Levol's homogeneous alloy	718·93	slow	1·2 ,,
IV.	$AgCu$	630·3	slow	21·1 ,,
V.	$AgCu_4$	333·3	slow	12·8 ,,

In I. *a* and II. *a*, the centres of the cubes were the richest and the corners the poorest.

In I. *b* and II. *b*, the slight variations followed the same law.

In III., the corners were generally richer than the centre.

In IV., Roberts-Austen supposes that gravity has influenced the alloy, the lower parts being richer than the upper.

In V., the variations do not follow any known law.

From the above it will be seen that slow cooling of I. and II. renders them almost homogeneous.

(*b*) Alloys of silver with copper heated in a current of air become oxidised in proportion to the copper present, so that some indication of the amount of each may be obtained from the intensity of the discoloration. Chaudet gives the following table :—

Silver in 1000 parts of Alloy.	Colour of Surface after Heating to Redness.
1000 *i.e.*, pure silver,	Dull, but white.
950 - - -	Uniform grey-white.
900 - - -	Dull grey-white ; black at edges.
880 - - -	Grey, almost black.
860 - - -	,, ,,
840 - - -	Quite black.
820 - - -	,,
800 - - -	,,

(*c*) The amount of alloy now taken for assay is generally 12 grains, which must be very accurately weighed on a delicate balance. Although the amount taken is of no great consequence, yet the above quantity is convenient, as it saves trouble in computing the results; it

is known as the "assay pound." The silver assay pound is subdivided into aliquot parts, *i.e.*, into 12 ounces, each ounce into 20 pennyweights, and these again into halves, so that each nominal half pennyweight weighs $\frac{1}{40}$th part of a troy grain, when the pound = 12 grains. The decimal system in relation to the above weights is also used—the ounce, dwt., and half dwt. are represented by 1 grain, ·05 grain, and ·025 grain respectively. This is shown by the following table :—

Silver				Assay	Silver				Assay
oz.	dwt.	gr.		Grains.	oz.	dwt.	gr.		Grains.
12	0	0	-	12	0	10	0	-	0·500
11	0	0	-	11	0	5	0	-	0·250
6	0	0	-	6	0	3	0	-	0·150
3	0	0	-	3	0	2	0	-	0·100
2	0	0	-	2	0	1	0	-	0·050
1	0	0	-	1	0	0	12	-	0·025

The assay piece is enclosed in an envelope of sheet lead, the amount of which depends on the quantity of copper present.

(*d*) The following table gives the amount of lead which should be used for various alloys of silver and copper :—

Amount of Silver.	Amount of Copper.	Quantity of Lead for 1 part of Alloy.
1000	0	1
950	50	3
900	100	7
800	200	10
700	300	12
600	400	14
500	500	16-17
400	600	
300	700	
200	800	
100	900	
0	1000	

As metallic lead invariably contains silver, the amount of that metal introduced into the assay must be ascertained and deducted from the quantity of silver obtained.

(*e*) A number of assays having been prepared, they are placed in the compartments of a wooden tray containing nine to twelve divisions, from which they are transferred to a copper tray in the same order; this tray has forty-five to sixty depressions (Fig. 60), and from thence into previously heated cupels occupying a corresponding position in the muffle. In a short time the lead melts and becomes covered with greasy-looking drops of litharge which are rapidly absorbed and replaced by others, the oxidation and absorption then continue until the base metals are removed. In from ten to twenty minutes,—iridescent films appear, showing that the last traces of lead are being oxidised, which quickly disappear, leaving the bead of silver bright, known as "brightening."

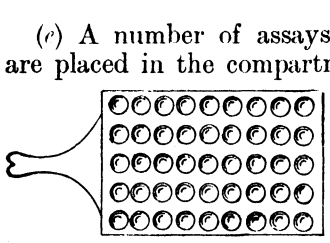


Fig. 60.

The brightening, when the operation has been successfully performed, should commence with the first row, and finish with the back row. If the brightening occurs irregularly, or commences at the back of the muffle, it shows that the draught has not been properly regulated, and the results cannot be so thoroughly relied on as in the former case. The muffle is now completely closed, and the whole allowed to cool slowly to avoid "spitting," which would render the assay useless when anything like accuracy was desired.

It is advisable to keep the temperature as low as possible to prevent volatilisation of silver and absorption by the cupel. The heat should be so adjusted that only slight fumes are visible over the cupels, and the fused metal should be highly luminous and clearly distinguish-

able from the cupel. Too high a temperature causes fumes to rise to the top of the muffle; with too low a temperature, crystals of litharge will be deposited round the edge of the cupel.

(*f*) A certain amount of loss of silver always occurs in cupellation, which loss increases with the temperature and the amount of lead used.

To ascertain this loss, a check is used with every nine or twelve assays placed as in Fig. 61. This consists of a known weight of pure silver made up to 12 grains by copper, equal in amount to the copper probably present in the assays, and assayed with same quantity of lead in the same heat. The loss of silver in the check piece is then added to the weight of silver obtained from the assay. In places where large quantities of standard silver assays are made, a specially prepared alloy, known as trial plate, is used for checks.

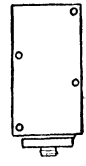


Fig. 61.

(*g*) The silver beads or "prills" should be round on the top, or only slightly depressed in the centre; should be readily removed from the cupels, and have a bright appearance. A flattened appearance indicates the presence of copper; also when they adhere firmly to the cupel, or throw out projections near the bottom, it shows they are not "fine," and that an insufficient amount of lead has been used.

Before weighing the button of silver, it should be squeezed laterally with a pair of round-nosed pliers, or tapped on the edge with a clean hammer, to detach any adhering bone ash, and brushed with a hard tooth brush. If this fails to remove all foreign matter, soak in dilute hydrochloric acid, and brush till clean.

(*h*) It is always an advantage to the assayer to know the approximate composition of an alloy before proceeding to

obtain a correct estimate of the silver. The character, and roughly the amount of other metals, may be judged by the indications of the cupel in a preliminary assay. Thus lead produces an orange red colour; manganese a bluish black stain and corrosion of cupel; iron a reddish brown stain at the commencement and dark stain at finish; copper a dark green or brown; cobalt a dark green incrustation and green stain; chromium a dark brick red stain; arsenic a white or pale yellow; antimony a red-brown incrustation, which, if present in any amount, cracks the cupel; nickel a dark green slag and green stain; platinum a greenish stain and crystalline button; tin a grey incrustation; zinc a yellow ring on cupel, the metal burning with a brilliant flame, emitting copious vapours and corroding the cupel.

(*i*) The presence of platinum, palladium, iridium, and rhodium requires a higher temperature for the cupellation. The surface also of the button is dull after the operation has terminated. Iridium always sinks to the lower part of the button, so that on rolling out the button into a strip a black spot or streak will be observed on the under surface.

Second Method. SILVER ORES.

§ 127. (*a*) The fluxes and re-agents employed are red lead, or litharge, granulated lead, and sheet lead. These should be tested previously to ascertain the amount of silver they contain, if that metal is present in notable quantity. For this purpose the above oxides may be reduced by heating with charcoal at a low red heat, and the buttons of lead obtained, cupelled. Red lead is preferable to litharge, the common varieties of which contain more silver than red lead.

Carbonate of soda and carbonate of potash in powder, charcoal, and anthracite.

Tartar or red argol, which has a higher reducing power than pure cream of tartar.

Nitre in powder.

Fluor-spar, free from lead, which is argentiferous.

Hoop iron or wrought nails for reducing sulphides.

(*b*) *Sampling.*—The ore must be roughly crushed, an average sample of ½ lb. taken and weighed. This portion is then dried at 100° C. and re-weighed, so that the return may be made on the dry or wet sample. The ore is then finely crushed in an iron mortar, and passed through a sieve with 80 meshes to the inch. It sometimes happens that metallic particles remain on the sieve; these are assayed separately, and the proportionate amount of silver added to each aliquot part assayed.

§ 128. *Estimation of the Silver.*

This may be determined by one of two methods, or by both, as a check on each other.

(*a*) 1st. *By Fusion in a Clay Crucible.*—This method is suitable for ores of silver containing much gangue and only a small proportion of other metals. The following quantities are suitable proportions for an average ore:—

Ore, 200 grains; red lead, 500; charcoal, 25; sodium carbonate, 300; borax, 200.

This mixture, however, would not be suitable in all cases, as carbonate of soda, being a basic substance, must be increased when a large excess of silica or other acid material is present, and the borax increased in case of much lime, oxide of iron, etc. When barytes, gypsum, or phosphate of lime is in the gangue, fluor-spar must be added.

The materials are mixed together, transferred to the crucible, covered with part of the borax, and placed well down in a moderate fire. For the first ten minutes a medium temperature is best, then gradually increase for another eight or ten minutes until the liquid becomes tranquil; then pour into a round mould, allow to cool,

and detach the slag, which, on account of its brittleness, readily separates on hammering from the malleable button of lead. It occasionally happens that the reduced lead is covered with a regulus, or speise, which may contain silver, in which case it would be advisable in assaying another portion to add a strip of iron to decompose the sulphide or arsenide present. But this omission may be remedied by adding iron to the mixture used for cleaning the slag.

The slag is generally glassy, but varies with the nature of the ore, and should be uniform in colour and composition.

(*b*) *Cleaning the Slag.*—The slag is pounded in a mortar covered with a duster to prevent loss, and mixed with 300 grains red lead, 15 grains charcoal, and 20 grains carbonate of soda. Fuse for about fifteen minutes in the same crucible in which the ore was smelted, and pour into round mould as before. The slag obtained in this case is thrown away, and the lead button after cleaning saved for cupellation.

(*c*) The two lead buttons are then cupelled, particulars of which have been given in § 124.

§ 129. (*a*) Sulphides of copper, iron, lead, etc., containing silver, may also be assayed by the crucible method just described; but the sulphur, arsenic, etc., must be oxidised by a preliminary roasting, or a large quantity of red lead must be added in the fusion mixture.

The oxidation is effected by heating the powdered ore at a low temperature at first, in a roasting dish made of fire clay, constantly stirring with an iron rod, as the material, especially in the presence of lead, has a great tendency to fuse and clot together, which prevents oxidation to a great extent. In about fifteen minutes the greater part of the volatile matters will be expelled, and the temperature may then be raised to complete the operation.

(*b*) The quantity taken for roasting should vary with the richness of the ore, but the following may be taken as an average sample.

Take 200 grains and roast as above, then mix with red lead, 1000 grains; charcoal, 35 grains; borax, 400 grains; and carbonate of soda, 200 grains.

The above mixture is placed in a clay crucible, covered with borax, a strip of iron introduced to decompose any sulphides, and the operation conducted precisely as described in § 128.

(*c*) If the ore is fused direct without roasting, then take: ore, 200 grains; red lead, 2000 grains; charcoal, 35 grains, and white sand, 150 grains. When there is much sulphur present, the charcoal is unnecessary, and a little nitre may be added with advantage to assist the red lead in its oxidation.

This method of assaying is objectionable because of the large amounts of lead obtained for cupellation; for one part of iron pyrites requires $8\frac{1}{2}$ times its weight of lead, and grey copper ore 6 to 7 times its weight. The nitre, however, may be judiciously used to assist oxidation. The sand diminishes the action of the bases on the crucible, and may be omitted if an iron crucible be used.

§ 130. As a check on the two preceding methods, digest 200 grains of the ore with strong nitric acid and heat for an hour, adding nitric acid occasionally as it evaporates. Then add water and boil; filter off any insoluble matter; dilute the solution with water, if necessary; boil, and add sufficient hydrochloric acid to precipitate the silver as chloride. If lead is present it will also be partly precipitated, unless the liquid is kept near boiling. Filter off the insoluble silver chloride; well wash with boiling water, which also dissolves out any lead chloride; dry, and heat in a weighed porcelain crucible till the chloride just begins to fuse, then allow to cool and weigh. After deducting the weight of crucible and

filter-ash, the amount of silver is obtained by the following proportion :—

143·5 : 108 : : Weight of precipitate : x.

As 200 grains have been taken $\frac{x}{2}$ = the percentage.

The insoluble residue is mixed with 300 grains red lead, 15 charcoal, 50 borax, and 100 carbonate of soda. Fuse as before in clay crucible, cupel lead, and add the weight of silver button, if any, to the quantity obtained above.

§ 131. In experiments performed on a sample of pyrites to test the three modifications just described, the following results were obtained :—

With prelim. calcination	Direct fusion.	Solution in nitric acid.
* ·546 grains Ag.	·541 grains Ag.	·491 grains Ag.
oz. dwt. grs.	oz. dwt. grs.	oz. dwt. grs.
89 3 14 per ton.	88 7 6 per ton.	80 17 0 per ton.

For the mode of calculating the amount of silver per ton of ore see Lead Assay, § 124 *d*.

§ 132. 2nd. *By Scorification in a Fireclay Dish.*

(*a*) This operation is very simple and rapid in its action, but more experience is required to obtain trustworthy results than by fusion in a crucible. It depends on the principle that molten oxide of lead has the power of uniting with infusible silicates such as fireclay, dissolving other bases which may be present, such as oxides of copper, iron, antimony, etc., and forming a fusible slag, leaving unoxidisable metals, such as silver and gold, in combination with the metallic lead present in excess.

(*b*) All ores and products containing silver may be assayed by this method, but as scorifiers are much

* In calculating the results, allowance must be made for any silver contained in the red lead employed. See § 139 *d*.

smaller than crucibles in capacity, a less quantity of ore can be operated on, so that very poor ores are best treated by the crucible plan. It has been explained that oxide of lead in sufficient quantity completely oxidises sulphur, arsenic, etc., as well as base metals, so that this method is well suited for pyritic ores containing silver. Moreover, the lead can be scorified to any convenient size suitable for cupellation. The oxidation of impurities is partly effected by the air and partly by the litharge, which occasionally causes spurting by the effervescence ensuing on this reaction. The lead employed should be in fine grains, which are obtained by pouring lead near its point of solidification into a rectangular box previously blackleaded to prevent the metal sticking, and then vigorously shaking to granulate it. Uniformity of grain is desirable, and may be obtained by passing the above through a fine sieve.

(*c*) The following proportions may be taken, when the ore or product is of medium quality :—

Finely crushed ore passed through No. 80 sieve, 100 grains.

Granulated lead, ...	1000 grains.
Borax, ...	10 „

Mix the ore with half the lead; place in the scorifier (Fig. 41); then spread the remaining lead on top, and on this put the borax, whose function is to lessen the action on the vessel and make a more liquid slag. The scorifier and its contents are now placed in a muffle, previously raised to a bright red heat, the door closed until the mass is in full fusion; then the upper half of the door is opened to admit air for oxidation of lead, etc. White vapours now rise from the surface and litharge is rapidly formed. This action is continued until the slag formed just covers the lead beneath; the temperature being now raised the slag becomes very liquid. The size of the

scorifier employed should be such that the contents about half fill it. The slag contains a little silver which is separated by adding 5 to 8 grains of anthracite powder wrapped in tissue paper, and placed quickly on the top of the slag; this causes effervescence and rising of the contents, which, with too small a vessel, will pass over the sides and vitiate the assay. When all action ceases the scorifier and its contents are removed, both metal and slag being poured into the same dry mould. When cold, the slag is detached as usual by hammering on an anvil. The cleaned button of lead is then cupelled and the amount of silver calculated to the ton as before.

(*d*) The lead obtained should be soft and malleable. If brittle, too little lead has been used, or the scorification has not continued long enough. If the slag is not uniformly liquid when ready to pour, add more borax. In some cases it may be necessary to stir the slag with an iron rod to incorporate any lumps with the slag.

(*e*) Instead of cleaning the slag with anthracite, it may be cleaned after detaching from the lead, in the manner described under the crucible method, § 128*b*.

§ 133. Gold is occasionally present with the silver obtained by cupellation of the lead. The button should then be flattened and heated with dilute nitric acid for fifteen minutes, the liquid poured off, and the residue boiled with strong acid for a few minutes; the gold is washed, dried, ignited, and weighed. The difference gives the silver.

Full particulars relating to parting gold from silver are given with gold assaying, § 136*e*.

§ 134. *3rd Method. Treatment of Regulus, Litharge, Old Cupels, Slags, Sweep, and other Waste Matters.*

(*a*) The fluxes employed will of course vary with the

nature of the foreign matter, and the quantity with the amount of matter to be scorified. The following proportions may be taken for jewellers' sweep :—

1 oz. of sweep.
1½ oz. of potash.
1½ oz. of borax.
1¼ oz. of salt.
¼ oz. of nitre.
40 grains anthracite.
2 oz. of red lead.

If the substance contains much coal or other carbonaceous matter, omit the anthracite, and substitute ½ oz. of lime.

If the substance contains lime, then add ½ oz. of white sand to the above mixture.

In the presence of sulphides, add a piece of hoop iron or a large wrought iron nail.

Another excellent flux is :—

2 oz. potash.
1 oz. salt
1½ oz. borax.
40 grains nitre.
40 grains anthracite.

Well mix the fluxes with the assay sample, leaving the salt as a covering. Commence with a gentle heat, raising the temperature gradually. Towards the close, when the violence of the action has nearly ceased, place a cover on the pot, and finish with a strong heat. About twenty minutes are required. Remove the iron ; allow crucible to cool ; break open ; detach button of lead ; and cupel for silver and gold as before. Clean the slag as in previous cases.

(*b*) *Treatment of Old Cupels for Silver and Gold.*

The crushed bone-ash containing litharge and other oxides is mixed with sufficient charcoal to reduce the

metallic oxides, and as fluxes, the following proportions may be taken :—

Old Cupels, 100 grains ; fluor-spar, 150 ; borax glass, 150 ; carbonate of soda, 150.

Fuse in a clay crucible, gradually raising the temperature as the operation proceeds, finishing with a strong heat. Pour into mould ; allow to cool ; tap away the slag, and cupel the button of lead for silver and gold in the usual way.

(*c*) *Metallurgical Products, Sweep, etc.*

The following system is used at the Royal Mint. 2400 grains are weighed, dried and reweighed ; the difference between the two weighings giving the moisture. Calling the second weight found W, and the weight of moisture M, then $W = (2400 - M)$ grains. The dried sample is ground in an iron mortar, passed through a sieve of 60 holes to the linear inch, and the metallic residue cupelled separately. Calling the weight which passes through the sieve W_1, it is evident that $\frac{W_1}{4}$ will be the proportion obtained from 600 grains of the initial sample. This weight $\frac{W_1}{4}$, is now roasted at a red heat in a muffle to remove all combustible matter. It is again weighed on cooling and its weight W_2, divided into three equal portions for scorification. Each portion $\frac{W_2}{3}$ will thus correspond to 200 grains of the original sample.

For each scorification charge are taken 800 grains granulated lead, and 50 to 100 grains of borax. Half the lead is mixed with the charge, and the other half is placed on the top. The scorification is then conducted as described on page 240.

ASSAY OF GOLD ORES, PRODUCTS, AND ALLOYS.

§ 135. As gold is so closely connected with silver, both metals frequently existing in the same material, and as the same process may generally be applied to both, it follows that much of what has been said concerning silver assaying, applies also to gold. However, this metal having a much higher value, substances containing it even in minute quantities may be profitably treated for its extraction, so that in many cases much larger quantities require to be operated upon to obtain the precious metal in a weighable amount, and consequently crucibles of large capacity are required.

§ 136. 1ST. ESTIMATION OF GOLD IN ALLOYS.

(*a*) In places where a large number of assays have to be conducted, a special set of weights is employed as with silver, the unit quantity being termed the assay pound, which is sub-divided into carats, carat grains, eights, and excess grains. The amount taken as a unit may be 10 grains or half a gramme = 7·716 grains. The relation of the parts are well shown in the following table by Prof. Roberts-Austen :—

				Excess grains.	Decimal equivalent.
			Eighths	1	·1736
		Carat-grains.	1	7.5	1·3021
	Carat.	1	8	60	10·416
Assay pound.	1	4	32	240	41·6
1	24	96	768	5760	1000·0

The excess grains in one assay pound are the same as the number of grains in the troy pounds. Gold is reported to the trade according to the above table in carats or the decimal equivalent; thus pure gold is 24 carat or 1000 fine; standard gold, 22 carat $= \frac{22 \times 1000}{24} = 916{\cdot}66$ fine. When an alloy is slightly "worse" than the standard, it is said to be "worse so much." When above the standard, the alloy is called "better so much," the difference being expressed in carat grains, eighths, and excess grains, or in its decimal equivalent. In both cases the excess grains represent gold present in excess of the report.

(*b*) In America assays of gold ores and bullion are reported in money value per ton. One troy ounce of gold 1000 fine = \$20·67.

Phillips gives the following standard values for different countries:—

Countries.	1000 (24 Ct.)	916·66 (22 Ct.)	900 (21·6 Ct.)
United Kingdom, troy oz.,	£4 4 10	£3 17 10	£3 16 6
United States, ,,	\$20·67	\$18·95	\$18·6
France, kilogramme,	Fr. 3444·44	Fr. 3157·40	Fr. 3100
Germany, ,,	Mk. 2790	Mk. 2474·16	Mk. 2511

The principal standards for coinage are:—

	Gold, per 1000 parts.
Austria and Holland (old ducat gold), .	986 and 983
United Kingdom, India, Russia (old), Portugal, Turkey, and Brazil, . .	916·66
France, Germany, United States, Italy, Spain, Russia (new), ...	900
Egypt, Mexico, Spanish Philippine Islands,	875

Most other countries 900 fine.

(*c*) Alloys of gold chiefly contain copper and silver,

but other metals are occasionally present. In the case of silver alone, the alloy is simply adjusted by fusion with silver, so that the silver equals $2\frac{1}{2}$ times that of the gold, and the latter separated by its insolubility in nitric acid. With copper, cupellation is necessary, and with notable quantities of nickel, antimony, tin, etc., scorification may be required before cupellation.

(*d*) *Method of conducting the process when Silver, Platinum etc., are absent.*

Weigh out either 10 grains, or $\frac{1}{2}$ gramme, and wrap in a quantity of sheet lead, the remaining lead being introduced in the form of a bullet, which may be ascertained by reference to the following table :—

Amount of gold in alloy.	Lead required for cupellation for one part of alloy.
1000	1
900	10
800	16
700	22
600	24
500	26
400, 300, 200, 100	34

The prepared samples are then transferred to trays and thence to the heated cupels in the muffle, as described for silver in § 126*e*, but as gold has a much higher melting point than silver the temperature required to finish must be higher. After brightening, the assay should be cooled in the closed muffle, although it may be removed as soon as it is solid. It is then cleaned and weighed. As most gold contains silver it is better to proceed as follows :—

(*e*) *Silver being present.*

The great majority of alloys employed by jewellers and

goldsmiths contain silver as well as copper, in which case the 10-grain sample is wrapped in an envelope of sheet lead, together with 2½ times as much silver as the gold supposed to be present (which in an unknown alloy is determined by a rough preliminary assay), a lead bullet added as before, and the whole cupelled. Then the cupel is allowed to cool in muffle as before, and the button cleaned from any adhering bone ash by squeezing with pliers or hammering and brushing with a hard tooth brush, or immersing in warm hydrochloric acid; then dried and weighed. It is then flattened on a bright steel anvil with a heavy round-faced hammer whose head is polished bright and smooth. The button is first struck in the centre, then near the edge to elongate it so that it may be more readily gripped by the rolls. It is then annealed and rolled out into an oblong strip about two inches long, again annealed, and coiled into a spiral, the outer surface of which should be that which formed the bottom of the bead. This side of the strip is easily recognised by being less brilliant than the other.

The spiral or "cornet," as it is termed, is then placed in a glass flask having a long neck and capable of holding

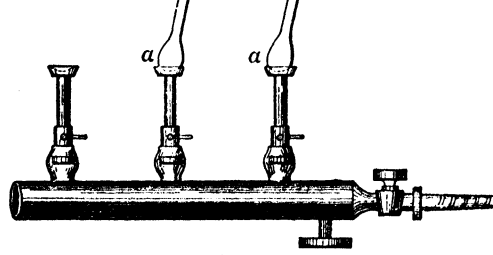


Fig. 62.

about 5 to 6 ounces (Fig. 62). Two ounces of dilute nitric acid, containing two parts water to one of strong

acid, are added, and gently boiled for ten minutes, until all brown fumes have disappeared, then the silver solution is poured off. A small ball of fireclay about the size of a pea is placed in the flask to prevent irregular ebullition, which might break up the cornet and cause loss by spurting. Stronger acid, of the proportion 1 : 1, is then added and boiled for ten minutes. The cornet is boiled in strong acid to finish. Pour off the liquid, wash the gold with pure distilled water, and fill up the flask to the top with same. Now cover the open end with the thumb, invert, and place in a small crucible full of water. This operation of inverting without spilling any liquid may, after a little practice, be easily done, without stopping with the thumb. The gold cornet and any detached fragments fall to the bottom of the crucible in virtue of the high specific gravity of gold; the greater portion of water can now be poured off and the rest evaporated. The dry crucible with the cornet, which is of a dull brown colour, is then placed in a red hot muffle for a short time, when the gold acquires the usual yellow colour with a considerable shrinkage in bulk. The gold is allowed to cool and then weighed.

The amount taken was 10 grains. The weighing after cupellation = silver and gold present, plus the silver added for parting, which was 2½ times that of the gold. The weighing after parting = gold; and the difference from former weighing = silver.

(*f*) The accuracy of an assay cannot be relied on without a "check" assay being made at the same time, as silver or copper may be retained, or gold absorbed by the cupel, so that the error may be in excess, or below the true amount. The "check" contains the same amount of pure gold as is supposed present in the alloy, made up to 10 grains (or whatever weight is used in the sample) with pure copper so as to make it completely comparable.

Prof. Roberts-Austen points out "that as absolutely pure gold cannot be obtained, the results of assays indicate an amount of pure gold in excess of that actually present. But the opposite cannot occur, as gold cannot be more than pure. The correction is shown by the following formula:—

Let 1000 represent the weight of alloy taken.

" p " " " " gold obtained.

" x " " actual amount of gold in alloy in thousandths.

" a " " weight of gold (almost pure) taken as a check which approximately = x.

" b " the loss or gain in weight experienced by (a) during the assay, expressed in thousandths.

" k " the variation of the 'check gold' from purity.

Then the amount of fine gold in check = $a\left(1 - \frac{k}{1000}\right)$ and x the corrected weight of assay will

$$= p - \frac{ak}{1000} \pm b$$

(b) being subtracted or added according as it is loss or gain. If (a) be assumed = x this equation becomes

$$x = \frac{p \pm b}{1 + \frac{k}{1000}}$$

Example. Let p = 917·1 thousandths.

a = 920·0

b = ·3

k = ·1

Then by first formula,

$$x = 917{\cdot}1 - \frac{920 \times 0{\cdot}1}{1000} - 0{\cdot}3$$

for as (b) is a gain in weight it must be deducted. Hence $x = 917{\cdot}1 - 0{\cdot}092 - 0{\cdot}3 = 916{\cdot}708$, and by second formula

$$x = \frac{917{\cdot}1 - 0{\cdot}3}{1 + \frac{0{\cdot}1}{1000}} = 916{\cdot}708.$$

These results show that although (a) does not exactly = x, no sensible error is introduced." (Percy's *Gold and Silver*, p. 274.) From the foregoing table it will be seen that gold sometimes retains a little silver by which its weight is increased. This is known as "surcharge," and most commonly occurs when only a small quantity of copper is present, as when the latter is considerable, much lead is required for cupellation, which causes more gold to be absorbed by the cupel. It will also be readily understood that with a medium quantity of copper, the surcharge and absorption may just balance each other.

(*g*) The following table, showing results of experiments made at the Paris Mint, illustrates this point:—

Copper.	Gold.	Results.	Difference.
100	900	900·25	+0·25
200	800	800·5	+0·5
300	700	700	0·0
400	600	600	0·0
500	500	499·5	
600	400	399·5	
700	300	299·5	−0·5
800	200	199·5	
900	100	99·5	

Having weighed the gold obtained from assaying the "check pieces," the excess or deficiency in weight is subtracted or added to the weight of the gold obtained from the assayed sample.

(*h*) In places where a large number of assays are frequently being made, platinum vessels are often used for parting instead of glass. A shallow platinum dish is

furnished with a rack containing a number of divisions, each holding a small perforated thimble-shaped vessel

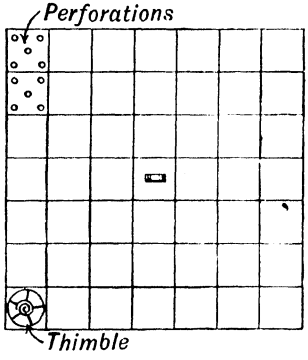


Fig 63.

made of platinum, which admits of free entrance of the acid contained in the dish. The dish is heated from beneath to boil the acid, and covered at the top with an inverted glass funnel to carry off the fumes. By raising the rack the acid is drained off from all the vessels at once. The apparatus is shown in plan and section in Figs. 63 and 64.

§ 137. *Assay by the Touchstone, etc.*

(*a*) This is a rough and rapid method of approximately ascertaining the quality of a gold alloy without injury of the article as is the case in dry and wet assaying. An experienced person may determine the correct standard within 1 per cent. of the truth. The method is based on the fact that the richer an alloy is in gold, the more clearly does a streak drawn with it on a black ground exhibit a pure golden yellow colour and the less is it attacked by a test acid.

(*b*) The touchstone is a hard siliceous stone of a black

colour obtained from Bohemia, Saxony, and Silesia, its surface being prepared and left so that it will just abrade

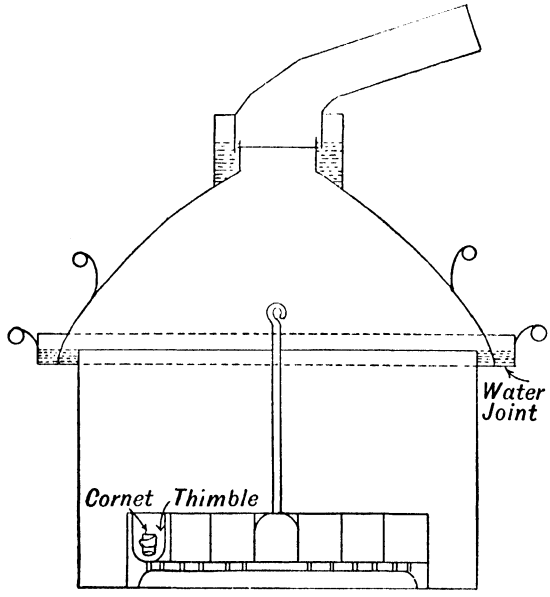


Fig. 64.

the metal from any sharp angle of the alloy when the latter is drawn over the stone.

(*c*) In order to ascertain the quality of the alloy, its streak is compared with streaks drawn by alloys of known fineness called "touch needles," of which five series are required: 1. *Red series*, consisting of gold and copper, the gold increasing by half carats in successive needles. 2. *White series*, contains gold and silver. 3. *Mixed series*, in which the quantities of silver and copper alloyed with the gold are equal. 4. *Unequal mixed series*, in which the silver is to the copper as 2 : 1. 5*th series*, in which the silver is to the copper as 1 : 2. Besides these, special

needles are prepared for different kinds of work. The mark left on the stone having been matched with the corresponding mark of one of the "touch needles" is assumed to have the same composition. To confirm this assumption a drop of acid is placed on each streak, allowed to work for some time, and its effect observed in each case; then wiped off to see if the mark is left unchanged. The test acid consists of 98 parts pure nitric, 2 parts pure hydrochloric, and 25 parts distilled water. The first streak made by a body is discarded, as in the case of coloured gold, for example, the surface has a different composition to the general mass. The above test mixture has no effect on alloys of 18 carats and upwards, so that streaks made by these alloys will not be wiped off with linen rag after treating with acid. Pure nitric acid has no effect on alloys of 15 carats upwards.

2nd. ESTIMATION OF GOLD IN ORES.

§ 138. Gold as a rule exists in minerals and bye-products in much smaller quantities than silver, and as stated before can be economically extracted when present in small quantity, such as would not pay if its value only equalled that of silver; therefore a much larger amount of matter must be operated upon to obtain an amount of gold capable of being accurately weighed. Bodies containing gold frequently contain silver also, so that it is usual to examine the button of gold for that metal, which, if present, must be parted from the gold and both metals estimated.

(*a*) *Sampling.* The greatest care should be taken to obtain a typical sample, which must correctly indicate the average richness of the whole vein. This is an easy matter when the metal is in fine grains uniformly distributed throughout the rock, which is a rare case; but more often it occurs in irregular grains, pockets, nuggets, etc., so that two tons or more should be crushed

and thoroughly mixed in order to select about 20 lbs. for the assay sample. This must be crushed very small and passed through a fine sieve of 80 meshes to the inch. Any flattened grains remaining which cannot be sifted, must be assayed separately, and the proportion of gold and silver added by calculation to the results of the assays.

(*b*) The assay may be performed in a crucible or in a scorifier as with silver assays, by taking advantage of the solvent power of molten lead, and afterwards cupelling and parting if silver be present.

The matrix may be sand or quartz; pyrites, galena, blende, and other sulphides; granite; oxides of iron, etc. The rocks enclosing gold veins are mostly chloritic, talcose, and argillaceous slates. Gold *in situ* is most frequently found in quartz veins, intersecting metamorphic rocks, and almost invariably associated with pyrites. The most abundant supply of the gold of commerce is obtained from alluvial deposits by washing it from its associated sand.

§ 139. *Assay of Gold Quartz.*

Pass 3000 grains of the finely-powdered ore through a sieve with 80 meshes to the inch; collect any "metallics" to assay separately; well mix, and take the weight separately of what has passed the sieve and the metallics that remain.

(*a*) Weigh out 500 grains ore, 500 grains red lead, 20 to 25 grains charcoal, and 600 grains carbonate of soda. Mix and introduce into a clay pot, which should not be more than half full; cover with a layer of salt, and place well down in a hot fire, a hole having been made previously to receive it, so that the mouth of the crucible is below the lower level of the draught hole; well pack round with red hot coke, the object being to insure as

far as possible a uniform temperature in all parts of the crucible, which will prevent bubbles rising to the top and carrying a portion of the charge over the sides. Raise the temperature gradually as the operation proceeds, by opening damper and closing the back brick on top of furnace, which may be drawn from the wall a little way at first. In about twenty minutes the charge settles down tranquilly in the pot, and should then be poured into a half-round mould; allowed to cool and the button of lead detached, cleaned, and put ready for cupelling.

The button of lead should weigh at least 300 grains or there will be a danger of gold being left in the slag. If less than this amount, it indicates an insufficiency of reducing agent, or the oxidation of foreign matter by the oxide of lead and passage of latter into slag along with these oxides.

(*b*) *Instead of the foregoing* fluxes take 500 grains of ore, 500 grains red lead, 25 grains charcoal, 400 grains carbonate of soda, and 200 grains borax. Fuse and extract button of lead as before. Weigh the lead obtained.

(*c*) *Or smelt* 500 grains of ore with 1500 grains red lead and 30 grains charcoal. Treat as before and weigh the lead.

(*d*) Experiments were made on a given ore with the above mixtures with the following results:—

Weight of lead, -	380	362	770
,, silver, -	·020	·019	·011
,, gold, -	·027	·027	·028
Wt. of Ag in red lead,	·012	·012	·036

The following shows the mode of calculation:—

Weight of silver and gold, -	·059	·058	·074
Weight of silver in red lead, -	·012	·012	·036
Gold and silver in ore, - -	·047	·046	·038
Weight of gold alone, - -	·027	·027	·028
Weight of silver, - - -	·020	·019	·010

(*e*) The amount of silver and gold per ton was obtained by the following calculation :—

As 500 : ·027 : : 7000 × 2240 : Au per ton.
500 : ·020 : : 7000 × 2240 : Ag per ton.

Table showing results :—

Ore.	Silver.	Gold.	Silver, per ton.			Gold, per ton.		
			oz.	dwts.	grs.	oz.	dwts.	grs.
500	·020	·027	1	3	3	1	15	7
500	·019	·027	1	2	10	1	15	7
500	·010	·028	0	13	2	1	16	4

The above results are given here to show that with a large proportion of oxide of lead a larger amount of gold is obtained, but as silver is lost in cupellation in proportion to the quantity of lead operated upon, the amount of that metal is too low in the 3rd method. Also in the second case the amount of carbonate of soda was too small to flux the acid gangue present ; therefore a preliminary assay should be made to ascertain the nature of the foreign matter before making the true assay.

(*f*) Having obtained the gold in the button of lead the latter is cupelled as before described, the gold weighed and calculated to the ton as in § 139 (*e*). If the bead is yellow in colour, add 2½ times its weight of silver ; wrap both in lead, and cupel to obtain the

alloy in a single bead ; flatten with hammer ; roll out thin, and part with nitric acid as described in § 136, to ascertain the amount of silver, if any, as well as the gold.

§ 140. *Assay of Pyritic and other Sulphur Ores.*

(*a*) Ores containing a large amount of sulphur, arsenic, zinc, etc., should undergo a preliminary roasting to remove the excess of these volatile impurities, or there is danger of the formation of oxysulphides, which, being very fusible, resist reduction and carry silver with them into the slag. The same result may be achieved by adding nitre to the fluxes in smelting, but too much of this re-agent causes effervescence with the consequent liability to boil over. Arsenic and antimony produce arseniates and antimoniates which convey silver into the slag. Zinc increases loss of silver by volatilisation.

(*b*) The roasting is performed in a fire-clay roasting dish placed in a muffle, gradually raised to a bright red heat and occasionally stirred for about half an hour until no further odour of sulphur dioxide is perceived, when the dish is taken out and a current wafted to the nose by means of the hand, in the same way as in roasting copper regulus.

(*c*) Make two assays, using the following proportions, which must be increased according to the paucity of precious metal present :—

(1) Ore,	1000	(2) Ore,	1000
Carbonate of soda,	1200	Carbonate of soda,	800
Red lead,	500	Borax,	400
Carbon,	30	Red lead,	500
		Carbon,	35

Proceed as in the former case with gold quartz. After introducing the ore mixture into the crucible and covering with salt, force to the bottom a piece of hoop

iron to reduce lead sulphide, etc., which might otherwise retain some of the silver. Even if lead sulphide be absent from the ore, it would be formed by the reaction of lead on iron pyrites.

(*d*) When the ore contains sufficient pyrites to reduce a suitable quantity of lead for cupellation, the reduction may be effected by fusion with red lead or litharge and carbon, thus :—

(3) Ore, 1000 ; Red Lead, 3000 ; Carbon, 75.

These three proportions were applied to a suitable ore, the lead cupelled ; the bead alloyed with silver, and parted.

(*e*) The following results were obtained :—

Weight of lead, - -	430	385	Not weighed.
Silver and gold, - -	·116	·103	·184
Silver in red lead, - -	·024	·024	·072
Gold and silver in ore, -	·092	·079	·112
Gold after parting, -	·066	·058	·078
Silver in ore, - -	·026	·021	·034

Ore.	Gold.	Silver.	Gold, per ton.			Silver, per ton.		
			oz.	dwts.	grs.	oz.	dwts.	grs.
1000	·066	·026	2	3	3	0	17	0
1000	·058	·021	1	17	21	0	13	17
1000	·078	·034	2	10	3	1	2	5

§ 141. *Assay of Gold Ores by Scorification.*

This method is carried out in the same way as with silver ores, § 132, but larger quantities as a rule require to be operated upon. With poor ores, eight or ten separate scorifications are carried on simultaneously with

the same ore, each scorifier containing 50 to 100 grains of ore and the resulting buttons of lead placed in one scorifier and re-scorified until the lead is reduced to a sufficiently small bulk for cupellation. The quantity of lead required varies with the nature of the gangue. Argentiferous and auriferous lead ores only require five times their weight of lead, while arsenical and pyritic ores require fifteen or sixteen times their weight. The following table may be used as a guide:—

Quartzose,	8
Basic (oxides),	8
Lead ores,	5
Arsenical and antimonial,	16
Fahl ore,	12 – 16
Pyritic ores, Blende,	10 – 15

The borax must be used very sparingly, in just sufficient amount to form a liquid slag, or it may form a crust over the ore and lead, preventing oxidation. It is better to add a few grains at first, and the remainder at intervals as the process advances.

ASSAY OF TIN ORES, ETC.

§ 142. The tin of commerce is obtained from its oxide, known as cassiterite or tin-stone, which may generally be recognised by its appearance and high specific gravity which varies from 6·3 to 7·1 in good specimens. When pure, it contains 78·62 per cent. of tin. Tin pyrites is of a yellowish grey colour with strong metallic lustre, having a specific gravity of 4·35, but does not occur in sufficient quantities to be used for extracting the metal on the large scale. It is chiefly found mixed with other sulphides. The following analyses show the composition of good specimens of tin ores:—

Cassiterite.		Tin pyrites.	
Tin, - - -	77·50	Tin, - - -	27·55
Oxygen, - -	21·50	Copper, - -	29·39
Ferric oxide, -	0·25	Iron, - - -	12·44
Silica, - - -	0·75	Sulphur, - -	29·64

Tin ore as taken from the lode contains from 2 to 5 per cent. of cassiterite, which is often associated with one or more of the following bodies:—Quartz felspar, chlorite, schorl, and other stony minerals, mispickel, iron and copper pyrites, iron oxide and wolfram. Cassiterite, having a high specific gravity, is separated from its gangue by a series of washings, which remove the lighter materials. The mispickel and pyrites are converted into oxides by roasting and removed by a subsequent washing. The concentrated product is known as "black tin" (varying from 60 to 72 per cent. of pure tin), and the common impurities are silica, copper and iron oxides, and wolfram. In certain stream tin ores there may be as much as 7 per cent. of titaniferous iron ore.

(*a*) Before any variety of tin ore is assayed it is necessary to separate the oxide from its associated gangue, which is very skilfully accomplished by an experienced person on a "vanning shovel" (Fig. 23). For this purpose the ore is very finely crushed and sifted so as to obtain all the particles of the same size. The amount of ore taken for the purpose varies with the richness. With poor ores an ounce or 250 grains may be taken; with rich ores half or even a quarter of this amount is used. The weighed portion of ore is placed on a vanning shovel. The vanner stands in front of a tub of water, and allows a little water to run on to the ore. He then raises the shovel a little above the surface of the water, and, holding it nearly horizontal, imparts to it a circular motion until the whole is brought to the centre: by this motion, too, the lighter portions will travel to the top and the

heavier ore pass to the bottom. The top finer mud is then run off. This is repeated until the water standing for a moment is tolerably clear. Water is again added, and the shovel is rotated, the workman imparting to it an elliptical motion at the front and back positions. Besides the elliptical motion, at certain points a jerk is added in one direction throwing the earthy matter forward and the heavier minerals backwards. This jerk is produced just as the wave of water is returning so that it carries forward the lighter matter, whilst the heavier portions at the bottom are hardly affected by it, but the jerks gradually throw them backwards. When the washing is complete the residue is dried on the shovel, then transferred to a hot crucible and roasted till free from sulphur. The roasted mass is then put on the shovel again, the hard particles rubbed to powder by a clean flat hammer-head, the adhering particles washed from the hammer, and the vanning repeated until everything except the tin oxide is, as far as possible, removed. The cleaned ore is dried, freed from particles of iron by a magnet, and weighed. By this means a close approximation to the real amount of tin present in the ore can be ascertained. A complete set of appliances for vanning purposes will include a shovel (Fig. 23) having a bent deal handle, 3 feet long; a bruising hammer weighing 2½ pounds; two sets of scales and weights, one for heavy weights, the other for weighing the "black tin"; a furnace such as shown in Fig. 1; and a water box, 4 feet long, 2 feet 6 inches wide, and 8 inches deep.

§ 143. *Assay of Tin Stone* (Cornish method).

For this purpose take 12,000 grains of washed ore as delivered by the miner; grind in an iron mortar, and pass through No. 60 sieve. Well mix; remove 5000 grains, and pass the whole of this through a sieve with 80 meshes to the inch.

(*a*) Weigh out 1000 grains of oxide, and 200 grains of

anthracite powder which has also been passed through No. 80 sieve; place in a plumbago crucible which should be smooth inside (those sold by Messrs. Morgan of Battersea are especially suitable for this purpose), and put well down in the furnace. Gradually raise the temperature as the operation proceeds; in about twenty minutes remove the crucible, and rub down the inside with a piece of wood to remove any adhering particles of metal or oxide, replace in the fire and heat strongly for another ten minutes; then withdraw, impart to the pot a circular motion to collect all the metal in one mass, scrape the excess of anthracite and slag to one side and pour the metal into a rectangular mould, Fig. 17*g*, by which means a strip is produced long enough to test its physical properties, such as the character of the "cry" when bent, its softness, malleability and fracture when broken. After pouring the metal, the residue must be thoroughly scraped out of the pot; the particles of carbon, etc., ground very fine in an iron mortar, and any particles of metallic tin picked out and added to the main portion. The residue is then sifted and vanned on a shovel, or it may be placed in a porcelain or similar dish, and a gentle stream of water allowed to run on, by which the carbon, etc. is washed away. The dry residue is mixed with an equal bulk of carbonate of soda, placed in a small clay crucible (not plumbago), and fused for ten minutes. Now pour into mould; powder the slag and pick out any shots of metal, which must be weighed with the main quantity obtained in the first smelting. The weight divided by ten gives the percentage of black tin. In Cornwall the results are generally expressed in cwts. per ton of ore. A small quantity of borax or fluor-spar is occasionally used to flux refractory slags.

(*b*) To get a better idea of the quality of black tin; it may be re-melted and allowed to remain in the pot after removing from the fire until the scraped surface ceases

to oxidise, then poured into a rectangular mould made of marble and allowed to cool undisturbed. If pure, the surface will be bright, smooth, rounded at the sides, and free from spots. (See § 25.) A frosted appearance indicates the presence of iron, copper, zinc, lead, antimony, etc. Low quality ores containing these metals, in combination with arsenic, sulphur, and oxygen, will give too high results, as they are reduced and alloy with the tin.

(*c*) A purer assay product from the above process may be obtained as follows:—Place 1000 grains of ore in a porcelain dish; moisten with hydrochloric acid, and add sufficient water to cover the powder. Heat gently for half an hour; fill up with hot water; filter; wash once or twice; dry the residue; mix it with anthracite, and smelt as before. If wolfram be present in the ore it increases the apparent amount of tin. It may be removed by boiling the assay sample in aqua-regia and dissolving out the tungstic acid, which has been liberated, by means of ammonia.

§ 144. *Assay of Tin Ores containing Silica, as Tin Slags.*

This assay is conducted on the principle, that iron displaces tin from its combination with silica, forming silicate of iron and metallic tin. If, however, the iron be in excess, an alloy of tin and iron will be formed, but the slag will be free from tin. Take 500 grains of ore, 200 grains of forge scales or hematite, 100 grains fluor-spar, and 100 grains of anthracite powder, place in crucible and cover with lid. Heat for half an hour moderately, then for another half hour at the highest temperature of the furnace; remove crucible from fire; allow to cool; break open the pot; remove slag, and clean the button of tin. The amount of pure tin in the button can only be obtained by a wet method.

§ 145. *Assay of Tin Oxide by fusion with Potassium Cyanide.*

This re-agent is expensive when pure, and very objectionable from its poisonous nature, and the obnoxious fumes liberated when it is heated. The common variety is more effective as a reducing agent because it contains potassium carbonate. When used alone, 100 grains of oxide require 500 to 600 grains of the cyanide, so that the following mixture may be substituted with economy and good results: 100 grains ore, 200 grains common cyanide, 30 grains charcoal. It is well to place a little cyanide in the bottom of a small clay crucible, then add the ore mixture (the cyanide need not be crushed to powder); place in a fire at low red heat for ten minutes, then increase the temperature for another five minutes; remove from furnace and pour into a half-round mould. Allow to cool; detach the button of tin; wash away any adhering slag, and weigh. The following equations show the reactions:—

$$SnO_2 + 2KCy = 2KCyO + Sn.$$
$$KCyO + C = KCy + CO.$$

A purer button of tin may be obtained by a previous digestion with dilute hydrochloric acid as in § 143 (*c*). The results obtained by this method are accurate and the assays rapidly performed, but the quantity of tin obtained is too small to test its physical properties, which are such reliable guides to the operator as to the quality of the tin. A Cornish sample of oxide of tin was submitted to assay by the anthracite method and by the cyanide method with the following results:—

	Tin.	Tin.
With anthracite, and 1000 grains ore,	71·0%	71·5%
With cyanide and carbon, and 100 grains of ore, - - - - -	72·0%	72·0%

The former method after treatment of ore with dilute

hydrochloric acid yielded 71·0 per cent. of tin, and the latter method, 72 per cent. It will be seen by these results that with good tin oxide the cyanide method yields a higher result, especially as the button is free from oxide, while the ingot obtained from the anthracite method is covered with a black scale of oxide.

§ 146. *Assay of Ores containing Tungsten, Arsenic, and Sulphur.*

(*a*) When tungsten is absent, the ore, after crushing very fine, is roasted in a clay dish, with frequent stirring, until all volatile matter is removed, by which means the arsenic and sulphur are largely removed and the tin left as oxide, which can then be assayed by one of the foregoing methods.

(*b*) Tungsten is present. Weigh out 200 grains and roast until as free as possible from sulphur and arsenic. Place in a crucible and reduce by the potassium cyanide method. The tungstic acid undergoes no reduction by potassium cyanide even at a high temperature, but unites with the alkali to form a compound soluble in water. The amount of tungstic acid may then be estimated by a wet method.

The following is an example of the composition of "black tin."

Tungstic oxide,	1·5
Tin oxide,	72·1
Silica,	4·6
Titanium oxide,	·8
Copper oxide,	1·0
Ferric oxide,	18·6
Sulphur,	·6
Arsenic,	·3
	99·5

ASSAY OF ANTIMONY ORES.

§ 147. For the purposes of assay, the ores may be divided into two classes, viz., those which contain sulphur and those free from sulphur, such as oxides. The former are by far the most abundant and are generally associated with iron, lead, zinc, silver, quartz, and sulphate of barium. They have a lead grey colour and give a similarly coloured streak. The formula of the pure sulphide is Sb_2S_3.

§ 148. 1*st Class.—Sulphides.*

(*a*) These may be assayed by roasting to oxide and reducing with carbonate of soda and carbon, or by direct reduction with metallic iron as in the case of galena. The roasting must be conducted at a low red heat, otherwise the ore will fuse and sublime, and with constant stirring to prevent the particles clotting together. The operation takes about three quarters of an hour, being complete when no further odour of sulphur-dioxide is perceived.

(*b*) The direct method is preferable to the foregoing, both on account of economy of time and the less liability to loss, but a series difficulty will arise if certain precautions are not attended to. When sulphide of antimony is heated with iron in amount according to the following equation,

$$Sb_2S_3 + 3Fe = 3FeS + Sb_2,$$

the whole of the antimony is set free, but if the iron be in excess, an alloy of antimony and iron will be formed. Now sulphide of iron has a density only a little less than that of antimony, so that complete separation of the two bodies can only take place by keeping the contents of the crucible for a considerable time in a state of fusion, by

which means the white crystalline button of antimony remains at the bottom, covered with the bluish-yellow iron regulus. It is better to let the crucible cool and then break to remove the metal from the slag button.

Assuming the ore to be pure sulphide of antimony, 50 grains of iron will be required for each 100 grains, producing theoretically 71·43 grains of antimony; but 60 to 65 grains is about the amount practically obtained, the loss being due to volatilisation.

(*c*) A rough estimate of the amount of sulphide of antimony in stibnite may be obtained by liquating it from the earthy and siliceous gangue with which it is associated. Place the lid of a clay crucible or the side of a broken crucible in an inclined position on a tripod stand, and on the top, 100 grains of ore. Heat from beneath by means of a large Bunsen burner and allow the fused sulphide to flow into a weighed vessel, then cool and weigh the liquated sulphide. Instead of the above, the apparatus Fig. 47 may be employed.

(*d*) Suppose 50 per cent. of sulphide present, then the following mixture may be used for the assay:—

200 grains ore, 35 grains clean iron filings or thin iron wire cut up very small, 50 grains carbonate of soda, and 10 grains charcoal. Place in a black lead or a brasqued crucible; cover with lid or a piece of coke and heat moderately for fifteen minutes, then raise the temperature for another quarter of an hour; remove from fire and pour into a half-round mould, or allow to cool and break the pot as before described. Carefully detach slag and regulus, and weigh the white crystalline button of metallic antimony.

(*e*) Antimony sulphide may also be assayed by mixing 50 grains of ore with 200 grains of potassium cyanide and heating in a clay crucible. The reduction takes

charcoal furnace. The former is more convenient, as the end *b* can be warmed first, and the heat gradually carried to the ore mixture. As the temperature rises the mercury sulphide is decomposed, the metal being carried forward by the gas into the drawn out part *b c*, which is kept cool, and there condensed together with a little water; but the latter is carried out by the continual stream of gas. The tube is then allowed to cool, the end cut off and weighed as before. If any of the condensed mercury cannot be removed with water it must be treated with nitric acid, washed out clean with water, and the mercury estimated by the wet way.

§ 159. (2) *Method by Difference.*—Cinnabar when in combination with fixed earthy matter may be roughly estimated by heating 100 grains of the dry ore in a covered crucible for fifteen minutes at a strong red heat; then remove from fire; allow to cool, and weigh the residue. The difference indicates the amount of mercury sulphide volatilised. HgS contains 86·25 per cent. of mercury.

ASSAY OF BISMUTH ORES.

§ 160. This metal occurs native, frequently containing small quantities of arsenic, and often associated with silver, sometimes with iron and other metals. It also accompanies various ores of silver, copper, lead, zinc, nickel, and cobalt.

The other ores of bismuth are the oxide, sulphide, silicate, and carbonate. It is also found in combination with tellurium ores.

§ 161. (1) *Native Bismuth.*

This assay is a simple liquation process, the metal being separated by raising the mixture to a little above

the melting point of bismuth, when the metal flows out and may be collected in a suitable receptacle.

(*a*) Weigh 200 grains of the crushed ore; place in a small crucible, the bottom of which is perforated with a number of small holes; cover with a clay lid, and lute it on with clay. Place this in another crucible which leaves sufficient space for the liquated bismuth to collect, and lute the two together. (Fig. 47.) Then raise the inner crucible to a red heat, when the molten metal will run through the perforations into the bottom crucible. Remove the source of heat; allow to cool, and weigh.

(*b*) In most cases the native metal is associated with oxide or sulphide, so that it is necessary to add a certain amount of flux and reducing agent, the nature and quantity of which will depend on the amount of bismuth compound and earthy matter present. The following proportions may be taken as a guide:—

200 grains of ore, 200 grains of carbonate of soda, 20 grains of tartar, and a little iron to reduce any bismuth sulphide. Place the mixture in a clay crucible; cover with a layer of carbonate of soda, and fuse at a moderate temperature for about fifteen minutes; pour into half-round mould; allow to cool; carefully detach the slag, and weigh the button of bismuth obtained.

§ 162. (2) *Bismuth in Copper Ores.*

The separation of bismuth from copper may be effected by taking advantage of the great affinity of copper for sulphur, by which a regulus is formed containing the whole of the copper, any iron passing into the slag, while bismuth is reduced to the metallic state.

In the case of copper pyrites, take 200 grains of ore, 150 grains of borax, 150 grains of powdered glass, 200 grains of lime, 200 grains of fluor-spar, 50 grains of

sulphur, and 30 grains of charcoal. Place the mixture in a large copper assay pot and fuse in furnace till tranquil; then pour into mould, cool, detach button of bismuth from regulus and slag, and weigh.

In the case of oxidised ores, take 100 grains of ore, 200 grains of sodium carbonate, 80 grains of sulphur, and 20 grains of charcoal. Well mix together; place in crucible, and cover with 80 grains of common salt. Fuse and pour as in former case.

The metal obtained by either of the above methods is very liable to be impure, and as some of the metal is lost by volatilisation, only approximate results can be obtained.

The pure metal has a reddish white colour and bright crystalline structure when fractured. Copper may be detected when present, as it does not alloy with bismuth. Antimony makes the lustre duller, and sulphur imparts a black tinge.

ASSAY OF NICKEL AND COBALT ORES.

§ 163. The ores of these metals are often of a very complex nature, being generally associated with ores of other metals. The most important compounds are those with arsenic and sulphur.

The assay of nickel and cobalt by the dry way is based on their affinities for arsenic, by which means they are first concentrated in the form of a speise, and the cobalt afterwards removed by the superior affinity of nickel for arsenic. This method has already been described in § 119 in dealing with the valuation of copper ores containing nickel and cobalt.

(*a*) First form nickel speise, containing nickel, cobalt and iron. Take 100 grains of ore crushed very fine and passed through No. 80 sieve and mix with 20

grains of arsenic, 100 grains of carbonate of soda, 80 grains of tartar, and 30 grains of borax glass. The mixture is then fused in a clay crucible for about fifteen minutes, and when tranquil poured into a half-round mould and allowed to cool. The speise must then be detached from the slag and weighed. This should be repeated with a second portion of ore. The following results were obtained from two experiments:—

1st, - - - - - -	66·310 grains.
2nd, - - - - - -	65·630 grains.

(*b*) *Treatment of the Speise.*

The action is based on the fact that when an arsenide of iron, cobalt, and nickel is heated in a muffle in contact with air and borax, the cobalt and nickel remain unaffected until the whole of the iron is oxidised and passed into the slag. Then in the same way, the nickel does not leave the speise until the cobalt has been scorified.

A piece of about 10 grains must be accurately weighed and the exact weight noted. An inverted crucible lid, Fig. 34, may be used as a scorifier; a very hot muffle being employed. Then 15 grains of borax glass wrapped in tissue paper is added to the scorifier, and when fused the button of speise is added, also wrapped in paper. The temperature must be sufficiently high to melt the speise at once, or some of the nickel and cobalt will oxidise and pass into the slag. In a short time the surface brightens; allow it to remain until the action stops, then lift out the scorifier and quench gradually in water. If all the iron has been removed, and the operation stopped at the right stage, the slag will be slightly coloured blue, showing that the cobalt was beginning to scorify. Remove the bead from the slag and place it in a small brasqued crucible; cover with lid, and heat until no odour of arsenic is perceived. Allow to cool and weigh.

(*c*) Repeat the above operation in another scorifier

with the weighed nickel and cobalt speise, using several scorifiers if necessary and less borax. When the whole of the cobalt has passed into the slag, a green cap will appear, indicating that the nickel is beginning to scorify; then quench in water as before, and weigh the bead which contains nickel arsenide only. (Ni_2As.)

The loss between this and the last weighing gives the amount of Co_2As.

(*d*) The following results were obtained from one of the samples of nickel speise mentioned in § 163 (*a*):—

Speise.	Nickel, per cent.	Cobalt, per cent.
1. 11·37 grains	yielded 31·75	—
2. 10·326 ,,	,, 31·76	—
3. 11·159 ,,	,, 31·80	and 8·28
4. 11·396 ,,	,, 31·80	,, 8·01

The method of calculation is as follows:—

Weight of speise taken = 11·37 grains.
,, Ni_2As = 5·914 ,,

Then as 11·37 : 100 :: 5·914 : 52·014 (Ni_2As).

Ni_2 = 117·52 (Ni = 58·8)
As = 75 (As = 75)

192·52

As 192·52 : 117·52 :: 52·014 : 31·75 Ni.
Co_2As in No. 3 = 1·516 (Co = 58·8)
,, in No. 4 = 1·494 (As = 75)

§ 164. *Assay of Speise containing Nickel, Cobalt, Copper, and Iron.*

(*a*) Take 100 grains of speise and mix with 100 grains carbonate of soda, 30 grains borax, 80 grains tartar, and 30 grains arsenic. Fuse in crucible; pour and detach speise as before, and weigh. Weigh accurately a piece of about 10 grains, and scorify the iron and cobalt as before, when a speise is left containing nickel and copper. Weigh, and

then wrap the bead in paper with ten times its weight of fine gold, and place the mixture in a hot scorifier containing molten borax, when the nickel gradually oxidises and passes into the slag. The operation is repeated until the slag ceases to be coloured with nickel oxide. Then remove the gold-copper alloy, which must be malleable; weigh and cupel with 35 times its weight of lead. The loss in weight gives the copper.

The first weighing after removing iron gives the combined weight of Co_2As, and Cu_3As.

The second weighing gives the amounts of Ni_2As and Cu_3As, and the difference between the first and second gives the Co_2As.

The third weighing gives the gold and copper.

The fourth weighing gives the gold, and the copper by difference between third and fourth.

The quantity of copper being found, the amount of arsenic originally associated with it may be computed. Then the difference between the Cu_3As and the second weighing gives the amount of Ni_2As.

(*b*) The following example will make the method clearer:—

Weight of speise taken,	10·168 grains.
„ after removing iron and arsenic,	6·845 „
„ „ Co_2As,	3·378 „
Weight of Co_2As,	3·467 „

	Grains.
Weight of gold added,	34·182
„ „ and copper after removing Ni_2As,	35·090
„ copper present,	·908

But the copper exists in the speise as Cu_3As:—

$Cu_3 = 189$	(Cu = 63)
As = 75	(As = 75)
264	

As 189 : ·908 :: 75 : ·36 arsenic. Therefore the Cu_3As = ·908 + ·36 = 1·268 grains, and 3·378 − 1·268 = 2·110 Ni_2As.

The 10·168 grains of speise contains :—

Iron and arsenic, -	-	3·323 grains.
Co_2As, -	-	3·467 ,,
Ni_2As, -	-	2·110 ,,
Cu_3As, -	-	1·268 ,,

§ 165. *Assay of Cobalt Speise.*

Assuming the speise to consist of the following ingredients :—

30 grains of cobalt.
4 ,, nickel.
10 ,, iron.
56 ,, arsenic.

Well mix the speise with 10 grains of arsenic, 100 grains of carbonate of soda, 80 grains of tartar, and 30 grains of borax glass. Place in fire, and fuse at a bright red heat; pour when tranquil; allow to cool; extract the speise and weigh.

The speise is then assayed in the same way as nickel speise. A very high temperature is required to start with, but as the cobalt scorifies off, a lower temperature will suffice. When a large amount of cobalt, as in the present case, is known to be present, a larger scorifier may be conveniently used, and a greater amount of borax.

DRY ASSAY OF PLATINUM ALLOYS.

§ 166. (*a*) Take 3 or 6 grains of alloy according to the quantity of platinum present; add three quarters the amount of pure silver, and wrap the whole in the requisite quantity of lead to remove base metals by cupellation, and cupel until the bead brightens. Weigh

the bead obtained. The loss gives the amount of base metal originally present.

(*b*) Flatten; anneal; roll out thin; again anneal; roll into a cornet as in gold bullion assay; place in a parting flask, and boil for fifteen minutes with strong sulphuric acid, which dissolves out the whole of the silver. Wash, dry, and weigh the residue. The loss equals the silver originally present, plus the amount of pure silver added for cupellation.

(*c*) Add to the cornet twelve times its weight of silver and cupel with lead as before. Flatten bead; anneal; roll out again; anneal; coil into a cornet, and boil for a few minutes in dilute nitric acid, then with stronger acid as in gold parting. Wash thoroughly, dry, and weigh the residue. The loss gives the platinum, plus the silver added. The undissolved portion may be gold and osm-iridium.

Boil in aqua-regia, and weigh the residue if any, which is the osm-iridium. The loss in weight gives the gold.

(*d*) In platinum alloys containing much platinum not more than 2 grains should be taken for assay as the difficulty in cupelling is increased with the size of the button. Platinum will be dissolved in the sulphuric acid if too much silver is added, which would otherwise facilitate the cupellation.

PART III.

ASSAYING AND ANALYSIS BY WET METHODS.

Estimation of Bases and Acids with Methods of Separating Them from Each Other.

Group I.

Containing Silver, Mercurous Oxide, Lead.

Note.—In the following exercises, two portions of each substance should be worked as a check on each other.

§ 167. *Silver.*

Take 5 grains of pure silver; introduce into a conical flask; add sufficient dilute nitric acid to dissolve it; close the mouth with a small funnel, and heat gently till all is dissolved. Dilute with hot water and transfer to half pint beaker; add hot water till about half full; boil on sand bath; remove and add dilute hydrochloric acid with constant stirring as long as a precipitate is produced. A large excess of the precipitant must be avoided. Heat nearly to boiling with frequent stirring till the precipitate settles; pour off the supernatant liquid through a filter of known ash; wash the silver chloride twice in the beaker with hot water; then transfer to filter, and wash with water containing a little nitric acid, then with pure water. Dry thoroughly in water oven, and transfer precipitate to a dry watch glass. Incinerate the paper in a weighed porcelain crucible; add a few drops of nitric acid to dissolve any reduced silver; heat; then add a little hydrochloric acid; evaporate carefully to dryness; add the

precipitate from the watch glass, and heat the crucible till the edges of the chloride just begin to fuse; allow to cool in a dessicator and weigh. Then—

143·5 : 108 :: Weight of precipitate : x.

EXAMPLE.

	Grains.
Suppose the crucible with ppt. weighs - -	107·112
,, crucible alone ,, - -	100·520
Weight of precipitate =	6·592

$$\frac{108 \times 6{\cdot}592}{143{\cdot}5} = 4{\cdot}961 \text{ grains of silver.}$$

$$\text{Then} \frac{4{\cdot}961 \times 100}{5} = 99{\cdot}22 \text{ per cent. of silver}$$

See note, § 222.

§ 168. *Lead.*

Dissolve 5 grains of lead in nitric acid; remove excess of acid by evaporation; dilute with water; transfer to beaker, and add dilute sulphuric acid as long as a precipitate forms; then add twice as much alcohol as there is sulphuric acid present; allow to stand in a warm place till the lead sulphate completely subsides; pour the clear liquid on to a filter; wash the precipitate once or twice with dilute alcohol; transfer to filter, and wash till all free sulphuric acid has been removed. Dry; remove precipitate, and incinerate the paper in a weighed porcelain crucible; cool; moisten with nitric acid. Then add a few drops of sulphuric acid; cautiously evaporate; ignite moderately; add the main bulk of precipitate; again ignite; cool, and weigh.

In cases where alcohol cannot be used, a greater excess of sulphuric acid is requisite.

If the liquid contain nitric acid it is advisable to evaporate after adding the sulphuric acid until the nitric acid is removed.

If hydrochloric acid be present, the precipitate and filter ash must be treated with strong sulphuric acid, evaporated, and ignited to convert any lead chloride into sulphate.

The amount of lead is calculated thus—

As 303 : 207 : : Weight of ppt. : x.

§ 169. *Mercurous Oxide.*

If nitric acid be present the solution should be evaporated to a small bulk, diluted considerably with cold water; and then dilute hydrochloric acid mixed with twice its bulk of phosphorous acid added till all the chloride is precipitated; allow to stand a few hours in a warm place; filter on to weighed paper, which has been dried at 100° C.; dry at same temperature; cool in desiccator, and weigh. After deducting the weight of the paper—

235·5 : 200 : : Wt. of ppt. : x.

Mercurous oxide is generally converted into mercuric oxide for estimation, by heating with nitric acid, and adding hydrochloric acid by degrees till the mercury compound is dissolved.

§ 170. *Separation of Silver, Lead and Mercury in an amalgam.*

Take 25 grains and dissolve in nitric acid; evaporate to small bulk; dilute considerably with water; boil; add dilute hydrochloric acid in excess, with constant stirring till all is precipitated; heat nearly to boiling for some time till the liquid is quite clear; filter rapidly; wash with boiling water several times; dry; ignite; and weigh the silver chloride, with precautions as in § 167.

The filtrate contains the mercury and lead. Evaporate to small bulk and add pure sulphuric acid in excess. Evaporate till the sulphuric acid begins to volatilise; add

more sulphuric acid if necessary; then dilute with water; filter off the lead sulphate and treat it as in § 168.

Filtrate from lead sulphate must be evaporated to small bulk; diluted with water and a current of sulphuretted hydrogen passed into the liquid until all the mercury is precipitated as sulphide. The whole must be allowed to stand for some time in a warm place and filtered through a weighed paper (dried at 100°); washed with hot water; dried at same temperature as the filter paper and weighed.

If any nitric acid be present, the precipitate must be washed a few times with bisulphide of carbon or a hot solution of sodium sulphide to dissolve the free sulphur liberated by that acid.

As 232 : 200 : : Wt. of ppt. : x.

§ 171. *Another Method of Separation.*

Excess of nitric acid having been removed and solution diluted, sodium carbonate is added in slight excess, then potassium cyanide in excess; heat gently for some time and filter off the carbonate of lead. Wash the precipitate with water containing a little cyanide. Dry, ignite, and weigh as lead oxide.

As 223 : 207 : : Wt. of ppt. : x.

The filtrate containing silver and mercury is neutralised with nitric acid, and a little more added to insure complete precipitation of silver cyanide, which is filtered on to a weighed paper; washed; dried at 100° C., and weighed.

As 134 : 108 : : Wt. of ppt. : x.

The filtrate from the latter is evaporated to small bulk, neutralised with carbonate of soda, and sulphuretted hydrogen passed in till all the mercury is precipitated as HgS. This is allowed to settle; filtered; washed, and weighed as explained in § 170.

As free sulphur will be present, it should be treated with sodium sulphide, as described in § 170.

Group II.

Containing Mercury, Bismuth, Copper, Cadmium and Lead.

§ 172. *Mercuric Oxide.*

Twenty grains may be used to determine the mercury in the metallic state by distillation in a piece of glass combustion tubing about 12 inches long and ½-inch bore (Fig. 65). First put into the part *a b* a mixture of dry bicarbonate of soda and chalk, then the mercury compound mixed with excess of quicklime in the part *b d*, then another layer of lime, and lastly a loose plug of asbestos. The end *e g* is next drawn out with the blowpipe to a small jet which just dips beneath the surface of water in flask *g* during the operation. The tube and its contents are heated in an ordinary tube furnace till all the metal is volatilised. The part *a b* is then strongly heated and the carbonic acid liberated expels the last traces of mercury. The contracted portion is cut off and any adhering mercury washed into the flask. When the metal has settled, the water is decanted off, the mercury transferred to a porcelain crucible, the water removed by blotting paper, and the last remnants by standing some time under a bell jar over strong sulphuric acid; then the metal is weighed.

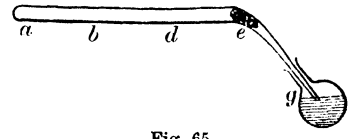


Fig. 65.

§ 173. *Bismuth Oxide.*

Dissolve 10 to 15 grains of the metal or compound in a little dilute nitric acid; dilute with water, disregarding any precipitate; boil; mix with carbonate of ammonia in slight excess and heat for some time nearly to boiling; filter; dry; and ignite, with the usual precautions, oxidising any reduced metal by nitric acid. Weigh the

Bi_2O_3. In the presence of sulphuric and hydrochloric acids, basic sulphide and chloride are precipitated, which are not decomposed by excess of ammonium carbonate, and thus give incorrect results. When this is the case, re-dissolve in nitric acid and re-precipitate.

As 464 : 416 :: Wt. of ppt. : x.

§ 174. *Copper.*

Dissolve 5 to 10 grains of copper in nitric acid and evaporate to dryness. Re-dissolve in hydrochloric acid; dilute; boil, and pass through the solution a current of sulphuretted hydrogen, keeping the liquid nearly to boiling in the meantime. When complete, allow to settle; test the supernatant liquid with sulphuretted hydrogen water; if it remains clear, filter quickly; wash continually with water containing sulphuretted hydrogen, and dry quickly on the filter. Burn the paper and transfer both ash and precipitate to a weighed porcelain crucible; add a little flowers of sulphur and ignite strongly in a stream of hydrogen, using gas blow-pipe; cool, and weigh as Cu_2S.

As 158 : 126 :: Wt. of ppt. : x.

The hydrogen may be introduced by having a hole in the cover of crucible, into which fits a fire-clay tube (Fig. 67) conveying the dry gas.

§ 175. *Cadmium.*

Five to ten grains of the metal may be dissolved in dilute acid; the solution diluted; boiled, and an excess of carbonate of soda added. The latter should be added cautiously till the solution is strongly alkaline; then boil; allow to settle; decant through filter, and wash the precipitate two or three times before transferring to the paper; wash well with hot water; dry; remove completely from paper; burn latter; allow to cool; oxidise with nitric acid; ignite; transfer precipitate and ash to crucible; ignite, and weigh the CdO.

128 : 112 :: Wt. of ppt. : x.

To avoid the loss of cadmium by volatilisation on ignition of the paper, the latter should be saturated with a solution of ammonium nitrate, dried, and then ignited.

§ 176. *Separation of Mercury, Bismuth, Copper and Cadmium in an alloy.*

Take 5 grains of each metal; dissolve in nitric acid; remove excess of acid by evaporation; dilute with water and add sodium carbonate in slight excess, then a solution of potassium cyanide; heat gently for some time; filter, and wash repeatedly. The precipitate is Bi_2O_3. Treat as in § 173.

The filtrate contains the mercury, copper and cadmium. Pass a current of sulphuretted hydrogen into the solution, or add sulphuretted hydrogen solution, as long as a precipitate forms. Allow to subside; wash repeatedly by decantation; treat precipitate once more with solution of potassium cyanide; heat gently; filter, and wash the sulphides of mercury and cadmium.

The filtrate contains the copper. Evaporate in fume chamber with the addition of nitric and sulphuric acids until all hydrocyanic acid is expelled; dilute with water; precipitate the copper as sulphide with sulphuretted hydrogen, and estimate as in § 174.

The precipitated sulphides of mercury and cadmium may be carefully washed off the filter into a porcelain basin and digested with dilute nitric acid until all the cadmium sulphide is dissolved. Filter the undissolved portion through a weighed paper, and well wash; dry at 100° C., and estimate mercury as in § 172.

Boil off excess of acid in filtrate; add excess of sodium carbonate, and determine the cadmium as described in § 175.

Group III.

Containing Tin, Antimony, Arsenic, Gold and Platinum.

§ 177. *Tin.*

Digest 10 grains of tin with dilute nitric acid at about 80° C. When all is converted to a white powder, dilute to four or five times the bulk with hot water and allow to stand in a warm place for several hours. Filter; wash with hot water; dry; remove to a watch glass; burn the paper; allow to cool; add 3 drops of nitric acid; dry; ignite; add the precipitate and strongly ignite, then weigh the SnO_2.

As 150 : 118 : : Wt. of ppt. : x.

§ 178. *Antimony.*

Digest 10 grains of antimony with dilute nitric acid, and proceed as with tin. But a little of the oxide of antimony is soluble in the nitric acid, so that the filtrate should be evaporated to dryness; the residue re-dissolved in hydrochloric acid; tartaric acid added; diluted with water, and a current of sulphuretted hydrogen passed through to precipitate the remaining antimony as sulphide. The latter is filtered, washed, and oxidised in a crucible with fuming nitric acid, and the main bulk added; dried; ignited, and weighed as Sb_2O_4.

As 304 : 240 : : Wt. of ppt. : x.

§ 179. *Arsenic.*

When ordinary nitric acid is used to dissolve arsenic or an arsenical compound the metal will be present chiefly in the form of arsenious acid. When fuming acid is employed, then the higher oxide is formed. Both oxides being present, adopt the following method. Evaporate the solution to remove nitric acid; reduce the arsenic acid by boiling with a solution of sodium sulphite; add

hydrochloric acid; largely dilute with water; heat to about 70° C., and pass sulphuretted hydrogen gas until the arsenic is precipitated as As_2S_3, together with free sulphur. Filter; wash; dissolve precipitate in ammonia; filter off sulphur, and well wash. The filtrate contains the arsenic. Add hydrochloric acid in the cold to re-precipitate the As_2S_3; allow to stand some time; filter on to weighed paper; wash; dry; dissolve any free sulphur with bisulphide of carbon; dry again at 100° C., and weigh.

As 246 : 150 : : Wt. of ppt. : x.

§ 180. *Gold.*

Take 5 grains of gold, dissolve in aqua regia at a moderate temperature; evaporate to dryness on water bath; re-dissolve in water and a little hydrochloric acid; add a solution of pure sulphate of iron in excess, and digest at a gentle heat in a porcelain dish for several hours; filter; wash; dry; ignite, and weigh the metallic gold.

Ammonium oxalate may be used instead of iron sulphate; or the gold may be precipitated with sulphuretted hydrogen as sulphide, which is readily decomposed by ignition.

§ 181. *Platinum.*

Dissolve 5 grains of platinum in aqua regia; evaporate cautiously to dryness; re-dissolve in the smallest quantity of water; add excess of ammonium chloride solution, then an equal bulk of alcohol. Allow to stand in a warm place for a few hours; filter; wash with alcohol; dry; ignite in a platinum crucible, and weigh the spongy platinum. Or collect precipitate on weighed paper; dry at 100°, and weigh.

Separation of the Constituents of Groups II. and III.

§ 182. *Principles on which the Separations are based:*— *Platinum and Gold* from all the rest by their insolu-

bility in nitric acid, and the subsequent volatility of the chlorides of tin and antimony when subjected to a stream of chlorine gas.

Platinum from Gold by the insolubility of the double chloride of platinum and ammonium.

Antimony from Tin by the insolubility of sodium antimoniate in alcohol.

Silver from all the rest, except Mercurous Oxide, by the insolubility of its chloride in hot dilute nitric acid.

Lead from all the rest by the insolubility of its sulphate in alcohol.

Mercury from all the rest, except lead, by the insolubility of mercury sulphide in dilute nitric acid.

Bismuth and Lead from all the rest by the insolubility of their carbonates in potassium cyanide.

Cadmium from Copper by the solubility of copper sulphide in potassium cyanide.

§ 183. *Separation of Gold, Platinum, Tin, Antimony, and Arsenic in an alloy.*

Take 20 grains of the alloy, roll out very thin, and cut into small pieces. Introduce into a porcelain boat placed in a glass tube (Fig. 66), and pass a current of dry chlorine gas while the outside of the bulb is being heated gently with a Bunsen's burner, and finally increased to redness. The chlorides of gold and platinum will be left, and the chlorides of the other metals volatilised. The gold and

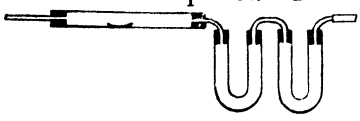


Fig. 66.

platinum chlorides are dissolved in water and a little hydrochloric acid, the platinum estimated as double chloride (§ 181), the gold in solution as metal (§ 180). The volatile chlorides are received in U-tubes containing water, and condensed. Transfer the solution to a beaker, and precipitate the three metals as sulphides with sulphuretted hydrogen; filter; transfer to beaker, and digest with a large excess of a saturated solution of oxalic acid; filter, and thoroughly wash. The filtrate contains the tin; add ammonia till alkaline; then add warm ammonium sulphide until the precipitate just re-dissolves; add excess of warm acetic acid, and allow the precipitated SnS_2 to settle in a warm place; then filter. As this precipitate has a great tendency to pass through the pores of the paper, the washing is effected by a solution of ammonium acetate containing a slight excess of acetic acid. Dry; ignite paper separately; then add the precipitate; cover the crucible with lid, and heat gently for some time; remove lid, and gradually increase the temperature, finishing with a strong heat; cool; then heat repeatedly with ammonium carbonate to a high degree to remove any sulphuric acid; cool again, and weigh the SnO_2.

As 150 : 118 : : Wt. of ppt. : x.

The precipitated sulphides of arsenic and antimony contain a little tin. They may be dissolved in ammonium sulphide, excess of oxalic acid added, and then boiled with sulphuretted hydrogen water. Filter and wash; extract tin from filtrate as before, and add the sulphide to the main bulk of precipitate. The separation of antimony and arsenic will be explained in the next paragraph.

§ 184. *Separation of Tin, Antimony, and Arsenic in an alloy.*

Oxidise the alloy with strong nitric acid in a porcelain crucible, adding the acid drop by drop till the oxidation is

complete. Dry on water bath; transfer to silver dish, rinsing out the crucible with a solution of sodium hydrate; dry again; add eight times the bulk of solid sodium hydrate, and fuse for some time. Cool and treat with hot water till the undissolved residue has the appearance of a fine powder; dilute with water; add one third the volume of alcohol; allow to stand several hours with frequent stirring; filter; wash with alcohol and water containing a few drops of carbonate of soda; continue the washing until the colour of a portion of the fluid running off remains unaltered on being acidified with hydrochloric acid and mixed with sulphuretted hydrogen water.

Rinse the antimoniate of soda from the filter; wash with hydrochloric and tartaric acids; heat gently till dissolved. Precipitate with sulphuretted hydrogen; filter through a weighed paper, wash rapidly with water containing a little sulphuretted hydrogen; dry at 100° C., and weigh. The precipitate retains a little water and free sulphur. A portion should be placed in a porcelain boat which is then inserted in a glass tube and cautiously heated while a current of carbonic acid is passed, until the orange ppt. becomes black; cool in carbonic acid and weigh. From the amount of anhydrous sulphide found, the amount in the whole precipitate may be calculated. Then:—

$$\text{As } 336 : 240 : : \text{Wt. of ppt.} : x.$$

The filtrate from the insoluble antimoniate contains the tin and arsenic. Add hydrochloric acid in excess; pass a current of sulphuretted hydrogen until all is precipitated, and allow to stand till the odour of sulphuretted hydrogen disappears. Treat the precipitate as in § 183 for estimation of tin. The arsenic sulphide is then filtered off; washed; dried at 100° C., and weighed. If any free sulphur is present it must be dissolved by washing with bisulphide of carbon, the precipitate again dried and weighed, and the drying repeated until the weight is constant.

Group IV.

Containing Iron, Aluminium, Chromium, Zinc, Manganese, Nickel and Cobalt.

§ 185. *Iron.*

Dissolve 10 grains of iron in nitric acid; remove excess of acid by evaporation; dilute with water; add ammonia in slight excess; heat nearly to boiling; decant on to filter; wash with hot water; wash precipitate on to filter with hot water; dry thoroughly; ignite in platinum crucible, and weigh.

As 160 : 112 : : Wt. of ppt. : x.

The precipitate may be examined for silica by dissolving in strong hydrochloric acid, evaporating to dryness and re-dissolving in hydrochloric acid, when any silica will be rendered insoluble and may be filtered off, washed, dried, ignited and weighed, and the weight deducted from the weight of the original iron precipitate.

§ 186. *Aluminium.*

Dissolve 25 grains of crystallised alum, which has been coarsely powdered and dried by pressure between filter paper. The solution is then mixed with a large excess of ammonium chloride, and a slight excess of ammonia added. Heat for some time; filter; wash with hot water till free from sulphuric acid; dry; ignite in a platinum crucible, and weigh the Al_2O_3.

As 102 : 54 : : Wt. of ppt. : x.

Note.—Fixed organic matter prevents the precipitation of alumina, which is also the case in some measure with the oxides of iron and chromium.

§ 187. *Chromium.*

25 grains of chrome alum may be employed. Dry as in § 186. Dissolve; make the solution moderately

dilute; heat nearly to boiling and add a slight excess of ammonia; heat again nearly to boiling until the supernatant liquid remains colourless; filter; wash; dry; ignite in a platinum crucible, and weigh the Cr_2O_3.

As 152·8 : 104·8 : : Wt. of ppt. : x.

Note.—Organic matter interferes with the precipitation.

§ 188. *Zinc.*

10 grains of pure zinc may be dissolved in a little nitric acid, and the solution diluted to a moderate extent. Heat nearly to boiling in a porcelain vessel; add sodium carbonate cautiously till the solution is alkaline; boil; allow to stand some time; filter; wash with hot water; dry; ignite the paper; then add the precipitate; ignite strongly, and weigh the ZnO.

As 81 : 65 : : Wt. of ppt. : x.

§ 189. *Manganese.*

10 grains of pure black oxide of manganese may be employed for practice. Dissolve in hydrochloric acid; dilute, and proceed as in the case of zinc. Sometimes it happens that the filtrate is turbid, then evaporate to dryness; dissolve out the soluble matter with boiling water, and filter the residue on to a fresh paper. Dry and ignite both precipitates in a platinum crucible very strongly for fifteen minutes in an oxidising flame. Cool and weigh the Mn_3O_4.

As 229 : 165 : : Wt. of ppt. : x.

Note.—If iron is present, this must be precipitated first.

§ 190. *Nickel.*

Dissolve 10 grains of the metal in nitric acid; filter off any silica and carbon; remove excess of acid by evaporation; dilute with water; boil in porcelain dish, and add excess of sodium hydrate. Heat nearly to boiling for some time; allow precipitate to settle;

filter; wash with boiling water; dry; and ignite the NiO in a weighed platinum crucible.

As 74·6 : 58·6 : : Wt. of ppt. : x.

§ 191. *Cobalt.*

10 grains of pure cobalt nitrate may be taken for practice. The solution is mixed with an excess of a strong solution of sodium hydrate and heated until the precipitate has a brownish colour; allow to settle; filter; wash with hot water; dry; ignite, and finally reduce to the metallic state by means of a current of dry hydrogen. This is effected in a porcelain crucible (Fig. 67) having a hole in the cover, into which fits a porcelain tube conveying the gas, the crucible being ignited in the meantime.

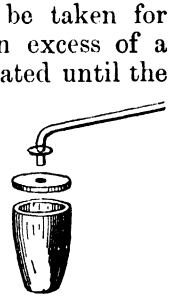


Fig 67.

§ 192. *Separation of the members of Group IV.*

Principles on which the separations are based.

Iron, Aluminium, and Chromium from the rest by the insolubility of their hydrates formed by ammonia or barium carbonate.

Aluminium and Chromium from the rest by the solubility of their oxides in tartaric acid and sodium sulphide.

Chromium from the rest by conversion to chromic acid on fusion with nitre and sodium carbonate.

Aluminium from Iron by the solubility of alumina in caustic potash.

Manganese from Zinc by the solubility of zinc carbonate in ammonium chloride.

Zinc from Nickel, Cobalt and Manganese by the insolubility of zinc sulphide in a solution made neutral with sodium carbonate and containing a little sodium acetate.

Nickel and Cobalt from Manganese and Iron by the insolubility of the sulphides of nickel and cobalt in very dilute hydrochloric acid.

Nickel from Cobalt by the formation of soluble cobalticyanide of potassium and of soluble double cyanide of nickel and potassium which is decomposed by bromine.

Ferric Oxide from Ferrous Oxide. First determining the total iron volumetrically by means of a solution of potassium bichromate, then dissolving another portion in sulphuric acid in an atmosphere of carbonic acid, and determining the FeO; the difference giving the amount of Fe_2O_3.

§ 193. *Separation of Iron, Aluminium and Chromium from Nickel, Cobalt, Zinc and Manganese.*

A chloride or nitrate solution may be employed, but not a sulphate.

Put the solution into a flask, which must contain a little free acid; add ammonium chloride; then add a moderate excess of freshly precipitated barium carbonate suspended in water. Cork the flask, and allow to stand some time in the cold, with occasional shaking. Iron and aluminium hydrates soon separate; chromium hydrate takes some time. Decant; wash two or three times by decantation with cold water; filter, and wash.

The precipitate and the filtrate contain baryta, which may be removed from each by adding dilute sulphuric acid after dissolving the precipitate.

§ 194. *Separation of Chromium from Iron and Aluminium.*

Fuse the oxides with two parts potassium nitrate and

four parts sodium carbonate in a platinum crucible; boil the mass with water; rinse the contents into a beaker; add several crystals of potassium chlorate, then hydrochloric acid in excess; evaporate to the consistence of syrup, adding potassium chlorate occasionally to remove free hydrochloric acid; dilute with water; boil till all soluble matter is dissolved. Filter off the residue, and add ammonia to the solution to precipitate the alumina which has been dissolved; heat till the ammoniacal fluid has almost lost its alkaline character; allow to stand some time; filter, and wash with hot water. The filtrate contains the chromium.

Mix the filtrate with sodium acetate in excess; add acetic acid until the solution is strongly acid; then add a neutral solution of acetate of lead as long as a precipitate forms. Allow to stand in a warm place till all has subsided; filter on to weighed paper; wash; dry at 100° C., and weigh the $PbCrO_4$.

As 323·4 : 52·4 : : Wt. of ppt. : x.

§ 195. *Separation of Aluminium from Iron.*

Mix the hydrochloric acid solution with sodium hydrate till neutral, and pour the solution gradually into excess of nearly boiling soda in a platinum or silver dish, stirring all the time; filter; well wash; dry, and ignite. Weigh the Fe_2O_3. This precipitate contains some alkali, and should be dissolved in hydrochloric acid; boiled with nitric acid if necessary, and re-precipitated with ammonia, as in § 185.

The alkaline filtrate contains the aluminium. Add hydrochloric acid in excess; boil with the addition of potassium chlorate (to destroy any organic matter); concentrate by evaporation; dilute with water; boil; add ammonium chloride in quantity, then ammonia in slight excess; boil till free ammonia is expelled; allow the precipitate to settle; decant; wash with boiling water two or three times, decanting through the filter; transfer

precipitate to filter; wash; dry; ignite in a covered platinum crucible, as particles may be lost by the violent escape of the last traces of water. Weigh the Al_2O_3.

Note.—As sodium and potassium hydrates generally contain alumina, this must be tested for before using, and allowed for in the result.

§ 196. *Another Method of Separating Iron from Aluminium.*

Neutralise the excess of hydrochloric acid with sodium carbonate, and add sodium thiosulphate in sufficient quantity to reduce all the ferric to ferrous oxide; then add more of the thiosulphate, and boil until the odour of sulphurous acid has disappeared, when the alumina is precipitated as hydrate along with sulphur.

$$Al_2O_3.3SO_3 + 3S_2O_3Na_2 + 3H_2O = Al_2H_6O_6 + 3Na_2SO_4 + 3SO_2 + 3S.$$

Filter, wash, dry, ignite, and weigh the Al_2O_3.

The iron in solution may be estimated by adding hydrochloric acid; boiling to decompose excess of the thiosulphite; filtering off the free sulphur, then adding ammonium chloride, ammonia in excess, and ammonium sulphide until all the iron is precipitated. Filter, wash, dry, and ignite with a little sulphur in an atmosphere of hydrogen. Weigh the FeS.

As 88 : 56 : : Wt. of ppt. : x.

§ 197. *Separation of Manganese from Zinc and Nickel.*

Use a slightly acid solution. Add ammonium chloride, then ammonium carbonate in excess, and allow the white carbonate of manganese to settle in a warm place; filter through a double paper; wash with hot water; dry; ignite strongly, and weigh the Mn_3O_4.

§ 198. *Separation of Zinc from Nickel, Cobalt and Manganese.*

Use a hydrochloric acid solution. Add sodium car-

bonate until a permanent precipitate forms, then a few drops of hydrochloric acid to just re-dissolve it. Now pass a current of sulphuretted hydrogen till all the zinc sulphide is thrown down; add a few drops of very dilute sodium acetate; pass the gas again for some time; allow the whole to stand some time; filter; wash with water containing sulphuretted hydrogen; dry; transfer to weighed porcelain crucible; add a little sulphur, and ignite in current of hydrogen. Weigh the ZnS.

As 97 : 65 : : Wt. of ppt. : x.

Small quantities of zinc sulphide may be converted to oxide by strongly igniting in an open platinum crucible.

§ 199. *Separation of Manganese from Nickel and Cobalt.*

Use a hydrochloric acid solution. Add sodium carbonate in excess, then a moderate excess of acetic acid; then add to the clear liquid 3 to 4 cubic centimetres of sodium acetate solution (1 of salt to 10 of water) for each grain of nickel or cobalt present; heat, and pass sulphuretted hydrogen to saturation. When precipitation is complete, filter, and wash the sulphides of nickel and cobalt.

The filtrate contains the manganese, together with some nickel and cobalt. Concentrate the solution by evaporation; add ammonium sulphide, then an excess of acetic acid, when the remaining sulphides of nickel and cobalt will be thrown down; filter, and wash as before. Boil the filtrate with hydrochloric acid to remove the acetic acid; neutralise with ammonia; boil; add ammonium sulphide; boil for fifteen minutes; cool; add more ammonium sulphide, and filter through double filter; wash, dry, and ignite with sulphur in a current of hydrogen. Weigh the MnS.

As 87 : 55 : : Wt. of ppt. : x.

§ 200. *Separation of Nickel from Cobalt.*

Use a hydrochloric acid solution; evaporate to remove

excess of acid; dilute; add potassium cyanide until the precipitate at first formed re-dissolves; add a little more cyanide; boil for some time; cool; add bromine, and well shake. Allow to stand for some time, adding potash occasionally, so that the solution may remain alkaline to the end. In about an hour the whole of the nickel will be precipitated as a black powder, the cobalt being in solution. Add a little more bromine to bring down the last traces, filter and wash. As the precipitate contains alkali, dissolve in hydrochloric acid; dilute with water; add sodic hydrate in excess; heat for some time near to boiling; filter; wash; dry; ignite, and weigh the NiO.

As 74·6 : 58·6 : : Wt. of ppt. : x.

The filtrate containing the cobalt is acidified with hydrochloric acid, evaporated to dryness in a fume chamber, re-dissolved in water, and the solution mixed with excess of a strong solution of sodium hydrate. Heat until the precipitate has a brownish colour, allow to settle; filter; wash with hot water; dry; ignite, and finally reduce to the metallic state by means of a current of dry hydrogen. See § 191.

§ 201. *Estimation of Ferric and Ferrous Oxides.*

(*a*) Dissolve in hydrochloric acid or aqua regia if necessary; dilute, and add pure zinc; allow to stand until the solution is quite colourless, and estimate the total amount of iron present by means of a standard solution of potassic permanganate. (See Volumetric Analysis, § 366.)

(*b*) Weigh another portion, and dissolve by heating with sulphuric acid in a flask through which a stream of carbonic acid is constantly passing; dilute with water, and determine the amount of ferrous oxide as above. The difference gives the ferric oxide.

For example—Suppose in the first case 40 per cent. of iron was found, and in the second case 30 per cent.,

then 30 per cent. is present in the form of FeO, and 10 per cent. in the form of Fe_2O_3.

Now 56 unites with 16 ∴ 30 unites with 8·6 = 38·6 per cent. of FeO. And 112 unites with 48 ∴ 10 unites with 4·3, which equals 14·3 per cent. of Fe_2O_3.

(*c*) Instead of passing a stream of CO_2, the oxides may be dissolved in a small flask as in Fig. 68, provided with a bent tube, and connected with another similar tube by a piece of india-rubber tubing, so that it may be closed when desired with a pinch tap. This tube dips beneath the surface of recently boiled water in the conical beaker (*b*). A lump of sodium bicarbonate is added to the flask (*a*) at the commencement of the experiment to expel residual air.

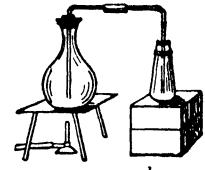


Fig. 68.

Group V.

Containing Barium, Strontium, Calcium and Magnesium.

§ 202. *Barium.*

Hydrochloric acid solution is employed. Heat nearly to boiling; add dilute sulphuric acid till complete precipitation is effected; allow to stand a few hours for the liquid to clear; decant the clear liquid; rinse on to the filter with a dilute solution of ammonium chloride to prevent any fine particles passing through the pores. The paper should never be more than half full as there is a tendency in the liquid to creep upwards. Wash till free from sulphuric acid; dry; ignite in platinum crucible, and weigh the $BaSO_4$.

As 233 : 137 : : Wt. of ppt. : *x*.

Where expedition is desired, the precipitation may be facilitated by continuous stirring for three or four minutes, and the solution at once filtered.

§ 203. *Strontium.*

Use a concentrated solution containing hydrochloric acid; boil; mix with sufficient dilute sulphuric acid to precipitate strontium sulphate; add an equal volume of alcohol; allow to stand several hours, and proceed as with barium. The precipitate should however be washed with alcohol to obtain a more correct result.

As 183·2 : 87·2 : : Wt. of ppt. : x.

§ 204. *Calcium.*

A sample of pure white marble may be analysed for practice. Dissolve in hydrochloric acid and filter off any insoluble residue. Evaporate to remove excess of acid; add ammonia until the solution is alkaline; then solution of ammonium oxalate in sufficient quantity to precipitate the calcium as oxalate; heat till the precipitate has subsided; pour the clear liquid through a filter; wash once or twice with hot water containing ammonia and ammonium oxalate; then wash the precipitate on to the filter; again wash with hot water; dry, and very gently ignite. Now add a little pure ammonium carbonate; moisten with water; dry and heat to very faint redness; cool, and weigh the $CaCO_3$.

Repeat this operation till the weight is constant.

As 100 : 40 : : Wt. of ppt. : x.

With the aid of a blow-pipe and platinum crucible the carbonate may be converted into oxide and weighed as CaO; but the temperature must be maintained at a white heat for some time.

§ 205. *Magnesium.*

Add ammonium chloride to the solution, then ammonia in slight excess. If any precipitate appears, add more ammonium chloride to re-dissolve it. Warm gently; add a solution of ammonium phosphate (microcosmic salt) in excess, and well stir with a glass rod, taking care not to touch the sides of the beaker; allow to stand

several hours in a warm place; filter; wash with water containing $\frac{1}{4}$th its volume of ammonia; dry; heat, gently at first, in a platinum crucible, then ignite strongly; cool and weigh the $Mg_2P_2O_7$.

As 222 : 48 : : Wt. of ppt. : x.

§ 206. *Separation of Barium, Strontium, Calcium and Magnesium.*

Principles on which the Separations are based:—

Barium, Strontium and Calcium from Magnesium by the solubility of magnesium carbonate in certain ammonium salts.

Barium from Strontium and Calcium by the insolubility of barium silico-fluoride.

Strontium from Calcium by the insolubility of strontium nitrate in alcohol and ether, or by the insolubility of strontium sulphate in ammonium sulphate.

§ 207. *Separation of Magnesium from Barium, Strontium and Calcium.*

Employ a nitric acid or an aqueous solution. Remove any excess of acid by evaporation; add ammonium acetate and ammonia in slight excess, then ammonium carbonate to precipitate the carbonates of barium, strontium and calcium (too much ammonium carbonate must be avoided); digest at a moderate temperature for a short time; cool, and filter.

To filtrate add hydrochloric acid; evaporate to dryness; re-dissolve in water, and estimate the Mg as pyrophosphate. (See § 205.)

The precipitated carbonates of barium, strontium, and calcium may be dissolved in hydrochloric acid, rendered nearly neutral, and hydrofluosilicic acid added in excess,

then $\frac{1}{3}$rd the volume of alcohol, and allowed to stand a few hours; precipitate collected on a weighed paper; washed with water and alcohol; dried at 100° C., and the BaF_2,SiF_4 weighed.

As 279·5 : 137 : : Wt. of ppt. : x.

The filtrate contains the strontium and calcium. Evaporate with nitric acid in a flask to dryness; cool; add equal volumes of alcohol and ether; close with a cork; allow to stand some time, with occasional shaking, and filter off the insoluble strontium nitrate; wash with alcohol and ether. Re-dissolve the insoluble nitrate in water and estimate the strontium as in § 203.

The filtrate containing the calcium is boiled with hydrochloric acid to remove alcohol, ether, and nitric acid; the solution diluted; neutralised with ammonia, and the calcium estimated as in § 204.

Group VI.

Containing Potassium, Sodium and Ammonium.

§ 208. *Potassium.*

The solution should be concentrated and made slightly acid with hydrochloric acid. If other acids are present the solution must be evaporated to dryness, re-dissolved in water and a little hydrochloric acid. Then add a concentrated solution of platinum chloride in slight excess; evaporate to a small bulk on a water bath; add an equal bulk of alcohol; filter through a tared paper; dry at 100° C., and weigh the $PtCl_4,2KCl$.

487·3 : 78 :: Wt. of ppt. : x.

§ 209. *Sodium.*

Ten grains of pure sodium chloride may be employed for practice. First clean, ignite, and weigh a platinum

crucible and lid; add the 10 grains of salt; place the crucible on a triangular support in an inclined position; partly cover the mouth with the lid; add sufficient sulphuric acid, drop by drop, very cautiously, to convert the salt into sulphate; very gently warm the crucible with a Bunsen flame, beginning at the top; as the fumes diminish, gradually increase the temperature to redness, and maintain at this point for about a quarter of an hour; allow to cool, and weigh the Na_2SO_4. Heat again, cool, and re-weigh. Repeat, if necessary, until the weight is constant.

142 : 46 :: Wt. of ppt. : x.

§ 210. *Ammonium* (NH_4).

The operation is conducted the same as for potassium, $PtCl_4$,2AmCl being precipitated; but all the constituents except platinum are volatile on ignition, so that the amount of ammonium may be calculated from the weight of spongy platinum obtained. 194·3 parts by weight of platinum are associated with 36 parts of ammonium.

§ 211. *Separation of Sodium, Potassium and Ammonium.*

Principles on which the Separations are based :—

Potassium and Ammonium from Sodium by the insolubility of the double chlorides of platinum with potassium and ammonium.

Potassium from Ammonium by the volatility of ammonia and ammonium salts.

§ 212. *Separation of Potassium, Sodium and Ammonium.*

Convert the salts into chlorides, if not already present as such. In case of nitrates, the evaporation must be repeated several times. In presence of phosphates, borates, and sulphates, special methods must be adopted (see Fresenius' *Quantitative Analysis*). The hydrochloric

acid solution must be evaporated and ignited to remove ammonium compounds; re-dissolved in water, and platinum chloride added to precipitate the potassium as ($PtCl_4$, 2KCl); filter, etc., as in § 208; dry at 100° C., and weigh.

§ 213. *Separation of Ammonium from Potassium and Sodium.*

Weigh the total quantity of the mixed salts in a tared platinum crucible; heat gently with the lid on, gradually increasing the temperature to a low, red heat, and maintaining it at that point till the ammonium salt has volatilised. The decrease in weight shows the amount originally present.

Ammonium may be estimated by boiling the substance containing it with sodium hydrate, conducting the evolved ammonia into hydrochloric acid, and estimating as in § 210.

ESTIMATION OF ACIDS.

GROUP I.

Containing Sulphuric, Phosphoric, Boracic and Silicic Acids.

§ 214. *Sulphuric Acid.*

Acidify the solution, if necessary, with hydrochloric acid; heat nearly to boiling, and add barium chloride in sufficient excess; heat for some time, with frequent stirring, until the liquid becomes clear, and proceed as in § 202.

As 233 : 96 : : Wt. of ppt. : the SO_4 present.

§ 215. *Phosphoric Acid.*

Take 5 grains of pure crystallised phosphate of soda for practice ($POHONa_2O_2 + 24OH_2$), and estimate the

P_2O_5 as phospho-molybdate of ammonia. Concentrate the solution by evaporation, if necessary, to a small bulk; make it slightly acid with nitric acid, and add 40 c.c. of the molybdate solution described in § 104*c*. (54 c.c. of this solution are required for 1 grain of P_2O_5.) Shake vigorously till the precipitate is well formed; heat to boiling, and allow to settle in a warm place for a few hours. Test a portion of the supernatant liquid, to ascertain if the precipitation is complete; filter and wash very thoroughly with a solution of ammonium nitrate (containing 14 grammes or 232 grains of salt in 100 c.c. of solution, slightly acidulated with nitric acid, and also containing a little molybdate solution). Now dissolve the phospho-molybdate precipitate in the smallest quantity of ammonia, and wash the filter with dilute ammonia. Add to the solution hydrochloric acid, until the precipitate formed just re-dissolves with difficulty, then add 2 c.c. of the magnesia mixture given in § 104*d*. Shake as before, and allow to stand some time; then add one-third the bulk of ammonia. Allow to stand a few hours; filter; wash with ammonia diluted with three times its bulk of water; dry; raise very cautiously to a strong red heat: cool, and weigh the $Mg_2P_2O_7$.

As 222 : 142 :: Wt. of ppt. : the P_2O_5 present.

Instead of the above double precipitation, the phospho-molybdate precipitate may be washed with dilute nitric acid; filtered; dried at 100° C., and weighed. It contains 1·63 per cent. of P_2O_5. Or the sodium salt could be at once precipitated with magnesia mixture.

§ 216. *Boracic Acid.*

There is no borate sufficiently insoluble to allow the acid to be precipitated in that form, so that this acid is usually estimated by loss.

When no other acid is present, the solution is mixed with a known weight, say 53 grains of pure anhydrous carbonate of soda, which must be sufficient to render it

distinctly alkaline, and evaporated to dryness. The residue is carefully dried, weighed, and the amount of carbonic acid determined. The amount of boracic acid may then be found by deducting the joint weights of the carbonic acid and soda from the weight of the dried residue.

§ 217. *Silica.*

This acid is determined by conversion into the insoluble modification. If the substance under examination is soluble in hydrochloric acid, it is gently heated with that acid till dissolved; then evaporated to dryness, and heated for some time to destroy any organic matter. The residue is well moistened with strong hydrochloric acid, and gently heated; then dilute hydrochloric acid is added, and the whole heated, until all soluble matter is dissolved; the silica is filtered off; well washed with hot water; dried; ignited, and the SiO_2, which must be white, weighed. The ash of the filter may, however, impart a slight colour, if not made of the best paper. The ignition is best performed in a platinum crucible.

If silver or lead be present, then nitric acid must be used instead of hydrochloric.

If the substance be insoluble in acids and other solvents, it must be very finely powdered; mixed with four times its weight of sodium and potassium carbonates, and fused in a platinum crucible (assuming easily reducible metals, as lead, bismuth, etc., to be absent), which should never be more than half full, and the mass kept in fusion for twenty minutes. The crucible is cooled; placed in a beaker, and digested with water at a gentle heat till its contents are dissolved. The crucible is then removed; well swilled, and the liquid very cautiously and gradually diluted with hydrochloric or nitric acid as above; carefully evaporated to dryness, and proceeded with as before.

As 60 : 28 :: Wt. of silica : x = Si.

Separation of Sulphuric, Phosphoric, Boracic and Silicic Acids.

§ 218. *Principles on which the Separations are based :—*

Sulphuric acid from the rest by the insolubility of barium sulphate in hydrochloric acid.

Silica from phosphoric acid by the insolubility of silica in hydrochloric or nitric acid after evaporation and ignition.

Silica from boracic acid by fusing with potassium and sodium carbonates.

Phosphoric from boracic acid, by the insolubility of magnesium pyrophosphate in water and alkalies.

§ 219. *Separation of Sulphuric Acid from the other Members of Group I.*

(*a*) The solution is clear and free from insoluble silica. Add hydrochloric acid, then a solution of barium chloride in excess; heat nearly to boiling; allow to settle, and proceed as in § 202.

(*b*) The substance is insoluble. Fuse with 4 parts of a mixture of sodium and potassium carbonates in a platinum crucible. Boil residue with water; filter. The silica is partly in the residue and partly in the solution. The latter contains nearly the whole of the sulphuric acid, and may be acidified with hydrochloric acid, and the sulphuric acid separated with barium chloride as above. The insoluble residue containing the silica is dissolved with hydrochloric or nitric acid; evaporated to dryness; re-dissolved in hydrochloric acid; any soluble matter filtered off, and barium chloride added to precipitate any sulphuric acid, which is then filtered and added to the main bulk.

§ 220. *Silica from Phosphoric Acid.*

(*a*) The substance is soluble in hydrochloric acid. Evaporate to dryness; treat the residue with acidulated water, and filter off the insoluble silica, which retains a little phosphoric acid. Wash it repeatedly with ammonia, which will remove the phosphoric acid. Evaporate the ammoniacal fluid; add a little hydrochloric acid; dissolve in water with the aid of a little nitric acid; filter off the small amount of silica which was dissolved by ammonia, and estimate the phosphoric acid in the two filtrates as in § 215. The silica as in § 217.

(*b*) The substance is insoluble. Fuse with potassium and sodium carbonates; treat with hydrochloric or nitric acid; evaporate to dryness, and proceed as before.

§ 221. *Silica from Boracic Acid.*

As chloride of boron is somewhat volatile, hydrochloric acid solutions cannot be evaporated for silica when it is desired to estimate the boracic acid. In this case fuse the substance with potassium and sodium carbonates; boil the residue with water; filter off the insoluble portion, which consists of silica, while the fluid contains the boracic acid and some silica; wash residue with boiling water, then with ammonium carbonate. Mix the filtrate with ammonium carbonate and heat, replacing the ammonium carbonate which evaporates. Filter off the precipitated silica and wash with ammonium carbonate. The filtrate from the latter still retains a little silica, which may be separated by adding a solution of zinc oxide in ammonia, evaporating until the ammonia is expelled, and then filtering off the silicate and oxide of zinc. The latter is then dissolved in nitric acid, evaporated to dryness; taken up with nitric acid, and the insoluble silica filtered off. The alkaline filtrate obtained from the zinc oxide precipitate contains the boracic acid. Neutralise with hydrochloric acid; add double

chloride of magnesium and ammonium in such quantity that one part of boracic acid may have at least two parts of magnesia; add ammonia, and evaporate to dryness. If a precipitate is formed with ammonia which does not dissolve on warming, then add ammonium chloride. Finish the evaporation in a platinum dish, adding a few drops of ammonia from time to time. Ignite the dry mass; treat with boiling water; collect the insoluble precipitate on filter, and well wash with boiling water. The filtrate and washings are mixed with ammonia; evaporated to dryness; ignited, and washed with boiling water. The two insoluble residues are ignited together in a platinum crucible for a long time in order to decompose any magnesium chloride. Cool; weigh, and determine the magnesia by dissolving in hydrochloric acid, and precipitating as pyrophosphate of magnesium and ammonium (see § 205)—the difference gives the boracic acid.

Group II.

Containing Hydrochloric, Hydrobromic, Hydriodic, Hydrocyanic Acids and Sulphuretted Hydrogen.

§ 222. *Hydrochloric Acid.*

Add dilute nitric acid; then add a solution of silver nitrate in excess; well stir with a glass rod, and heat nearly to boiling until the precipitate subsides. Allow to stand a few hours in warm place; filter, wash, dry, ignite, and weigh as in § 167.

As 143·5 : 35·5 : : Wt. of ppt. : the Cl present.

Note.—Exposure to light should be avoided, as it changes the composition of the precipitate.

§ 223. *Hydrobromic Acid.*

Precipitate with silver nitrate in presence of nitric acid, and proceed as with hydrochloric acid.

As 188 : 80 : : Wt. of ppt. : the Br present.

§ 224. *Hydriodic Acid.*

Precipitate with silver nitrate, etc., as with hydrochloric acid.

As 235 127 :: Wt. of ppt. : the iodine present.

§ 225. *Hydrocyanic Acid.*

Add to the solution silver nitrate and a little nitric acid; heat for some time with occasional stirring; then add water; heat, and test the clear filtrate with a little silver nitrate. Filter; well wash; dry at 100° C., and weigh. The precipitate should be quite white. Instead of weighing at 100° C. the precipitate may be transferred to a porcelain crucible and ignited till the weight is constant. The residue is metallic silver. When weighed as cyanide at 100° the calculation of the (CN) is as follows:—

As 134 : 26 :: Wt. of ppt. : (CN) present.

If weighed as metallic silver, then:—

As 108 : 26 :: Wt. of Ag : (CN) present.

§ 226. *Hydrosulphuric Acid* (Sulphuretted Hydrogen).

(*a*) *The Acid is in Solution.*—Add an excess of a rather dilute solution of arsenious acid in potash. Slightly acidify with hydrochloric acid; collect the precipitated sulphide of arsenic on a weighed paper; dry at 100° C., and weigh.

As 246 : 96 :: Wt. of ppt. : the S present.

(*b*) *The body is a Solid.*—Pulverise to a fine powder; then place it in a porcelain crucible and add 3 parts pure potassium nitrate, 3 parts dry sodium carbonate, and 4 parts pure dry sodium chloride in fine powder; then mix the whole together with a glass rod. Place the crucible and its contents on a pipe-clay triangle fixed on a tripod stand; cover partially with the lid, and heat gradually at first, and then keep the mass in fusion for some time; allow to cool; transfer to a porcelain dish; add water, and

digest at gentle heat till the mass is dissolved. Remove and wash crucible; filter off any insoluble residue; wash well with boiling water; acidify with hydrochloric acid very gradually; boil, and add a solution of barium chloride in excess. Allow to stand in a warm place until the precipitate has subsided; filter, wash, dry, and ignite the $BaSO_4$.

As 233 : 32 : : Wt. of ppt. : the S present.

Separation of Hydrochloric, Hydrobromic, Hydriodic, Hydrocyanic and Hydrosulphuric Acids.

§ 227. *Principles on which the Separations are based:—*

Hydrosulphuric Acid from the rest by the insolubility of sulphide of arsenic.

Hydrocyanic Acid from Hydrochloric, Hydrobromic and Hydriodic Acids by the decomposition of silver cyanide by sulphuric acid and zinc.

Hydriodic Acid from Hydrochloric and Hydrobromic Acids by the insolubility of palladium iodide.

Hydrochloric Acid from Hydrobromic Acid by the decomposition of silver bromide by chlorine.

§ 228. *Separation of Hydrosulphuric Acid from the other members of Group II.*

Proceed as in § 226*a*. to estimate the sulphuretted hydrogen as sulphide of arsenic. The filtrate contains the other acids.

§ 229. *Separation of Hydrocyanic Acid from Hydrochloric, Hydrobromic and Hydriodic Acids.*

Precipitate the whole with silver nitrate; filter on to a weighed paper; dry at 100° C., and weigh. Heat the precipitate or an aliquot part of it in a porcelain crucible, cautiously agitating the contents till completely fused. Cool; carefully add dilute sulphuric acid to the fused

mass, and then add a piece of pure zinc. Allow to stand some time until reduction is complete; filter and well wash. The filtrate contains the chlorine, iodine and bromine. Dilute if necessary, re-precipitate with silver nitrate, and determine the amount of the mixed chloride, bromide, and iodide of silver. The difference between this and the former weight gives the cyanide of silver.

§ 230. *Separation of Hydriodic Acid from Hydrochloric and Hydrobromic Acids.*

Add a little dilute nitric acid to acidify the solution, and then a solution of palladium nitrate as long as a precipitate forms; let the whole stand for twenty-four hours; filter; wash the dark brown precipitate; dry at 100° C., and weigh the PdI_2.

As 360·2 : 254 :: Wt. of ppt. : the I present.

Or the palladium iodide may be ignited in a current of hydrogen gas and the iodine estimated from the residuary palladium. (See § 191, Fig. 67.)

§ 231. *Separation of Hydrochloric from Hydrobromic Acid.*

Precipitate both acids with silver nitrate; filter and well wash. Transfer to a porcelain crucible; evaporate to remove the liquid present; dry; fuse, and weigh. If the precipitate is bulky take an aliquot part, place in the bulb part of a hard glass bulb tube which has been weighed, and weigh so as to obtain the amount of mixed chloride and bromide present. Now pass a current of dry chlorine gas, gently heating the tube in the meantime, and gradually raise the temperature until the contents of the tube are in fusion, occasionally shaking the tube. In about twenty minutes the whole of the bromine will be volatilised. Cool and expel any free chlorine by a current of air and weigh. Repeat until the weighings are constant.

Then 44·5 : 80 : : difference of weight : the Br. originally present.

§ 232. *Silver iodide* is decomposed by chlorine and bromine.

Silver chloride is converted into bromide by potassium bromide (KBr).

Silver chloride and bromide are converted into iodide by potassium iodide (KI).

Iodine may be removed in the same way, or the iodine precipitate treated with bromine water is converted into bromide. Hydrochloric, hydrobromic, and hydriodic acids may be estimated in admixture by precipitating with silver nitrate, converting the iodide into bromide by bromine water, and subsequent conversion of the bromide into silver chloride by means of chlorine. By multiplying differences of weight by appropriate factors the relative weights can be obtained.

Any two or more can be estimated as follows: Suppose HCl, HBr and HI present; divide solution into a number of equal parts and treat each with silver nitrate. Filter and place one to dry. Take each of the others and treat one with potassium bromide solution, the other with potassium iodide solution; filter, wash, dry, and weigh in each case.

First precipitate = AgCl + AgBr + AgI.

Second precipitate = AgBr + AgI.

Third precipitate = AgI.

Difference of first and second = Br − Cl (*a*).

Difference of second and third = I − Br (*b*).

44·5 : 143·5 : : difference (*a*) : AgCl present in first precipitate.

47 : 188 : : difference (*b*) : AgBr present in second precipitate.

$$\text{Then second ppt.} - \frac{188 \times \text{difference}(b)}{47} = \text{AgI present.}$$

$$\text{And first ppt.} - \frac{143{\cdot}5 \times \text{difference}(a)}{44{\cdot}5} - \text{AgI} = \text{AgBr.}$$

The results are multiplied by number of parts taken.

§ 233. *Estimation of Carbonic Acid.*

When carbonates are heated in presence of stronger acids, carbonic acid is expelled, and by causing the liberated gas to pass by aspiration through a series of U-tubes containing absorbents, its amount may be readily determined.

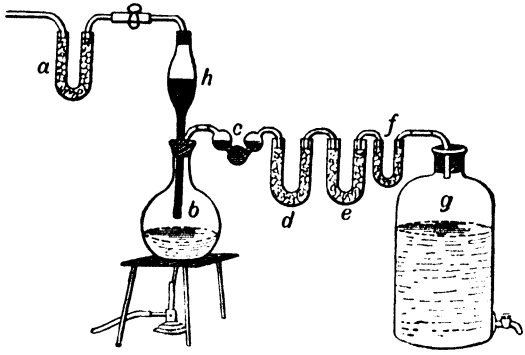


Fig. 69.

The substance to be examined is placed in the flask *b* closed with caoutchouc bung perforated with two holes, into which are inserted the tube *h* containing hydrochloric acid, and the bent tube leading to the drying bulbs *c* containing strong sulphuric acid. The tube *d* is 12 centimetres high and half filled with pumice saturated with copper sulphate solution and heated until all the water has been expelled, its use being to absorb any vapour of hydrochloric acid; the other half is filled with small pieces of calcium chloride. The tube *e* is filled with soda-lime for the absorption of the carbonic acid, and is connected with *f* containing calcium chloride, which prevents any atmospheric moisture passing into the weighed tube *e*.

The actual estimation is carried out as follows: Weigh out 25 grains of the carbonate; place in the flask *b*, and cover with water. Weigh the tube *e* with its contents

and connect up as in Fig. 69. Open the pinch-tap so that a little hydrochloric acid may fall into the flask, adding a little more as the action in the flask diminishes; finally run the whole acid in from the bulb tube *h*; gently heat the flask to boiling; remove the Bunsen burner and open the tap of the aspirator *g* cautiously, so as to aspirate a current of air through the apparatus. Allow the tubes to cool; detach tube *e*, and weigh. The increase in weight indicates the amount of carbonic acid. A set of Mohr's potash bulbs may be used in place of the tube *e*.

§ 233A. Anhydrous carbonates may be determined very accurately by fusing with borax as follows:—

Fuse some borax glass in a weighed platinum crucible; cool and weigh. Then add 15 grains of the well dried carbonate. The amount of borax should be four times as much as the carbonate. Heat gradually to perfect fusion; cool and weigh. The loss gives the amount of carbonic acid in the substance examined.

Instead of fused borax, fused potassium bichromate may be employed in the proportion of 5 parts bichromate to one of the carbonate.

ANALYSIS OF ORES, FLUXES, SLAGS, ALLOYS, ETC.

LEAD ALLOYS.

§ 234. *Plumbers' Solder containing only Lead and Tin.*

Take a piece of solder weighing about 500 grains and roll out very thin, so as to insure greater uniformity of composition. Cut up small, and weigh two portions of 20 grains, or 1 gramme each; place in beakers; add moderately strong nitric acid; cover with a glass plate or clock glass, and digest at a gentle heat till the metal is dissolved and oxide of tin formed. Evaporate to small bulk to remove excess of acid; dilute to about a quarter of a pint with water, and allow the whole to stand in a

warm place for a few hours. Filter; well wash with hot water; dry; ignite the filter paper on the lid of a weighed porcelain crucible; transfer precipitate and ash of paper to crucible, and ignite first with Bunsen burner, finishing with gas blowpipe. Allow to cool in desiccator and weigh the SnO_2; then deduct weight of crucible and ash.

The filtrate contains the lead. Evaporate to a small bulk on sand bath or water oven; add sulphuric acid and alcohol, then proceed as described in § 168.

§ 235. *Pewter, containing Tin, Lead and a little Copper and Antimony.*

Roll out a large piece. Cut up small and weigh two portions of 20 grains each; place in beakers; cover and digest with nitric acid containing an equal bulk of water. The oxide of tin will contain oxide of antimony, the remainder of the antimony being in solution. Expel excess of acid; dilute and allow to stand a few hours. Filter, wash and transfer precipitate to a beaker, then add a saturated solution of oxalic acid in such quantity that the oxalic acid equals twenty times the weight of the tin present. Boil, and pass sulphuretted hydrogen gas through the hot solution till all is precipitated; allow to stand for half an hour in a warm place, and filter the sulphide of antimony. Wash rapidly with water containing sulphuretted hydrogen, and dry. Moisten the precipitate with nitric acid; transfer to a weighed porcelain crucible and add eight to ten times its quantity of fuming nitric acid. Cover with lid, and gradually evaporate the acid; then ignite to form Sb_2O_4 and weigh. (See § 178.) The filtrate from the oxalic acid solution contains the tin. Render the solution slightly alkaline with ammonia; add sufficient ammonium sulphide to re-dissolve the precipitate first formed; then add acetic acid in excess to decompose the sulphosalt and allow the liquid to stand in a warm place until the precipitate

of bisulphide of tin has settled down. Filter; wash with a solution of ammonium acetate containing a small excess of acetic acid to prevent the precipitate passing through the filter. Dry; burn the paper in a weighed porcelain crucible; moisten with nitric acid and ignite. When cold, add the precipitate; cover and heat gently for a time; then remove the lid, and again heat until sulphurous acid has ceased to come off. Allow to cool and heat repeatedly with pieces of ammonium carbonate at a high temperature to expel all sulphuric acid; cool in desiccator and weigh the SnO_2. (See § 177.)

The nitric acid solution from which the oxides of tin and antimony have been removed contains copper, lead, and a little antimony. Evaporate to dryness; re-dissolve in water containing a few drops of nitric acid; filter; wash with very dilute nitric acid; ignite and weigh the Sb_2O_4 with the main precipitate. The filtrate contains lead and copper. Precipitate lead as sulphate, as in § 168. Evaporate the filtrate from the lead sulphate to expel alcohol; dilute, and pass a current of sulphuretted hydrogen to precipitate sulphide of copper. Filter, and treat precipitate as in § 174.

§ 236. *Fusible Alloy containing Tin, Lead and Bismuth.* Take two portions of the finely divided alloy, about 20 grains each. Treat with nitric acid as before to oxidise the tin, and filter off the oxide formed. The filtrate contains lead and bismuth.

The oxide of tin will contain oxide of bismuth. Fuse with 3 parts carbonate of soda and 3 parts sulphur in a covered porcelain crucible. When the excess of sulphur is volatilised, allow to cool and dissolve out the sulphosalt of tin with water, leaving the insoluble sulphide of bismuth. To the solution containing the tin add hydrochloric acid in excess; allow the precipitate to settle; filter, and treat as § 235.

Dissolve the sulphide of bismuth in nitric acid and

add the solution to the filtrate containing the lead and the remainder of the bismuth. Evaporate to a small bulk and add hydrochloric acid to dissolve any precipitated oxide of bismuth. Add sulphuric acid and proceed for lead as in § 168. Add to the filtrate from lead sulphate a large quantity of water, when the basic chloride of bismuth is precipitated. Filter, dry, and fuse in a porcelain crucible with five times its quantity of commercial potassium cyanide. A gentle heat is sufficient, and in about ten minutes the compound will be reduced to the metallic state. Wash rapidly with water, then with weak spirit, and lastly with strong spirit. Dry, and weigh the metallic bismuth.

§ 237. *Shot Metal containing Lead and Arsenic.*

Dissolve two portions of 20 grains each in nitric acid, and separate lead as sulphate. (See § 168.)

Evaporate the filtrate to dryness; re-dissolve in water and a little hydrochloric acid, and estimate the arsenic as in § 179.

COPPER ALLOYS.

§ 238. *Brass and Bronze containing Copper, Zinc, Tin and Lead.*

Take two portions of the alloy, about 20 grains each, and dissolve in nitric acid with an equal bulk of water. When all soluble matter is dissolved, evaporate to a small bulk; dilute to a convenient quantity with hot water, and allow to stand in a warm place for some time for the oxide of tin to settle. Filter; wash with hot water; dry; ignite and weigh the SnO_2.

The solution contains lead, copper, and zinc. Add strong sulphuric acid in excess; evaporate until the sulphuric acid begins to volatilise in order to expel nitric acid, and filter off the precipitated sulphate of lead; wash

with very dilute sulphuric acid, then with alcohol; dry; burn paper in a weighed porcelain crucible; add precipitate; ignite and weigh the $PbSO_4$.

The filtrate contains copper and zinc. Evaporate to dryness; take up with water and hydrochloric acid; boil, and pass a current of sulphuretted hydrogen until the whole of the copper is precipitated as sulphide. Allow the precipitate to settle; filter and wash with water containing sulphuretted hydrogen. For greater accuracy, re-dissolve the CuS and re-precipitate it, adding filtrate to the previous one. Dry; ignite paper in a weighed porcelain crucible; add the precipitate and a little pure flowers of sulphur; cover, and ignite. When cool, weigh the Cu_2S.

The filtrate contains zinc. Evaporate nearly to dryness; dilute; boil and add carbonate of soda cautiously until the solution is strongly alkaline; boil; allow precipitate to subside and decant through filter; add water; boil and again decant, repeating this three times; transfer precipitate to filter; wash; dry; ignite paper in a weighed platinum crucible, then add precipitate; strongly ignite and weigh the ZnO when cool.

§ 239. *Delta Metal containing Copper, Zinc, Tin and Iron.*

Take two portions of the alloy, about 20 grains each, and dissolve in nitric acid. Proceed for tin as in § 238. Filter off the oxide of tin, which may contain a little copper and iron. If a very exact analysis is required the oxide may be fused with 3 parts of sodium carbonate and 3 parts sulphur in a covered porcelain crucible. When the excess of sulphur is volatilised the mass is allowed to cool, and treated with water which dissolves the tin salt, leaving the sulphides of copper and iron undissolved. Sulphide of iron being soluble in hydrochloric acid may be thus separated from sulphide of copper. The solution containing the sulphide of tin is neutralised

by hydrochloric acid, when the sulphide of tin is precipitated. Filter; wash; dry and ignite the paper in a weighed porcelain crucible; then add the precipitate. Heat gently at first, with lid on; then remove the lid, and heat strongly until sulphurous acid ceases to come off. Allow to cool; add some pieces of pure ammonium carbonate and heat strongly to expel the residual sulphuric acid. Repeat this twice; allow to cool, and weigh the SnO_2. (See § 235.)

The nitric acid filtrate from the oxide of tin contains the copper, zinc and iron, except the small traces retained by the oxide of tin. Evaporate to expel nitric acid; add dilute hydrochloric acid and pass a current of sulphuretted hydrogen until all the copper is precipitated as sulphide. Filter; wash; dry; ignite paper in a weighed porcelain crucible; add precipitate together with some pure flowers of sulphur; cover with lid and ignite; allow to cool and weigh the Cu_2S. (See § 238.) The ignition with sulphur should be repeated until a constant weight is obtained Add also the copper sulphide obtained from the tin oxide.

The filtrate from the copper sulphide contains the iron and zinc.

Evaporate to remove sulphuretted hydrogen and excess of acid. Transfer to a flask; dilute, and nearly neutralise with carbonate of soda, or ammonia; add a concentrated solution of ammonium acetate in excess and boil. Allow the precipitate to settle; decant through filter and wash twice by decantation and filtration with boiling water containing a little ammonium acetate. After well washing on the filter, dry and ignite in a platinum crucible. Weigh the Fe_2O_3. A more exact result is obtained by dissolving the above precipitate in hydrochloric acid, and re-precipitating with ammonia, as in § 185.

Evaporate filtrate nearly to dryness, and estimate the zinc, as in brass § 238.

§ 240. *Phosphor Bronze, which may contain Copper, Zinc, Tin, and Phosphorus.*

Take 50 grains of the alloy, and dissolve in nitric acid. The tin and phosphorus are oxidised and, according to Reynoso, the two oxides combine, forming an insoluble compound when the tin is in excess; the other metals remain in solution. Filter; wash and dissolve the tin oxide containing the phosphorus in a small quantity of concentrated potash solution, when the two oxides dissolve as metastannate and potassium phosphate. The solution is then saturated with sulphuretted hydrogen, a small quantity of pentasulphide of ammonium added, and then acetic acid in slight excess. The tin is precipitated as sulphide; filtered and oxidised as before by ignition and the SnO_2 weighed. The phosphoric acid remains in the filtrate. Evaporate to a small bulk and estimate the phosphorus, as in § 215.

The solution containing the copper and zinc is treated for the estimation of those metals, as in the case of brass and bronze.

§ 240A. *Tin Phosphide* (Phosphor-tin).

Weigh out 10 grains or ½ gramme, and place in a large porcelain crucible, which has been previously accurately weighed. Add 5 c.c. of nitric acid and 2 c.c. of water. Cover with a watch glass, and heat gently on water bath till all is oxidised. Carefully evaporate to dryness on water bath and gently ignite the residue over Bunsen flame and finish at a red heat. Cool in a desiccator and weigh quickly to avoid absorption of moisture. The substance consists of stannic oxide SnO_2 and phosphoric acid P_2O_5. The increase in weight of the substance taken gives the weight of oxygen taken up by the phosphorus and tin. Now, 1 grain of tin combines with ·271 grains of oxygen and 1 grain of phosphorus with 1·29 grains of oxygen, so that the proportion of tin and phosphorus can easily be compared. For example, 1

gramme of the sample gave 1·313 grammes of mixed oxides, which is ·042 grammes in excess of that which would be got with pure tin. If the substance were all phosphorus the excess would be 1·02 gramme; therefore the proportion of phosphorus in the substance is ·042 ÷ 1·02 = 4·1 per cent.

The number 1·02 is obtained by deducting the amount of oxide formed from 1 gramme of tin, from the amount of oxide formed from 1 gramme of phosphorus, *i.e.*, 2·29 – 1·27 = 1·02.

§ 240B. *Tin Arsenide* (Arsenical-tin).

An easy method of approximately estimating these metals is based on the same principle as described for phosphor-tin in § 240A. The alloy is dissolved in nitric acid in a weighed porcelain crucible, evaporated, ignited, and the double oxide weighed. 1 grain of arsenic will yield 1·533 grains of arsenic oxide As_2O_5, and 1 grain of tin oxide will yield 1·271; consequently, the excess of weight of the mixed oxides over 1·271 must be divided by ·262, and if 10 grains were taken, the result, multiplied by 10, gives the percentage. This method is not so accurate for arsenical-tin as for phosphor-tin. Care must be taken to weigh quickly so as to avoid absorption of moisture.

§ 241. *Silicon Bronze, which may contain Copper, Zinc, Tin, and Silicon.*

Take two portions, 25 grains each, and dissolve in nitric acid, when tin and silicon are oxidised. Allow to stand some time; filter off the insoluble oxides and well wash. Evaporate the filtrate to dryness; cool and re-dissolve in hydrochloric acid, when any silica will be rendered insoluble and is removed by filtration. The filtrate contains the copper and zinc.

The tin oxide and silica are to be fused in a platinum vessel with four times their weight of carbonates of

potash and soda. (The addition of a little nitre to the fusion mixture will prevent the possibility of any tin oxide being reduced and attacking the crucible.) The fused mass is then dissolved in water and filtered; hydrochloric acid is then added to the filtrate, which is evaporated to dryness, when any soluble silica is rendered insoluble; treat with hydrochloric acid; filter, and wash. The different portions of silica obtained as above are mixed together; strongly ignited in a platinum crucible, and the SiO_2 weighed. Through the acid solution containing the tin, pass a current of sulphuretted hydrogen gas to precipitate sulphide of tin. Filter, wash, dry and ignite, as described in § 235. Weigh the SnO_2.

The solution containing copper and zinc is treated with sulphuretted hydrogen to precipitate the copper, and as the original solution has been evaporated to dryness and re-dissolved in hydrochloric acid, the solution may be boiled, and the gas passed into the boiling solution, which considerably hastens the process. Filter, wash, dry and ignite with sulphur. Weigh the Cu_2S. (See § 238.)

Filtrate contains the zinc; evaporate nearly to dryness and precipitate the zinc with carbonate of soda, as in § 238.

§ 242. *Manganese Bronze, which may contain Copper, Zinc, Tin, Manganese and Iron.*

Take two portions of 25 grains each; dissolve in nitric acid; evaporate to remove excess of acid; dilute; allow to stand some time in a warm place and filter off the oxide of tin which contains some iron, copper, and manganese. Fuse it with 3 parts sodium carbonate and 3 parts pure sulphur in a platinum vessel until the excess of sulphur is volatilised; allow to cool and boil with water, which dissolves the sulpho-salt of tin; filter off the insoluble sulphides of copper, iron, and manganese. Neutralise the filtrate with hydrochloric acid to precipitate sulphide of tin, which is then filtered, ignited and weighed as SnO_2. (See § 235.)

Dissolve the sulphides of copper, iron, and manganese in nitric acid, and add the solution to the main filtrate obtained from filtering the oxide of tin. This solution contains copper, zinc, manganese, and iron.

Evaporate to dryness; re-dissolve in hydrochloric acid; dilute with water; boil and filter off any insoluble silica which may be present. Then pass a current of sulphuretted hydrogen to precipitate sulphide of copper; filter, ignite, etc., and weigh the Cu_2S. (See § 238.)

The filtrate contains iron, manganese, and zinc. Transfer to a flask; boil off the sulphuretted hydrogen; nearly neutralise with carbonate of soda; then add a concentrated solution of sodium acetate, then ammonia in small excess and boil. Allow the precipitate to settle; decant through filter; wash twice by decantation and filtration; transfer all the precipitate to the filter; wash with hot water containing a little acetate; dry; ignite and weigh the Fe_2O_3.

The filtrate contains manganese and zinc. Add excess of acetic acid and pass a current of sulphuretted hydrogen. When the whole of the sulphide of zinc is precipitated, filter, wash and dry the precipitate. Burn the paper in a weighed porcelain crucible, then add the precipitate with some pure flowers of sulphur; cover with lid and ignite. Weigh the ZnS.

If the quantity of zinc sulphide be small, it may be ignited in an open platinum crucible and converted entirely into zinc oxide ZnO.

The filtrate contains the manganese. Evaporate to dryness; re-dissolve in a little strong hydrochloric acid; dilute and neutralise with carbonate of soda; then add a little excess and boil; allow precipitate to settle; test the clear liquid to ascertain if all the manganese is precipitated; then filter, wash, dry and ignite strongly in a platinum crucible. Weigh the Mn_3O_4. (See § 189.)

§ 243. *Aluminium Bronze, which may contain Copper, Tin, Zinc, Iron and Aluminium.*

Take two portions of 25 grains each and dissolve in nitric acid. The tin forms oxide, which must be tested for iron, etc., as in § 242.

The copper is then separated as sulphide.

The filtrate from copper sulphide contains iron, aluminium and zinc. Evaporate to dryness; re-dissolve in hydrochloric acid, using the minimum quantity of acid; dilute and transfer to a flask. Nearly neutralise the acid with sodium carbonate and add a neutral concentrated solution of sodium or ammonium acetate in small excess; boil; allow the precipitate which contains the iron and aluminium to settle; filter, wash, etc., as in the previous example.

The filtrate contains zinc. Precipitate with sulphuretted hydrogen and estimate the zinc as in manganese bronze.

The precipitate containing iron and aluminium should be dissolved in hydrochloric acid in a flask. Neutralise any excess of acid with sodium carbonate; add sodium thiosulphate in sufficient quantity to reduce the ferric salt to ferrous, that is, till the solution is decolourised; then add more thiosulphate and boil until all odour of sulphurous acid has disappeared. The alumina is precipitated as hydrate, thus—

$$Al_2Cl_6 + 3Na_2S_2O_3 + 3H_2O = Al_2H_6O_6 + 6NaCl + 3SO_2 + 3S.$$

Filter; wash; dry; ignite in weighed platinum crucible and weigh the Al_2O_3.

The filtrate contains the iron. Add hydrochloric acid to decompose the sodium thiosulphate; filter off the free sulphur; evaporate to dryness; re-dissolve in hydrochloric acid and precipitate iron with ammonia, as in § 185.

In the case of bronze not containing iron, the above

method is not suitable for separating aluminium from zinc. In such a case adopt the following method.

The filtrate from copper sulphide contains zinc and aluminium. Evaporate to dryness; re-dissolve in hot water; add acetic acid, and pass a current of sulphuretted hydrogen to precipitate zinc sulphide; filter and estimate the zinc as in manganese bronze.

Boil filtrate to remove sulphuretted hydrogen; add ammonia in slight excess. Boil until the odour of ammonia is barely perceptible; wash two or three times by decantation; filter, wash, dry and ignite the alumina in a platinum crucible and weigh the Al_2O_3.

NICKEL AND COBALT ALLOYS.

§ 244. *German Silver, containing Copper, Zinc and Nickel.*

Dissolve 20 grains of the alloy in nitric acid, using the smallest possible quantity of acid. Evaporate to expel excess of nitric acid; re-dissolve in dilute hydrochloric acid; dilute with water; boil and pass a current of sulphuretted hydrogen until all the copper sulphide is precipitated. Allow to settle; filter; wash; burn paper in a weighed porcelain crucible; then add the precipitate together with some pure flowers of sulphur; ignite with lid on and weigh the Cu_2S. This should be repeated until two consecutive weighings are constant.

The filtrate contains nickel and zinc. Boil till all sulphuretted hydrogen is expelled, and the solution is reduced to a small bulk; add sodium carbonate until all is precipitated, then add acetic acid until the precipitate is re-dissolved. Pass a current of sulphuretted hydrogen until the zinc is precipitated as sulphide; then add a few drops of very dilute sodium acetate and pass the gas again for a short time. Allow the solution to stand

some time in a warm place; filter; wash with water containing sulphuretted hydrogen; dry; cautiously ignite in a covered crucible with some flowers of sulphur and weigh the ZnS. If the precipitate is not white, re-dissolve and re-precipitate.

The filtrate contains the nickel. Evaporate to small bulk to remove sulphuretted hydrogen; dilute if necessary and add a strong solution of sodium hydrate in excess. Heat near to boiling for some time; allow precipitate to settle; filter; wash with hot water; dry and ignite in a weighed platinum crucible. Weigh the NiO.

§ 245. *German Silver, containing Cobalt and Iron, in addition to Copper, Zinc and Nickel.*

Dissolve 25 grains in nitric acid as usual. Precipitate copper as sulphide; filter and weigh the Cu_2S. (See § 238.)

Filtrate contains iron, nickel, cobalt, and zinc. Boil to expel sulphuretted hydrogen; dilute with water and add ammonium chloride in large excess (20 of AmCl to 1 of NiO, CoO, etc.), then ammonium carbonate till just neutral without any iron being permanently precipitated; then heat slowly to boiling and keep boiling for a short time after the carbonic acid has been expelled. The iron is precipitated as a basic salt, which rapidly settles if the solution is sufficiently dilute. Pour liquid through a filter and wash two or three times by decantation; then transfer precipitate to filter; wash with boiling water containing a little ammonium chloride. Re-dissolve the precipitate in hydrochloric acid; precipitate with ammonia; filter; wash; dry; ignite and weigh the Fe_2O_3 in a platinum crucible (See § 185.)

The filtrate contains zinc, nickel, and cobalt. Evaporate to dryness; re-dissolve in hydrochloric acid; dilute and neutralise with sodium carbonate, re-dissolving any precipitate which permanently forms with a few drops of hydrochloric acid and precipitate sulphide of zinc

with sulphuretted hydrogen as in last example. Weigh the ZnS.

The filtrate contains nickel and cobalt. Evaporate to a small bulk and add a concentrated solution of potassium nitrite (previously neutralised with acetic acid, and filtered from any silica and alumina which may have separated) in excess; then add acetic acid till the solution is acid; allow to stand several hours in a warm place. Test again with the nitrite to ascertain whether the whole of the cobalt is precipitated. Filter; wash with a dilute solution of potassium acetate containing some nitrite. Dissolve in hydrochloric acid; precipitate with potassium hydrate, and estimate cobalt as described in § 191.

The filtrate from the first cobalt precipitate contains the nickel. Boil with excess of hydrochloric acid; then precipitate the nickel with potash or soda and estimate as in § 190.

It is better to re-dissolve in hydrochloric acid, precipitate with ammonium sulphide and then convert into oxide as above.

Another method due to Liebig for separating nickel and cobalt and estimating the amount of each present, is described in § 200.

ASSAY OF NICKEL AND COBALT ORES.

§ 246. The ore should be examined to get some idea of the amount of arsenic, nickel and cobalt present. The arsenic may be roughly estimated by roasting a portion, and observing whether arsenic readily sublimes; the nickel and cobalt by the depth of the blue or green colour on solution in aqua regia.

Take 20 to 50 grains of the ore, according to its richness, and roast in a scorifier, to expel excess of sulphur

and arsenic. Transfer to a porcelain dish; add hydrochloric and a little nitric acid and heat until the soluble matter is dissolved, adding nitric acid from time to time. Dilute; allow to settle; decant clear liquid and wash the residue once or twice by decantation. Evaporate remainder to dryness and ignite to burn off globules of sulphur; again digest with nitric acid; dilute; filter and add the filtrate to the main bulk of decanted solution.

Nearly neutralise with ammonium carbonate; add excess of sodium acetate and boil, when the iron, arsenic, alumina and any phosphoric acid will be precipitated. Allow to settle; wash twice by decantation; then filter and well wash. (The washing of this precipitate is very tedious, owing to its slimy character; but the addition of a little sodium sulphate greatly facilitates the operation.)

Pass a current of sulphuretted hydrogen through the filtrate, till the nickel and cobalt are completely precipitated. Allow to settle; filter; well wash and cautiously re-dissolve the precipitate in nitric acid. Dilute; cool and pass a current of sulphuretted hydrogen to precipitate any metals of the copper group. Filter; wash and treat the filtrate, which contains nickel and cobalt, as in § 200 or 245. Should the ore contain zinc, that metal will be precipitated as sulphide along with the sulphides of nickel and cobalt. Dissolve precipitate in nitric acid; evaporate to small bulk and add a large quantity of ammonium chloride (5 grammes to 0·2 grammes of zinc); evaporate, and heat until all the ammonium chloride is removed and with it the zinc. Re-dissolve residue in hydrochloric acid, with the aid of a little nitric acid; boil off excess of acid and proceed for separation of nickel and cobalt.

When much nickel and little cobalt are present, estimate as cobaltio-potassium-nitrite. (See § 245.) If, on the contrary, there is much cobalt and little nickel, treat as in § 200.

§ 247. *Nickel-glance.*

Take 20 grains of the finely powdered mineral and fuse with 80 parts sodium carbonate and an equal bulk of sulphur. Allow to cool and digest with boiling water, which dissolves arsenic and antimony compounds; filter and well wash the residual metallic sulphides. Ignite filter paper; add residue; digest with fuming nitric acid and evaporate to dryness. Re-dissolve in hydrochloric acid and pass a current of sulphuretted hydrogen to precipitate copper and lead. Filter; wash; add crystals of potassium chlorate and evaporate filtrate to small bulk. Dilute with much water; nearly neutralise with ammonium carbonate; precipitate iron by sodium acetate and proceed as in the previous method. As the iron precipitate may retain some nickel, re-dissolve and re-precipitate; add the two filtrates together and evaporate to a small bulk. Boil and add sodium hydrate to precipitate the nickel as in § 190.

§ 248. *Cobalt Speise, containing Nickel, Cobalt, Arsenic, Sulphur and Silica.*

(*a*) *Estimation of Arsenic.*—After crushing, sampling, and passing through a sieve with 80 holes to the inch, take 10 to 15 grains to determine the arsenic. Boil in a large flask with concentrated nitric acid till no further action takes place. Dilute the solution with water; filter; mix filtrate with excess of ammonia and digest with colourless ammonium sulphide at a moderate heat for some time to obtain the whole of the arsenic in solution. Filter and wash precipitate with ammonium sulphide. (If yellow ammonium sulphide were used, some nickel sulphide might be dissolved.) The filtrate which contains the arsenic is decomposed with a slight excess of acetic acid, the solution being digested at a gentle heat until the odour of sulphuretted hydrogen has disappeared. The precipitated As_2S_3 is then collected on a weighed

filter; well washed with water; dried at 100° C., and weighed.

As this precipitate contains free sulphur, transfer to a flask; add a little nitric acid and after the violence of the action is over, heat until the precipitate has dissolved. Dilute and collect any globules of sulphur on a weighed filter paper; well wash; dry at 100° C., and weigh. Boil the solution and add barium sulphate until all the sulphuric acid is precipitated; filter; wash; dry; ignite and weigh the $BaSO_4$. The total amount of sulphur associated with the arsenic in the weighed arsenic precipitate being thus ascertained, the quantity of arsenic is obtained by the difference in weight.

(*b*) *Estimation of the Sulphur.*—Take 10 to 15 grains of the ore and digest; add water, then bromine (15 parts by weight of bromine being required for 1 part of sulphur), with constant stirring, so that the action may not be too violent.

When all the sulphur has been oxidised, evaporate to dryness to render any silica insoluble; take up with hydrochloric acid and water; dilute; boil and precipitate the sulphuric acid with barium chloride. Filter; wash; dry; ignite and weigh the $BaSO_4$. (See § 202.) From this precipitate the sulphur is computed.

(*c*) The nickel cobalt and iron may be separated and estimated by the method given in § 246 or that in § 245.

WET ASSAY OF ZINC IN ORES AND SLAGS.

§ 249. These substances are conveniently classified into oxides, silicates, and sulphides. The foreign metals with which zinc is likely to be associated are iron, lead and manganese, and sometimes copper and cadmium.

§ 250. (1) *Oxidised Ores free from Silica.*

Take 25 grains of the properly sampled and finely sifted ore; place in a conical beaker; add sufficient nitric acid and digest at a gentle heat for about half an hour, or until all soluble matter is dissolved. Evaporate just to dryness; allow to cool and then digest with a little dilute nitric acid for fifteen minutes; dilute with water and filter off the insoluble residue. If cadmium, copper, or lead be present, pass a current of sulphuretted hydrogen to precipitate these metals as sulphides; allow to stand some time and filter. Boil till all sulphuretted hydrogen is expelled and the solution is reduced to a small bulk; then add an excess of solution of ammonia; gently warm; allow the precipitate to settle and filter off the iron oxide; well wash with water containing ammonia and lastly with hot water. To the filtrate, which contains zinc and manganese, add acetic acid in excess and then pass a current of sulphuretted hydrogen, which precipitates the white zinc sulphide, leaving the manganese in solution. Add a little very dilute solution of sodium acetate and then pass the gas again for some time, then allow to stand a few hours; filter; wash with water containing sulphuretted hydrogen; dry the zinc precipitate, then transfer to a weighed porcelain crucible; add a little pure sulphur and ignite in a current of hydrogen. Weigh the ZnS obtained. Zinc sulphide, being of a light slimy nature, is difficult to wash thoroughly. Mr. J. H. Talbot has overcome this difficulty by neutralising the solution of zinc with ammonium carbonate; boiling and adding ammonium sulphide in sufficient quantity to precipitate the zinc. The zinc sulphide on boiling becomes granular, readily settles, and may be easily washed.

Zinc sulphide may also be converted into oxide for weighing by prolonged ignition in a porcelain crucible, the last traces of sulphuric acid being removed by drop-

ping in pieces of ammonium carbonate and afterwards strongly igniting. Weigh the ZnO.

§ 251. (2) *Silicates (Slags and Ores).*

Take 25 grains of the finely powdered sample and dissolve in strong hydrochloric acid, to which a little nitric acid has been added. When the whole is decomposed, evaporate to dryness; take up with hydrochloric acid; dilute; filter off insoluble residue and proceed as in former method.

§ 252. (3) *Sulphides (Zinc Blende, etc.).*

Take 25 grains of finely sifted ore, place in a muffle and roast until all odour of sulphur dioxide ceases; then digest in a conical beaker with hydrochloric and nitric acids and proceed as in § 250.

See also Methods for Zinc in Volumetric Analysis.

WET ASSAY OF COPPER IN ORES AND SLAGS.

§ 253. The simplest of all methods for estimating copper, although by no means the quickest and most exact, is to precipitate it from its solution by means of metallic iron or zinc. This method is not applicable to ores containing more than small quantities of arsenic.

If the ore be a sulphide or pyrites, it will be advantageous to roast it first to remove sulphur and other volatile matters and convert the metals into oxides.

Take 50 to 100 grains of the finely sifted ore, according to its richness in copper; place in a porcelain dish and roast at a low temperature at first in a muffle, occasionally stirring with a platinum wire, and as the operation proceeds gradually increase the temperature until no more odour of sulphur dioxide is perceived. Allow to cool; grind in an agate mortar; transfer to

dish and cautiously add nitric acid; cover with a clock glass and gently heat; then add hydrochloric acid and gently boil for some time till the ore is completely decomposed. Evaporate to dryness with the usual precautions; then allow to cool and add a little hydrochloric acid, heat gently; then add water; well wash down the sides and carefully boil till all soluble matter is dissolved. Filter off the residue; allow the filtrate to run into a beaker and well wash with hot water.

Now lower into the solution a strip of bright and perfectly clean wrought iron attached to a platinum wire; cover the beaker with a clock glass and keep the liquid just boiling until the whole of the copper is precipitated. The iron must be completely covered with the solution or some of the metal may become oxidised and vitiate the result. The completion of the process may be ascertained by taking a drop of the liquid and testing whether a blue tint is imparted by adding excess of ammonia.

When the whole of the copper is thrown down, carefully clean the iron with a feather; allow all flakes of copper to settle down, and syphon off the clear liquid. Wash several times with hot water; decant; dry in water oven, or on a hot iron plate, at such a temperature that the copper may not be oxidised. When dry, brush the precipitated copper on to a weighed watch glass and weigh.

If lead be present in quantity, it must previously be removed by adding sulphuric acid and filtering off the lead sulphate which is precipitated.

A more correct result may be obtained by re-dissolving the copper in nitric acid; evaporating to dryness, and igniting to obtain oxide, CuO; then weigh and calculate the amount of copper present from the above formula.

A still better plan would be to estimate the copper by means of a standard solution of potassium cyanide. (See Volumetric Analysis, § 352.)

§ 254. Copper may be very accurately estimated as sulphide. Take from 25 to 50 grains of the ore according to its richness in copper. In case of oxides, digest with hydrochloric acid; then add a little nitric acid and continue the digestion till the compound is decomposed. In case of sulphides, moisten with strong sulphuric acid; add nitric acid, and gently boil for about an hour, adding fresh nitric acid from time to time as required. Dilute and again boil for a short time.

Instead of dissolving sulphides direct, the ore may be roasted and then dissolved in nitric acid, as in the previous method. When the ore is decomposed, evaporate to dryness, take up with hydrochloric acid and water as before; filter off the insoluble residue; allow the filtrate to run into a beaker; well wash the residue; boil the solution, and pass a current of sulphuretted hydrogen through it until the whole of the copper is precipitated as sulphide. Filter, wash, dry and ignite with sulphur in a weighed porcelain crucible. (See § 174.)

Lead, if present, must be removed previous to the precipitation of the copper by adding sulphuric acid, if that acid has not been employed to effect the solution of the ore.

The two methods previously described take up a considerable amount of time, so that a more rapid plan of assaying was deemed advisable by the directors of the Mansfeld Copper Works, who offered a prize in 1867 for the discovery of a process which could be completed in a few hours and yield good results. The two following were considered the most important:—

§ 255. *Steinbeck's Process.*

Take about 50 grains of finely sifted ore, and if much sulphur and bitumen be present, roast previous to dissolving. Place the ore in a conical beaker; add 40 c.c. of hydrochloric acid, and when the action has ceased

add 5 c.c. of strong nitric acid diluted with an equal bulk of water. If the ore has been roasted, then 1 c.c. of nitric acid is sufficient. Digest for an hour at a gentle heat, then boil for a quarter of an hour, when the whole of the copper should be dissolved and the nitrous fumes driven off. Now filter the solution into a beaker in which has been placed a strip of platinum foil, and on this a bar of zinc free from lead weighing about 120 grains. In about three quarters of an hour the copper will be completely deposited; remove excess of zinc; well wash precipitate by decantation; re-dissolve the copper in 9 c.c. hydrochloric and 1 c.c. nitric acids; allow to cool; add 10 c.c. of a mixture of one part strong ammonia and two parts water, and titrate with a standard solution of potassium cyanide, 10 c.c. of which indicate one per cent. of copper. (See Volumetric Analysis, § 352.)

§ 256. *Luckow's Process.*

This experimentalist discovered that even a weak voltaic current could completely precipitate copper from nitric acid solutions containing less than 1½ grains of the anhydrous acid in each c.c. of the liquid (nitric acid of 1·2 sp. gr. contains 4·9 grains of anhydrous acid per c.c.), and that the action is less dependent on the strength of the current than when free sulphuric acid is present. Zinc, iron, nickel, cobalt, chromium, the earthy, alkaline-earthy and alkaline metals are not precipitated in a nitric acid solution. Lead and manganese are precipitated at the positive pole as peroxides, silver partially; easily oxidisable substances retard the precipitation at the negative pole. Mercury, silver, copper and bismuth are deposited in the reguline form, the mercury forming an amalgam with the copper. Arsenic and antimonic acids do not yield up their metals until some time after the precipitation of the copper.

For an assay by this method take 25 grains of the

finely divided ore and roast sweet in a porcelain crucible, then transfer to a beaker; add 2 or 3 c.c. of nitric acid and with this mix a few drops of sulphuric acid; cover with a clock glass and heat on sand bath until the sulphuric acid is expelled, at last strongly, adding nitric acid as required. A little hydrochloric acid is an advantage and necessary when silver is present. This operation takes about an hour and a half. Allow to cool; swill down with nitric acid 1 : 6; add a little tartaric acid, or if much iron is present add oxalic acid instead, and allow the residue to settle.

The copper is then precipitated by a voltaic current

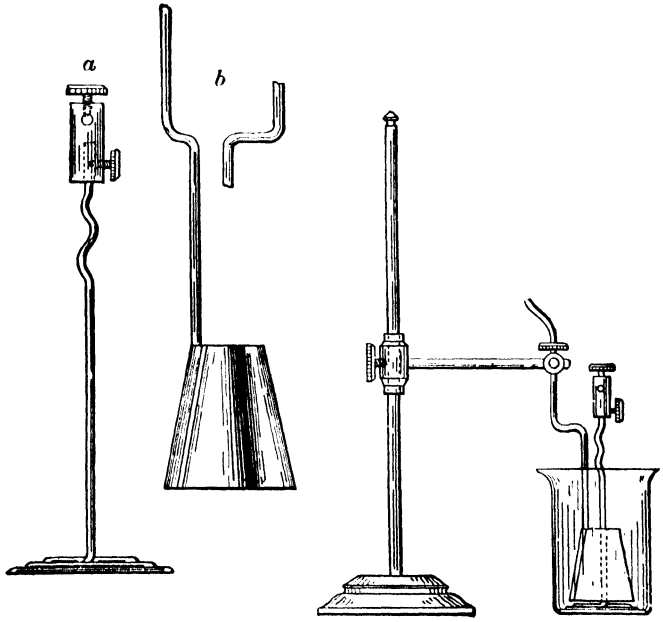


Fig. 70 *a*, *b*, *c*.

passing through the solution by means of platinum terminals. The positive pole consists of a platinum wire

(Fig. 70*a*) about $\frac{1}{12}$th of an inch thick and $7\frac{1}{2}$ inches long, $\frac{2}{3}$rds of its length being coiled into a flat spiral, and its upper extremity fixed in a binding screw. If the insoluble matter does not readily settle down, but causes the liquid to remain turbid, add 1 c.c. barium nitrate; well mix contents and allow to settle. The negative electrode, which consists of platinum foil in form of a cone or cylinder $2\frac{1}{2}$ inches long and $1\frac{1}{4}$ inches diameter (Fig. 70*b*) is then weighed and inserted in the liquid. This must not by any means be allowed to touch the spiral, or the current will cease to pass through the liquid. The cylinder or cone is immersed in the solution about three quarters of its length. The disposition of the apparatus is seen in Fig. 70*c*. Soon after the circuit has been closed the platinum cylinder or cone becomes covered with copper, while bubbles of hydrogen gas escape from the spiral, and assist in reducing any oxide of copper not dissolved and causing it to pass into solution. The strength and amount of the current is regulated according to the amount of copper supposed to be present and the requisite number of cells attached accordingly. The operation lasts from three to eight hours, but in order to make the process exact all test assays are left for eight hours. The termination may be ascertained by immersing the cone or cylinder lower in the liquid after adding a little dilute nitric acid, and observing whether any deposition takes place on the clean part.

When complete, the cone or cylinder is removed; well rinsed in cold water; then washed with alcohol from a wash bottle; dried at 100° C., and weighed. The increase of weight gives the amount of copper deposited.

§ 257. *Estimation of Copper in Cupriferous Iron Pyrites.* Take 50 to 100 grains of ore, roast in a porcelain dish placed in a muffle till sweet, *i.e.*, until the sulphur is burnt off; allow to cool; moisten with sulphuric acid; add nitric acid; cover with a clock glass and boil gently for

an hour, adding fresh nitric acid from time to time if necessary. When all action ceases, add a little hydrochloric acid; dilute with boiling water and filter off the insoluble silica and any silver chloride, allowing the filtrate and washings to run into a pint beaker; dilute with water until the beaker is one third full; add sufficient ammonia to precipitate the iron; boil; filter; and well wash with water containing ammonia, allowing the filtrate to run into a 30 ounce flask, which should be about half full. Cool down to 20° C., testing the temperature with a thermometer; then run in from a burette a standard solution of potassium cyanide until a faint lilac tint is left. From the amount of cyanide required the percentage of copper in the sample under examination may be calculated. For full particulars see "Volumetric Analysis of Copper," § 352.

If zinc, nickel, or cobalt be present, precipitate the copper (in the solution obtained from filtering off the silica and silver chloride), by a current of sulphuretted hydrogen; filter off the sulphide of copper; well wash with water containing sulphuretted hydrogen; dissolve the precipitate in dilute nitric acid; dilute with water; add ammonia until the solution is blue, and proceed as before with the standard solution of potassium cyanide.

§ 258. *Estimation of Sulphur in Burnt Pyrites, Purple Ore, etc.*

Take a quantity of the substance, say $\frac{1}{2}$ lb., crush very fine and pass through a sieve containing 80 meshes to the linear inch. From this sample weigh out 50 grains; place in porcelain dish; add a mixture consisting of 3 parts strong nitric acid and 1 part hydrochloric; boil gently till dissolved (about one hour being required); then add hydrochloric acid until nitrous fumes cease to be evolved and evaporate to complete dryness. When sufficiently cool, moisten with strong hydrochloric acid; allow to stand for an hour; dilute with water; wash down sides

of dish and bottom of glass cover; boil gently for some time and filter off any residue, allowing the filtrate to run into a pint beaker. Dilute considerably; heat to near boiling; add barium chloride in moderate excess; stir well for a few minutes and allow to settle. Decant clear liquid through a filter; wash precipitate by decantation with boiling water two or three times; transfer precipitate to the filter; wash with boiling water; dry; burn paper; ignite precipitate at a moderate red heat and weigh the $BaSO_4$.

The weight of precipitate, after deducting filter ash, multiplied by ·13734 gives the sulphur, and as 50 grains were taken, the product multiplied by 2 gives the percentage of sulphur in the sample taken.

§ 259. *Estimation of Arsenic in Copper Precipitate, Cake and Ingot Copper, etc.*

200 grains of the finely divided sample is taken for assay. Place in a large beaker; dissolve in the minimum quantity of nitric acid; evaporate to remove excess of acid; dilute largely with water; then add ammonia in excess and pass a current of sulphuretted hydrogen through the liquid until all the copper is precipitated. Allow to settle; filter; well wash with very dilute ammonia water, then with hot water.

To filtrate add hydrochloric acid in excess and allow to stand several hours. Filter and wash residue into a small flask; then add 1 oz. of nitric acid; evaporate nearly to dryness; add a little tartaric acid to keep any antimony in solution; break up any separated sulphur; filter, and well wash with hot water.

To the filtrate add 1 oz. of ammonia, 1 oz. of ammonic chloride and ½ oz. of the magnesia mixture described below. Allow to stand twelve hours, when the arsenic will be precipitated as $2(Mg,NH_4,AsO_4)+OH_2$; filter through a weighed paper previously dried at 100° C.; wash with dilute ammonia; dry in water oven at

100° C., and weigh. Deduct weight of filter paper, multiply by ·394, and divide the product by 2 to obtain the percentage of arsenic present.

Magnesia Mixture—5 ozs. magnesium sulphate and 5 ozs. ammonium chloride are dissolved in 2 pints water; then 1 pint of ammonia is added, allowed to stand a few days and liquid filtered off for use.

§ 260. *Estimation of Silver and Gold in Copper Chloride Liquors.*

Take 1 pint of the copper liquor obtained by roasting burnt pyrites with rock salt and dissolving the product in brine; add ¼ oz. of sodium iodide or zinc iodide (solution of 2 ozs. NaI dissolved in 20 ozs. of water) and 4 ozs. of a solution of lead acetate (solution of 1 lb. lead acetate in 40 ozs. of water); allow to stand for half an hour; filter; dry and place the precipitate with the paper in a clay crucible with the following mixture—

4 parts carbonate of soda.
1 part common salt.
1 ,, borax.
1 ,, argol.

Place in a moderately hot furnace and heat for about twenty minutes, when the mass should be in tranquil fusion. Pour into a suitable mould (semicircular is best); allow to cool; tap away the slag and cupel the button of lead as explained in the dry silver assay. The weight of the bead obtained multiplied by 8 gives the amount of silver and gold per gallon.

To separate the silver and gold in the cupelled bead, boil with nitric acid. (See parting of Silver and Gold, § 136, *e.*)

WET ASSAY OF MERCURY IN ORES, ETC.

§ 261. Take a convenient quantity according to the richness of the ore, say 25 grains, which must previously be very finely powdered and sifted. Assuming the ore to be cinnabar (which is usually associated with limestone, clay, and ironstone), digest for some time with hydrochloric acid to decompose the carbonates of lime and iron; allow to settle; decant the clear liquid; wash two or three times by decantation and digest the residue, which contains the mercury, with aqua regia to dissolve the mercury compound. Evaporate until the greater part of the free acid is removed; dilute; then add a solution of sulphurous acid and heat to convert any ferric oxide to the ferrous condition. Pass a current of sulphuretted hydrogen until the whole of the mercury sulphide is precipitated; filter on to a weighed filter; dry at 100° C., and weigh, using precautions as given in § 169.

§ 262. *Assay of Mercury in Amalgams.*

Mercury may be readily separated from its combinations with other metals, except antimony and arsenic, by volatilisation at a low temperature, and the mercury determined by the loss of weight. In the case of oxidisable metals the volatilisation must be effected in a current of hydrogen gas.

10 to 20 grains of the amalgam are placed in a weighed porcelain crucible (Fig. 67), having a hole through the cover, in which a porcelain tube is fixed to convey the perfectly dry hydrogen. Put the crucible on a pipe-clay triangle, and heat gently from beneath with a Bunsen's burner until mercurial vapours cease to come off. Allow the residual metal to cool in a current of hydrogen and weigh.

Mercury may be separated from antimony and arsenic by precipitating the mercury with yellow ammonic sulphide, the antimony sulphide being soluble in that liquid.

If excess of nitric acid is used oxide of iridium is deposited on evaporation. Evaporate to a syrupy condition allow to cool; heat with hot water until all soluble matter is dissolved and carefully decant off the liquid.

The distillate, containing some chloride of platinum which has spurted over, is poured upon the residue, and again distilled without boiling, whereupon a colourless distillate of dilute osmic acid is obtained.

(*b*) Separation of the other metals. The separation is based—first, on the insolubility of the double chlorides of platinum and ammonium, and the corresponding salts of iridium, osmium, and ruthenium in ammonium chloride; secondly, on the solubility of chloriridite of ammonium, and the corresponding rhodium salt in ammonium chloride solution; and, thirdly, on the convertibility of chloriridate of ammonium into chloriridite by sulphuretted hydrogen.

The solution containing the platinum, etc., after being separated from the residue is evaporated to dryness, and heated on a sand bath for some time from 140° to 150°, in order to convert the tetrachloride of iridium into trichloride. A small quantity of hydrochloric acid is then added; the whole dissolved in water; then mixed with a strong solution of ammonium chloride; the resulting precipitate of ($PtCl_4$, $2NH_4Cl$) collected on a weighed filter; washed with a dilute solution of ammonium chloride, then with alcohol; then dried at 100° C., and weighed. This precipitate may contain a trace of iridium, which may be removed by dissolving in aqua regia containing an excess of nitric acid; when the iridium is left undissolved, and may be calcined with the filter, reduced by hydrogen, weighed, and its weight deducted; or the platinum in the filtrate may be re-precipitated with ammonium chloride, and again weighed.

§ 274. Deville and Debray assay platinum ores by treating with aqua regia; evaporating the solution to dryness; then treating the residue with a small quantity of water, in which it should completely dissolve; then with twice the volume of alcohol; a large excess of pure crystallised sal-ammoniac is then added; the liquid warmed until the salt is nearly dissolved; then stirred and left at rest for twenty-four hours. The resulting precipitate containing the platinum and part of the iridium is collected on a filter washed with alcohol of 75 per cent.; dried; ignited at the lowest possible temperature, strips of paper moistened with oil of turpentine being repeatedly thrown into the crucible after the filter has been burned, in order to reduce the oxide of iridium and expel the last traces of osmium; and finally heated to whiteness until the weight comes constant. The mixture of platinum and iridium is then digested with aqua regia; diluted with four times its bulk of water at 40 to 50°, the liquid being renewed from time to time till it no longer becomes coloured; the undissolved portion is pure iridium. The decanted liquid which contains platinum and iridium is evaporated, till a great part of the sal-ammoniac has crystallised out, and filtered when cold; it then deposits a small additional quantity of platiniferous chloriridite of ammonium, which is washed with a solution of sal-ammoniac, then with alcohol, and treated as above with aqua regia to remove the last traces of iridium from the platinum.

ANALYSIS OF LIMESTONE OR DOLOMITE AND CLAY.

§ 275. These substances may contain lime, magnesia, oxide of iron, oxide of manganese, clay, sand, and water.

(*a*) *Determination of Water.*

Take 100 grains of the finely-powdered material and heat at a temperature below redness in a porcelain crucible for ten minutes. If the powder blackens, it indicates the presence of organic matter and the heat must be continued until the dark colour has disappeared. Allow crucible to cool; moisten the contents with a saturated solution of ammonium carbonate to re-convert any caustic lime again into carbonate; heat again at a low temperature until the weight remains constant. Should the residue, however, when moistened with water exhibit an alkaline re-action, the treatment with ammonium carbonate must be repeated. This method is not perfectly accurate, as some carbonic acid may be expelled from the carbonates of iron and manganese, and loss may occur from the volatilisation of organic volatile matter. (See Analysis of Iron Ores.)

(*b*) *Determination of Carbonic Acid.*

This may be effected by the method given in § 233, or by means of Schrötter's apparatus (Fig. 72). The mineral, acid, and apparatus are weighed before and after the experiment. The loss of carbonic acid is indicated by the difference of the two weighings. 20 grains of the mineral are placed in (*d*), a quantity of strong sulphuric acid in (*b*), and dilute sulphuric acid in (*a*), and the whole weighed. The tap (*c*) is now turned slightly, and a portion of the acid sucked into (*d*) by means of an india-rubber pipe connected to (*b*), the tap is then turned off again. The acid acts on the carbonate, liberating carbonic acid, which passes up the central portion of the tube (*b*), thence through the sulphuric acid, as shown by the arrows; this absorbs any water vapour. As the effervescence ceases, fresh acid is introduced from (*a*) until the whole is run in. The bottom of the bulb (*d*) is then gently heated over a

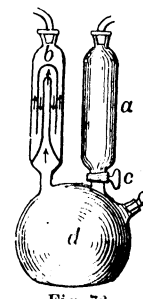


Fig. 72

water bath and the contents shaken. When the action appears complete, as shown by the absence of bubbles, open the tap (*c*) and suck a current of air through by means of india-rubber tube; wipe the apparatus and weigh. The loss gives the CO_2, and this multiplied by five gives the percentage, as 20 grains were taken.

(*c*) *Estimation of the Clay, Sand, Lime, Magnesia and Iron.*

Place 100 grains of the limestone in a large beaker; cover with distilled water and cautiously add dilute hydrochloric acid in small portions at a time until effervescence ceases; heat on sand bath till all soluble matter is dissolved; filter; well wash until the water is no longer acid; dry; burn the paper in a weighed platinum crucible; add the residue; well ignite and weigh. After deducting the ash, the remainder gives the amount of sand and clay present in the limestone. Reserve this for further examination.

The filtrate must now be evaporated, a few drops of nitric acid or crystals of potassium chlorate being added to oxidise the iron; take down to dryness; moisten with strong hydrochloric acid; allow to stand for an hour in warm place; add water; boil and filter off silica; well wash; dry; ignite and weigh the SiO_2.

The filtrate and washings contain iron, lime, and magnesia. Concentrate by evaporation; add ammonium chloride; then ammonia in slight excess; boil; allow to settle; filter; wash; dry; ignite and weigh the oxide of iron Fe_2O_3, which may contain small quantities of alumina and oxide of manganese. When much magnesia is present, it is very liable to be carried down with the iron, in which case the precipitate should be redissolved in hydrochloric acid; a quantity of ammonium chloride added and the iron re-precipitated with ammonia, the filtrate being mixed with the former one.

Test filtrate with ammonium sulphide for manganese,

and separate it if present. Boil off sulphuretted hydrogen; add ammonium chloride in excess; make alkaline with ammonia; then add ammonium oxalate in sufficient quantity to precipitate the calcium as oxalate; heat till the precipitate has subsided; pour the clear liquid on to a filter; wash once or twice by decantation; then wash precipitate on to filter; dry; burn paper and very gently ignite precipitate in a weighed porcelain crucible. Now add a little solid pure carbonate of ammonia; moisten with water; dry and heat to faint redness; cool in desiccator, and weigh the $CaCO_3$. Repeat this operation until a constant weight is obtained. The result multiplied by ·56 gives the amount of CaO.

Instead of weighing as carbonate, the precipitate may be converted into oxide by keeping at a white heat in a muffle for half an hour. A gentle heat must be applied at first, or loss will take place.

To the filtrate add excess of a solution of ammonium sodium phosphate; well stir with a glass rod without touching the sides; allow to stand a few hours; filter; wash with dilute ammonia; dry; burn paper in a weighed platinum crucible, then add precipitate; gently ignite at first, afterwards strongly; cool and weigh the $Mg_2P_2O_7$. The result multiplied by ·36 gives the MgO present.

The sand and clay forming the residue from (*c*) may now be examined. The proportions of each may be roughly judged by grinding in an agate mortar, then placing in a basin with water and allowing a gentle stream to run in from a tap, the clay floats away, while the sand falls to the bottom. To determine the silica and alumina accurately, fuse with four times their weight of potassium and sodium carbonates in a platinum dish, at a gradually increasing temperature and keep the mass in quiet fusion for half an hour, then cool; place the whole in a beaker; add water; cover beaker with a clock glass and gently heat, with frequent shaking, till the

mass is in a great measure broken up; add hydrochloric acid by degrees till effervescence ceases; heat on sand bath until no more bubbles of CO_2 are observed to come off; remove platinum dish; well wash it; then evaporate liquid to dryness in a porcelain basin. Moisten mass when cool with strong hydrochloric acid; allow to stand for an hour; add water; boil; filter off silica; wash; dry; ignite and weigh. The filtrate, which should be small in bulk, is treated with ammonia in excess, well stirred and allowed to stand for several hours in a warm place; then the alumina filtered off; washed; dried; ignited and weighed.

(*d*) If the amount of the sand be required, it may be ascertained by boiling the clay and sand repeatedly with strong solution of sodium carbonate, which leaves only sand; filter; wash; dry; ignite and weigh. The difference between this and the former weighing gives the clay.

ANALYSIS OF INSOLUBLE SILICATES, GLASS, SLAGS, ETC.

§ 276. (*a*) Reduce the silicate to the finest possible state of division; mix 20 grains with four times its weight of fusion mixture and fuse in a platinum crucible at a bright red heat until the fused mass appears clear and uniform. The operation must be carefully conducted at first, the temperature being gradually raised and the whole kept in a hot muffle for an hour. When cold, place the crucible and contents in a beaker; add water; cover with clock glass and boil until the mass is disintegrated. Now cautiously add hydrochloric acid and a little nitric acid drop by drop until effervescence ceases; then boil on hot plate; remove and wash crucible and evaporate to dryness. Take up with hydrochloric acid and water with usual

precautions; filter off silica; well wash; ignite and weigh the SiO_2.

(*b*) Pass a current of sulphuretted hydrogen. If any metals of the second group are present, such as lead, arsenic, etc., filter off and estimate as described in § 176. Boil off the sulphuretted hydrogen; add ammonium chloride; then ammonia in slight excess; boil until the odour of ammonia is barely perceptible and allow to stand until the oxide of iron and alumina are completely precipitated. Filter into a flask and well wash. Separate iron and aluminium as in § 195 or § 196.

(*c*) Add bromine to filtrate till the solution is red; well shake; cork up and allow to stand some time, then add ammonia in excess; then boil and filter off the hydrated oxide of manganese; ignite and weigh the Mn_3O_4.

(*d*) Concentrate the filtrate by evaporation to a small bulk; add ammonium chloride in excess; then ammonia, and ammonium oxalate to precipitate lime. Filter, wash and estimate the lime as in limestone. (§ 275.)

(*e*) The filtrate may contain magnesium, which is estimated as before with microcosmic salt, and weighed as magnesium pyrophosphate, $P_2O_7Mg_2$. (See § 275.)

(*f*) To estimate the alkalies, a fresh portion of 25 grains is taken and mixed with six times its weight of pure calcium carbonate in a large platinum crucible. Heat gently at first; then place in a muffle and keep at a bright red heat for an hour. Then allow to cool; place crucible and its contents in a platinum or silver dish; boil with water; then with hydrochloric acid; remove and wash crucible; evaporate to dryness; re dissolve in hot water; filter off insoluble matter and well wash. The solution contains the alkalies, together with calcium hydrate. Precipitate lime with ammonia

and ammonium oxalate as before. Filter, and evaporate filtrate to small bulk ; neutralise with hydrochloric acid ; add baryta water as long as a precipitate forms ; boil ; filter and well wash. The filtrate contains the potash and soda. Evaporate to dryness in a porcelain dish ; add pure nitric acid, and again evaporate to dryness to destroy ammonium chloride. Re-dissolve in water ; add hydrochloric acid and evaporate to dryness. Repeat this to remove all the nitric acid. Re-dissolve in water ; evaporate the solution to dryness in a weighed platinum dish ; heat gently and weigh the mixed chlorides. Re-dissolve in water and a little hydrochloric acid ; add platinum chloride and proceed for potassium as in § 208. The amount of potassium chloride deducted from the weight of the mixed chlorides gives the sodium chloride.

ANALYSIS OF ASHES OF WOOD, COAL, ETC.

§ 277. The following constituents may be expected to be present :—Potash, soda, lime, magnesia, oxides of iron, manganese, and aluminium ; sulphuric, phosphoric, hydrochloric, silicic, and carbonic acids. Sometimes baryta, strontia, copper, and cyanates.

(*a*) Estimate the carbonic acid either by the method given in § 233, or that in § 275. If the combustible matter of the fuel has been removed at a high temperature, the amount of carbonic acid will be very low owing to the decomposition of the carbonates, except in the case of the carbonates of the alkalies and baryta.

(*b*) Take 100 grains of the ash, place in a flask and digest with dilute hydrochloric acid in excess until the carbonic acid is expelled ; then gently boil for an hour ; transfer to an evaporating basin and evaporate to dryness. Take up with hydrochloric acid ; heat ; dilute ;

boil and filter off the insoluble silica and silicates. Treat this residue as described in § 276.

Concentrate the filtrate and washings by evaporation if necessary and make up the solution to a litre. Measure off 250 c.c. ; boil ; add barium chloride for the estimation of sulphuric acid, as in § 214.

(*c*) Take another 250 c.c., and estimate the alkalies as described in § 276 (*f*).

(*d*) The remaining 500 c.c. may be employed for the estimation of lime, magnesia, phosphoric acid, etc. Neutralise with ammonia ; heat gently and add 1 ounce of a saturated solution of ammonium acetate, when the solution should have a distinctly red colour ; transfer to a porcelain dish and boil until the red colour is destroyed, showing that the iron acetate has been decomposed ; filter and well wash with hot water.

The precipitate contains iron, aluminium, phosphorus, and manganese. Dissolve in dilute hydrochloric acid ; neutralise with ammonia and add ammonium sulphide Digest for two hours ; filter and wash with water containing ammonium sulphide.

The filtrate contains the phosphoric acid, which is estimated by magnesia mixture. (See § 215.)

The precipitate may contain iron, aluminium, and manganese. Dissolve in hydrochloric acid ; boil to expel sulphuretted hydrogen ; add a little nitric acid and again boil. Mix this solution with the filtrate from the basic iron acetate, precipitate the iron and aluminium as above, and concentrate by evaporation.

Add bromine to the filtrate ; cork up the flask ; allow to stand for an hour ; add ammonia ; boil ; filter off the precipitate of manganese oxide ; wash ; dry ; ignite and weigh.

Estimate lime and magnesia in filtrate as described in § 276.

(*e*) For the determination of hydrochloric acid, dissolve a portion of the ash in nitric acid; add silver nitrate and estimate the chlorine from the amount of AgCl obtained.

ASSAY OF SULPHUR.

§ 278. The substance must be dried at 100° C., ground very fine, and passed through a sieve with 80 meshes to the linear inch.

(*a*) Take 20 grains, or more if the amount of sulphur is small, mix with 500 grains of a deflagrating mixture, consisting of two parts common salt and one part nitre, previously powdered and dried.

Place the mixture in a platinum crucible in sufficient quantity to about half fill it, partly cover with lid; then gradually heat the crucible by means of a spirit lamp until the mass is completely deflagrated; add the remaining portions in small quantities until the whole is fused.

Allow to cool; place the crucible and its contents in a beaker; add water; boil; then add hydrochloric acid; remove crucible; well wash, and boil the solution until all action ceases. Filter off the insoluble silica, etc.; well wash; add a hot solution of barium chloride in sufficient amount to precipitate the sulphuric acid; well stir with glass rod; allow to settle; filter; wash; dry; burn paper in a weighed platinum crucible; ignite at a moderate temperature and weigh the $BaSO_4$. This multiplied by ·13734 gives the sulphur.

(*b*) Instead of the above fusion mixture the following may be used for 20 grains of the assay sample: 300 grains of salt, 100 grains of potassium chlorate and 100 grains of anhydrous carbonate of soda.

It is of the first consequence that the fluxes should be pure and free from sulphur, unless a check assay is made. A naked coal gas flame should never be used, or sulphur may be obtained from the gas.

§ 279. The author adopts the following plan, in which ordinary salts may be used :—

Weigh out two portions of fluxes, and add the assay sample to one of them; transfer each to a crucible; place both side by side in a gas muffle at a low temperature and regulate the temperature as required. The two portions are then dissolved, and the sulphur estimated in each. The amount of sulphur found in the blank experiment deducted from that found in the assay gives the true amount of sulphur. This method is suitable for estimating sulphur in coal, coke, pyrites, and other insoluble bodies.

§ 280. Sulphur in coke may be estimated by roasting 20 grains of the finely powdered coke with three times its weight of pure calcined magnesia. Introduce the mixture into a small porcelain dish; add a quantity of ammonium nitrate; place in a gas muffle; gradually raise the temperature to a red heat and maintain at this point until all the carbon is burnt off and the whole mass is white. Allow the dish to cool; transfer substance to a beaker; add hydrochloric acid and boil till the soluble portion of the mass is dissolved. Filter and well wash; then nearly neutralise the acid filtrate with ammonia; add sufficient barium chloride to precipitate the sulphuric acid; allow to stand for an hour, and treat $BaSO_4$ as in former methods. The sulphur by this plan is oxidised by the air, and absorbed by the magnesia forming $MgSO_4$, which is soluble in hydrochloric acid.

§ 281. Sulphur in ores, slags, etc., may be determined by dissolving the sample in aqua regia; evaporating to

dryness; taking up with hydrochloric acid and water; then filtering off the insoluble siliceous matter; evaporating to remove excess of acid; diluting largely with water and precipitating with barium chloride as usual. If barium should be present in the ore as well as sulphur, then the sample must be fused with alkalies as in §§ 278-9 and the sulphuric acid determined in the filtrate.

For mode of estimating sulphur in iron and steel see §§ 303-5.

§ 282. *Mr. A. H. Pearson's Method for Pyrites.*

Take 20 grains of the finely powdered mineral; mix with 2 grains of potassium chlorate; place in an evaporating basin; add pure nitric acid; cover with an inverted funnel, and keep the liquid gently simmering for at least half an hour, adding a crystal of potassium chlorate occasionally. When the oxidation is complete, well swill the funnel; wash down the sides of basin and evaporate the solution to a syrup; add strong hydrochloric acid and evaporate to dryness. Moisten the mass when cold with strong hydrochloric acid; allow to stand some time; add a little water; boil and filter off the insoluble silica.

Add 20 grains of solid tartaric acid to filtrate to prevent precipitation of iron salts and heat near to boiling. Then precipitate the sulphuric acid from the clear solution with barium chloride as usual. Filter; well wash by decantation with hot water; then with a hot solution of ammonium acetate to dissolve any barium salt that may adhere to the sulphate; transfer precipitate to filter; well wash with hot water; dry; ignite and weigh the barium sulphate, $BaSO_4$.

In all cases where nitric acid is employed to oxidise a body, it must be removed before adding the barium chloride, as barium sulphate is somewhat soluble in free nitric acid.

§ 283. Mr. P. Waage recommends the use of bromine in preference to nitric acid, chlorine, and potassium chlorate. He has for some time successfully employed bromine for pyrites, mispickel, nickel regulus and precipitated sulphides, both for the estimation of sulphuric acid and for the metals.

The powdered substance is shaken with bromine and water in a flask, the mouth of which is closed with a small funnel, adding fresh bromine if required until the substance is dissolved. A gentle heat is advisable towards the finish. 15 parts by weight of bromine are required for 1 part of sulphur. The solution is concentrated by evaporation, treated with hydrochloric acid, filtered, and the filtrate employed for the precipitation of $BaSO_4$ in the usual way.

Precipitated sulphides on a filter paper may be dissolved by bromine water. Perforate the paper, and wash the mass into a conical beaker by means of the same solvent.

ANALYSIS OF IRON AND STEEL.

Estimation of Iron.

§ 284. Weigh out 10 grains of the sample, which has been reduced to a fine state of division by drilling out about 100 grains from a piece of perfectly clean iron or steel; place in a porcelain basin; add 10 c.c. of pure hydrochloric acid and 5 c.c. of pure nitric acid. Boil at a very gentle heat until the metal is dissolved, and only a residue of free carbon and silica remains. Now evaporate carefully to dryness, keeping the top covered with a clock glass to prevent loss by spurting, and continue the heating until the residue is black; allow to cool; then moisten the contents with hydrochloric acid; swill down the sides and the clock glass cover (preferably with acid), using a glass rod, the end of

which is tipped with a piece of india-rubber tubing to remove any residue sticking to the vessel; again cautiously evaporate to dryness; cool and again add hydrochloric acid and digest until the soluble contents are brought into solution. Evaporate to a small bulk if necessary; dilute with water; boil for a short time and transfer the whole contents to a funnel the neck of which has been stopped with cotton wool to filter off the insoluble silica and carbon; well wash with hot water and dilute further if necessary to make the solution up to a quarter of a pint.

Mix the dilute solution with a large quantity of ammonium chloride (20 parts of AmCl to 1 of MnO, etc.), then add a saturated solution of ammonium carbonate gradually with frequent shaking as long as the precipitated iron re-dissolves, which takes place with difficulty towards the end. (It is best to finish with a dilute solution.) As soon as the liquid has lost its transparency without showing any signs of a precipitate the action is complete. When this point is reached, heat slowly to boiling and continue the boiling for a short time after the carbonic acid has been entirely expelled. The ferric oxide separates as a basic salt, which rapidly settles. Pour the clear liquid through a filter and wash several times by decantation and filtration with hot water.

The iron precipitate will probably contain alumina. Dissolve it in hydrochloric acid and neutralise the acid with a strong solution of sodium hydrate. Then pour the solution gradually into an excess of nearly boiling solution of sodium hydrate in a platinum or silver dish, stirring all the time. Then filter and well wash the precipitate. As the precipitate retains some alkali it should be re-dissolved in hydrochloric acid, boiled with some nitric acid, re-precipitated with ammonia, as in § 185, and the ignited Fe_2O_3 weighed. From this oxide the iron may be computed.

Another method of separating oxide of iron from alumina is given in § 196.

Iron may be much more rapidly, and as accurately, estimated by the volumetric methods afterwards described, when the standard solutions are once made and standardised.

§ 285. *Estimation of Ferrous Oxide in the presence of Ferric Oxide.*

The separation and estimation of these oxides separately in silicates is sometimes necessary. A process has been already described, see § 201.

The following method is due to Avery, who found that silica and many silicates could be completely dissolved by a mixture of some normal fluoride with a strong acid, either concentrated or dilute.

A sample of the silicate is first very finely powdered and sifted; then 25 grains are placed in a platinum crucible; 30 to 40 grains of powdered fluor-spar, free from iron, added and the contents well mixed. Pour in pure hydrochloric acid till the mixture is well covered and heat gently until the iron is dissolved.

During the process it is essential that the air should be excluded, or some of the protoxide of iron will be converted to sesquioxide. This is effected by placing the crucible in a small beaker, the edge of which is ground so as to fit tightly to a ground glass plate which covers it (Fig. 73). This glass plate is perforated with two holes through which pass two glass tubes. One tube is connected with a tap for delivering a constant stream of coal gas (which must be purified from sulphuretted hydrogen by passing through potash bulbs) and the other communi-

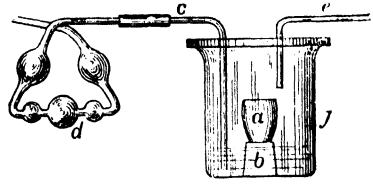


Fig. 73.

cates with the atmosphere; at the mouth of this tube the escaping gas may be burnt. *a* is the platinum crucible, *b* a lead support, *c* the gas delivery tube, *d* the potash bulbs, *e* the escape pipe. The beaker *f* containing a little water at the bottom through which the gas bubbles, is heated on a water bath. In from an hour to an hour and a half the decomposition is complete; the solution is then diluted, and the ferrous oxide determined by a standard solution of potassium bichromate, as described in § 365.

§ 286. Mr. Allen effects the solution of difficultly soluble ores by heating 10 to 15 grains in a sealed piece of combustion tubing half filled with fuming hydrochloric acid, which in this case dissolves the ore under pressure. It is first heated on a water bath for three hours, then for another hour at 150° C. The tube is then allowed to cool and the end broken under water. The ferrous oxide is then estimated by bichromate as in § 365. This method should only be used by persons who have had some experience in this kind of work, or a serious accident may happen.

ESTIMATION OF COMBINED CARBON.

§ 287. As carbon plays such a prominent part in modifying the character of iron it may be as well to remind the student that it exists in pig iron in two forms, viz., in the free state and in what is called the combined form, although this may simply be carbon in solution and not in true chemical combination with the iron. The effect of the combined form is to harden, increase its rigidity, make it brittle, and to reduce its tenacity when present beyond a certain amount. The effect of the graphitic condition is to make the metal softer and weaker than when in the combined form. The two

conditions may be produced by the rate of cooling, and by variations in the amount of other elements also present in the iron. Thus manganese, sulphur, and probably phophorus induce the carbon to pass into the combined form, while silicon has the contrary effect, causing it to crystallise out in the form of graphite. Hence it is probable that two samples taken from the same charge, unless cooled and mechanically treated under exactly the same conditions, will show different proportions of combined carbon, and even different parts of the same ingot may exhibit a difference, although the total quantity of carbon may be the same in all parts. In the case of iron containing less than ·15 per cent. of carbon, the metal is not sensibly hardened by sudden cooling, so that the results obtained from estimating the combined carbon in mild steels by the colour test, are much more reliable than those from the harder varieties, *i.e.*, those containing higher amounts of carbon. From the above remarks it will be seen that it is of the greatest importance to know, in the case of a sample of strong steel or cast iron, whether the assay has been made on a piece cast in a chill and cooled quickly, or cast in dry sand and cooled slowly.

§ 288. *Eggertz' Colour Test.*

(*a*) When iron, containing carbon in the combined form, is dissolved in nitric acid containing an equal volume of water a brown solution is obtained, the intensity of the colour being directly proportional to the amount of combined carbon present. When pure iron is dissolved in nitric acid and water, as above, and allowed to cool, a practically colourless solution is obtained. The nitric acid employed must be pure and especially free from chlorine, which communicates to the iron solution a yellowish colour. (Crookes states that ·0001 gramme of chlorine in a solution of ·1 gramme

of iron in 2·5 c.c. of nitric acid produces a decidedly yellow colour. Dilute this solution with 1·5 c.c. of nitric acid and 4 c.c. water, the colour is still observed, but less in proportion as the solution is diluted.) The quantity of nitric acid employed for dissolving the steel must be in proportion to the amount of carbon assumed to be present. Thus, with combined carbon under ·3 per cent. use 2 c.c. of acid; with ·5 per cent. and under, use 3 c.c.; under ·8 per cent., use 4 c.c.; for white cast iron use 5 c.c. The amount of metal taken for assay may be two grains for mild steel, 1 grain for strong steels, and not more than ½ grain for white cast iron.

(*b*) *Mode of conducting the Operation.*

In the first place a standard steel is necessary containing an amount of combined carbon, which has been very accurately determined by the combustion method, and a bottle containing nitric acid diluted with an equal bulk of water. Suppose this standard to contain ·35 per cent. of combined carbon.

Weigh out very accurately 2 grains of the standard steel, which must be in the form of very fine drillings, or filings and transfer, to a specially made narrow test tube, which must be dry, or some particles will stick to the sides, and it is essential they should all fall to the bottom. A good way of introducing the steel which avoids the necessity of a perfectly dry tube, is to cut a narrow strip of writing paper, fold it once down the middle so as to form a triangular trough. Place the steel in the paper, hold the tube in a horizontal position and pass the paper carefully to the bottom, then by tapping the paper the steel falls out without touching the sides (Fig. 74).

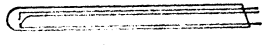


Fig. 74.

Now add 2 c.c. of the acid and place ready for dissolving. Then weigh an equal quantity of the steel to be assayed, introduce it into another tube similar to the former one and add the

same quantity of acid, or $\frac{1}{2}$ c.c. more if the steel is stronger than the standard, according to instructions in § 288 (*a*). Place the two tubes in a beaker containing hot water and keep the water just boiling until the steel in each case is dissolved; about twenty to thirty minutes being generally required. If a reddish yellow deposit is obtained, which somewhat clouds the solution, it may often be dissolved by shaking or carefully heating the tube in the flame of a Bunsen's burner. When the steel is thoroughly dissolved, and the solution quite clear, transfer the solution of the standard steel to a graduated tube; swill out the tube, in which the steel has been dissolved, with water, using only a few drops at a time. Dilute, until the solution stands exactly at 3·5 c.c in the graduated tube, the depth of colour in which may be taken to represent ·35 of carbon. Transfer this solution back again to the tube in which it has been dissolved and place in a test-tube rack for comparison. Now treat the assay steel in the same way, by transferring it to graduated tube, diluting with water and agitating until the same degree of colour is attained as in the standard. Suppose the reading to give 4·5 c.c.; then, as the same quantity of metal in each case has been taken, and the intensity of the colour is proportional to the amount of carbon present, and the proportion of the volumes indicates the relative proportion of colour, the steel contains ·45 of carbon. But the standard is known to contain ·35 per cent. of carbon, therefore the assay steel must contain ·45 per cent. of carbon.

The following tubes are 10 inches long with a bore of $\frac{3}{8}$ inch, which must be perfectly uniform throughout. The graduated tube must be exactly the same size and divided into $\frac{1}{10}$ c.c. The water for dilution is most conveniently added by means of a glass tube drawn out at one end so as to introduce it one drop at a time.

(*c*) It is not sufficient to have one standard for all kinds

of iron and steel when great accuracy is desired: thus Bessemer steel of ·5 per cent. combined carbon should be compared with a similar standard of Bessemer steel, and so for other varieties; so that a number of standards are

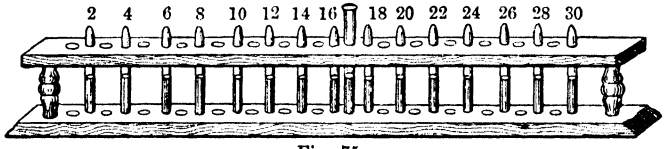


Fig. 75.

required for different varieties of metal. Instead of a single tube containing a standard solution for comparison, many steel works and laboratories, where a great number of carbon tests are being constantly made, keep a number of tubes containing coloured solutions, each corresponding to a different percentage of carbon. These are arranged in a wooden frame, with spaces between, to insert the tube containing the steel solution to be tested, the whole forming an instrument called a "colorimeter" (Fig. 75).

(*d*) Mr. J. B. Britton employs a rack containing 15 tubes, each charged with a solution made by digesting roasted coffee in alcohol and diluting with water, so as to obtain the desired tint. The tubes are $\frac{5}{8}$ inch in diameter and about $3\frac{1}{2}$ inches long. The tubes, after being filled, are hermetically sealed. The solution in the tube No. 2 has its colour to correspond exactly to one produced by 1 gramme of iron containing ·02 per cent. of combined carbon dissolved in 15 c.c. of nitric acid. The solution in the tube No. 4 has its colour to correspond with one produced by 1 gramme of iron containing ·04 per cent. of combined carbon, and so with each of the other tubes, each tube increasing in value by ·02 per cent. The last tube is equivalent therefore to ·3 per cent. The process is conducted thus:—1 gramme of the iron or steel, to be tested in the form of fine filings

or borings, is weighed out into a large test-tube, and digested with 10 c.c. dilute nitric acid in a beaker containing water maintained at 100° C. till all action ceases; the solution is then cooled by placing the tube in cold water and filtered without the residue being disturbed, through a small dry filter into a test tube of the same size, and made of the same glass as those containing the standard solutions. The insoluble matter is then treated with 5 c.c. of the nitric acid, gently heated and the solution added to the main portion. The entire solution is then agitated by shaking, so as to thoroughly mix and its colour compared. The holes in the rack allow the tube to be placed side by side with the standards; the number fixed to the tube with which it corresponds in colour indicates the percentage amount of carbon in the sample. If the iron or steel contains more than ·3 per cent. carbon, ½ gramme is taken for assay, or if 1 gramme, the solution is diluted with an equal volume of water, well mixed, and half of it poured away. If the metal contains a very small percentage of carbon, as in wrought iron, then 2 grammes are taken for assay.

At the back of the rack, for the purpose of partially screening the light and allowing the different shades of colour to be distinctly discerned, there is tightly stretched some fine white parchment paper. The determinations may be made by this method within ·01 per cent.

ESTIMATION OF THE TOTAL CARBON IN IRON AND STEEL.

As already mentioned, when speaking of combined carbon, this element exists in iron and steel in two forms—free and combined—so that any methods which indicate the amount of carbon in each state will of course give the total quantity of that body present in a given sample. Cast iron is produced in three varieties, the

condition of the carbon present modifying its physical properties. When the carbon is almost wholly in the combined form, white iron results; when in the free or graphitic form, grey iron results; and when about equal quantities of free and combined carbon are present, the iron is known as mottled. The method of estimating combined carbon by Eggertz' colour test has already been explained, and the following methods may be used for determining the quantity of free carbon:—

§ 289. *Estimation of Graphite and Silicon.*

In the case of grey pig iron considerable difficulty is experienced in obtaining a typical sample, as it is very possible to get an undue or insufficient amount of graphite in two portions weighed from the same drillings. Such iron should be reduced to as fine a state of division as possible by making the drill take a very fine cut, so that the particles may be exceedingly minute. It has been proposed by one chemist to place a well mixed quantity of such drillings in a porcelain crucible, well cover with pure alcohol, and allow the spirit slowly to evaporate. This causes all the particles loosely to adhere, from which a portion may be broken off for the assay and weighed.

Take 20 grains of grey or 50 grains of white pig iron; place in an evaporating basin; add strong hydrochloric acid; cover with glass plate, and heat until all action ceases. Add water and a little nitric acid, then evaporate to dryness. Heat the dry residue with hydrochloric acid, add water, and gently boil until all soluble matter is dissolved. Filter solution through a paper which has been dried at 110° C. and weighed; thoroughly wash with dilute hydrochloric acid, then with hot water; dry the residue and the filter at 110° C., and weigh when cool. Repeat the drying and weighing at intervals of half an hour until the results are constant. A weighing bottle will be found very convenient for this assay, as the paper and graphite rapidly absorb moisture. Deduct the weight

of paper: the remainder is the weight of the graphite, together with any insoluble silica.

Next weigh a clean and dry porcelain crucible; burn the filter paper; ignite the precipitate until every trace of carbon is burnt off; cool in desiccator and re-weigh. The result, after deducting the weight of the crucible and the known weight of the ash of the filter paper, is the amount of silica originally weighed with the carbon. The difference therefore of the two weighings gives the amount of graphite present in the iron. It will be noticed that by this method the silica is also determined at the same time as the graphite.

(*a*) Graphite may also be estimated by dissolving out the contained silica with potash. Take 20 grains, or more, of iron as before; dissolve in hydrochloric acid; add a little nitric acid, then evaporate to dryness; take up with hydrochloric acid; dilute; filter off the silica and graphite and thoroughly wash. Wash the contents of the filter into a porcelain, or better still, a silver dish; evaporate wash water to small bulk and add a piece of pure caustic soda. Digest for an hour; dilute and filter through a weighed paper. The graphite alone remains; thoroughly wash, then swill the graphite into a beaker, and heat for some time with aqua regia to dissolve out any mechanically enclosed matter; dilute; filter through a weighed paper; well wash; dry at 110° C., and weigh.

§ 290. *Estimation of Total Carbon.*

Mr. Thomas Turner, of the Mason Science College, Birmingham, has devised a neat and inexpensive method for the estimation of the total carbon in iron and steel, which is as follows:—

(*a*) For the solution of the iron, copper chloride or sulphate is still often used, and it is stated that the precipitated copper is rather an advantage than otherwise, as it assists in the combustion of the graphite; but this is

gradually going out of use since it is found that combustion of the carbon in the residue does not take place until the copper is thoroughly oxidised and this very often takes longer than the whole combustion when other methods are employed.

An excellent solvent is found in ammonium cupric chloride, and this is now extensively used. It may be prepared by dissolving 53·4 parts of ammonium chloride, and 85·4 of crystallised cupric chloride in hot water and crystallising. If the solution is not clear a little hydrochloric acid may be added; the crystals must then be washed with water and dried by pressure. The salt is permanent in air. One uses 15 grammes of the salt, dissolved in 50 c.c. of water per gramme of iron taken. After about fifteen minutes, a gentle heat is applied and the mixture occasionally stirred until the precipitated copper is entirely re-dissolved. After filtering, the residue is washed with warm dilute hydrochloric acid, and should burn white, or very nearly so.

A solution, which is cheaper, though not quite so effective, may be prepared by dissolving 360 grammes of crystallised copper sulphate in about 750 c.c. of hot water and gradually adding 310 grammes of common salt. If the temperature is raised to near the boiling point a precipitate of anhydrous sodium sulphate will form, but this is immaterial. The solution is allowed to cool, when sodium sulphate should crystallise out; the liquid is passed through a filter, and the filtrate made up to a litre. Then 50 c.c. of this solution is capable of dissolving 1 gramme of iron, leaving a residue free from copper. The solution is effected in the same way as before. When it is desired that the solution should be more rapid, a larger amount of the copper solution may be employed. For the estimation of graphite, the mode of procedure is exactly the same as for total carbon, with the single exception that the solvent is hydrochloric acid instead of copper salt. Generally 2 grammes of iron are taken, but

a somewhat larger quantity is used when the percentage of carbon is low. The iron being completely dissolved, the solution is allowed to subside for a few minutes and filtered.

(*b*) For filtration, a tube is employed, arranged as in Fig. 76.

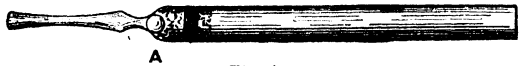


Fig. 76.

The tube is of ordinary glass combustion tubing, drawn out at one end, and constricted slightly at the junction of the broad and narrow part. The total length is 11 inches, the broad part being 8 inches long. At A is placed a small pea of baked clay, or some other suitable material, to act as a support; on this is placed about half an inch of sand, which has been heated strongly in a crucible with 5 per cent. of nitre to remove any organic matter. Upon this is placed a small plug of asbestos to act as a filter, and upon this again is about a quarter of an inch of white sand. By means of a small funnel the solution is introduced, while the narrow end of the tube passes through the cork of a flask connected with a filter pump. To ensure rapid filtration one should begin with a small pressure, and gradually increase this as necessary, and of course the precipitate should be put in last. The residue is washed twice with hot dilute hydrochloric acid and then with distilled water. The tube is then gently warmed by means of a Bunsen burner, and a stream of air aspirated through the residue until it is quite dry. The object of the lower layer of sand is chiefly to remove the residue from the constricted portion of the tube, because that part would be liable to collapse in the next part of the process in which the tube has to be very strongly heated. The upper layer of sand stops the larger particles of the residue and prevents the asbestos becoming clogged and so greatly assists in

the filtration; it also serves to distribute the residue, and thus causes it to burn more readily than it would do if it were compact. It is important, however, to avoid the use of too large a quantity of sand, as in that case the bulk of the residue which has to be dried is considerable, and much time is lost. When properly worked this method should give very little, if any, greater bulk of total residue, including the sand, filter, etc., than that obtained by solution in copper sulphate. If need be, in iron containing little silicon, solution and filtration may be completed in an hour, and the residue obtained in a form fit for direct combustion; and, as there is no transference, with a little experience a determination of total carbon may be performed in two hours. The tube itself should withstand a number of combustions, though it is preferable to remove the silica after each combustion, so as to avoid double error in case of any mistake. The residue being prepared and dried, it is ready to be burnt. For this purpose a special form of simple combustion furnace is employed. It consists of a stand made of sheet iron, about $4\frac{1}{2}$ inches broad, $8\frac{1}{2}$ inches high, 4 inches long at the top, and $8\frac{1}{2}$ inches long at the bottom, being made taper for greater steadiness and convenience. This stand supports a sheet iron trough, 5 inches long, for the purpose of carrying the combustion tube. Fire-bricks are used to obtain the necessary temperature and two fair-sized Bunsen burners are employed as a source of heat. This furnace stands upon an ordinary working bench, the temperature attained being sufficient to thoroughly soften good combustion tubing and to cause graphitic residues from cast iron to burn in less than an hour in a current of air.

(*c*) The operation of combustion is very similar to that usually adopted, except that all is in miniature and on a working bench. A drying tube and potash bulbs are attached to the narrow end of the glass tube, while a

cork and tube is attached to the open end. By means of an aspirator a slow stream of air, free from carbon dioxide, is drawn through the apparatus and heat gradually applied. The residue is noticed from time to time, and when the silica has turned white, or light brown with iron rich in silicon, the combustion is completed. This is accomplished in the case of steel in half an hour from the time when the full heat is applied and I have never yet had an iron requiring more than an hour. In other words, the whole combustion often takes less time than the mere oxidation of the copper alone in a stream of oxygen, when the copper sulphate method is employed. Fig. 77 shows the whole apparatus, the aspirator alone being omitted.

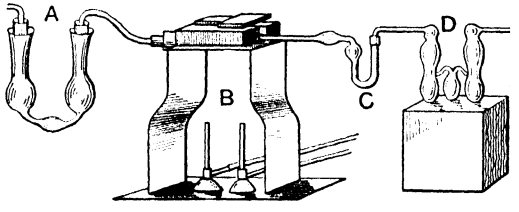


Fig. 77.

A. Potash tube. B. Combustion furnace. C. Drying tube. D. Potash bulbs.

ESTIMATION OF SILICON IN IRON AND STEEL.

§ 291. In treating samples of iron and steel in order to determine the amount of silicon present, it should be kept in mind that this element may exist in chemical combination with the iron or steel and also in the oxidised condition as silica in the enclosed slag, which, being a mechanical impurity, has no relation whatever to the real composition of the metal. It is therefore important to distinguish between these two amounts, so that some solvent is required which will dissolve the iron and leave

the enclosed slag (*i.e.* silicate) unaffected. Such a solvent was discovered by Dr. Eggertz in bromine, which, when mixed with water, dissolves the iron without the slightest action on the accompanying slag. But bromine is a most irritating and objectionable substance to have to deal with in large quantities, so that trials were made to substitute iodine in its place and with equal success, although the action of the iodine is slower than that of bromine in effecting solution. The silicon set free from the iron is oxidised to silica, which is soluble in a boiling solution of carbonate of soda; while that in combination in the slag is unacted upon.

§ 292. To estimate silicon in iron by the iodine method, take 25 to 30 grains in the state of very fine filings or drillings. Place in a conical beaker about 15 c.c. of distilled water; boil till the contained air is expelled to avoid oxidation of the iron and add gradually 200 grains of iodine, stirring at the same time with a glass rod, using as low a temperature as possible, which may be best effected by putting the beaker in a dish containing ice. The beaker must be covered with a watch glass. Add the iron and allow the solution to remain in the cold for several hours with occasional stirring. The low temperature enables the iron to be dissolved without evolution of gas and also to a great extent avoids the oxidation of the iron. When the iron is completely dissolved, wash any deposit from the sides by shaking the solution; then dilute to three times its bulk with very cold distilled water in order to prevent the separation of basic salts of iron; well mix and allow residue to settle. The lighter scales of graphite remain in suspension. Pour the liquid on to a filter, 2 inches in diameter, until there remains only a heavy dark powder of slag at the bottom of the beaker; then add a few drops of hydrochloric acid and stir with a glass rod. If this produces a disengagement of hydrogen it is a proof that all the iron has not been

dissolved, and a little iodine and sodium carbonate must be added to complete the solution. The acidified liquid must be quickly poured on to the filter to prevent the decomposition of the slag. Well wash the whole residue on the filter with cold water until the washings fail to give a precipitate with ferrocyanide of potassium, showing that all the iron has been removed. Evaporate filtrate to dryness with the addition of hydrochloric acid; boil the dry residue with hydrochloric acid to ascertain whether any silica has gone into solution with the iron, in which case, it must be filtered off, washed and added to the main residue.

The residue on the filter paper consists of graphite, silica and slag. Wash this residue into a platinum dish; evaporate the wash water cautiously to a very small bulk, then add a concentrated solution of sodium carbonate and heat for an hour on a water bath, adding fresh solution if necessary and stirring from time to time with a platinum spatula in order to divide any lumps in the insoluble residue. Then pour off the clear supernatant liquid from the insoluble mass in the dish on to a small weighed filter; add more sodium carbonate to the residue and boil for another hour; then pour the whole contents on to the filter and well wash with hot water.

The filtrate contains the silicon which was originally in combination with the iron, while the insoluble residue contains the slag, graphite and any oxide of iron. Acidify the filtrate with hydrochloric acid and evaporate to dryness. Digest with hydrochloric acid and again evaporate to render the whole of the silica insoluble; moisten with hydrochloric acid; add water; boil and filter; thoroughly wash, dry, ignite, and weigh the silica, if white.

The weighed filter containing the slag and graphite is dried at 110° C. and weighed. It is then ignited in a weighed crucible until all the carbon is burnt off,

allowed to cool and again weighed. The ignited residue is then boiled with water saturated with caustic soda, which dissolves silica. The solution is then filtered off and the residue washed and weighed.

§ 293. *Chlorine Process.*

This process was carried out by Mr. Watts with satisfactory results. A bottle is fitted with an india-rubber bung, having two holes and filled with oxide of manganese in lumps. Through one hole passes a tube to near the bottom of the bottle, its upper end being provided with a glass stop cock and bulb filled with hydrochloric acid; through the other hole passes a glass tube reaching just inside the bottle, bent at right angles and also provided with stop cock; this is the delivery tube for the chlorine gas and is connected with three wash bottles, the first containing water and the others strong sulphuric acid, so as to obtain the chlorine free from moisture. The oxygen of the air must also be removed; this is done by passing the gas through a tube containing lamp black, which has been previously strongly heated to free it from moisture and tarry matter; the column of lamp black is kept in position by plugs of gas carbon, and should be 6 or 8 inches long and occupy only the centre of the tube. This is followed by a combustion tube, the other end of which is bent at an angle of 110°, so as to dip into water placed in a flask. In this tube the iron to be assayed is placed. All the stoppers are of india-rubber and coated with paraffin to prevent leakage.

The iron in form of drillings or turnings is weighed into a porcelain boat and placed in the combustion tube. The air is expelled and the tube filled with dry chlorine, then it is heated to low redness, while a constant stream of dry gas is maintained. The chlorine is generated by placing the bottle containing the manganese oxide in a vessel of boiling water and running in a quantity of hydrochloric acid. The effect of chlorine on red hot iron

is to volatilise it as chloride, which condenses in the cooler part of the tube, while at the same time silicon tetrachloride is formed and being volatile, passes into the water and is decomposed. The water on evaporation yields silica, which represents the silicon originally in combination with the iron; the slag mixed with carbon remains unaltered in the boat.

This method was found by Turner to be attended with two great disadvantages; the total amount of silicon as compared with other methods is too low, and the residue left in the boat, even after boiling with dilute hydrochloric acid before burning off the carbon, contains variable and sometimes considerable amounts of substances other than slag. The source of error may be removed by adopting the following modification.

§ 294. The iron or steel is placed in a porcelain boat and burned in a stream of dry chlorine free from air. The excess of gas passing through the combustion tube is washed by passing through water contained in a Varrentrapp's bulb. When the combustion is completed as indicated by the entire absence of red vapours near the boat, the current is maintained for five or ten minutes and the solution afterwards evaporated to dryness. The residue is extracted with hydrochloric acid to remove any iron, etc., sometimes carried over, then filtered, washed and ignited. The residue left in the boat contains carbon, slag, a part of the manganese and a little iron as chloride. It may be transferred to a test tube; boiled with a little dilute hydrochloric acid; filtered; dried and ignited.

This residue consists of slag and other substances, so that it is necessary to estimate the silica by fusion with fusion mixture, as in § 297. The combined results furnish the total silicon present in the sample.

This process is well suited for the estimation of silicon in silicon-ferro-manganese and highly siliceous pig iron,

these varieties of metal burning readily in chlorine. The method is rapid and fairly accurate with all classes of iron, and it distinguishes between the unoxidised silicon and the slag.

§ 295. The usual method of estimating silicon in iron and steel is to dissolve a convenient quantity in hydrochloric acid, and when all action ceases, to add a little nitric acid and evaporate to dryness, by which means the silicic acid is dehydrated and becomes insoluble in hydrochloric or nitric acids. Fifty grains is a convenient quantity for steel and 25 grains for cast iron. In the latter case, graphite in greater or less quantity is present and even in steel a little carbonaceous matter is sometimes left behind after solution in acid. The carbon, however, left in the siliceous residue is entirely removed by ignition, when the silica can be weighed and the percentage of silicon computed. In cases where greater accuracy is desired, the graphite and silica may be washed into a silver dish; the excess of water evaporated; a lump of pure caustic soda added; the mixture digested on a water bath for an hour and the silicon determined as described in § 292. These methods give good results with steel, or with iron containing less than three per cent. of silicon, but are untrustworthy when the percentage of silicon is considerable, as in spiegel-eisen and silicon-iron.

§ 296. Another plan which is sometimes adopted on account of its rapidity, is to dissolve the iron or steel in concentrated hydrochloric acid and to filter without evaporation. This plan is quite unreliable and should never be used when any approach to accuracy is desired, as part of the silicon always remains in solution although the amount is less with strong acid than with dilute.

§ 297. A third method consists of dissolving in hydrochloric acid as before; evaporating to dryness; dissolving

the iron compound in hydrochloric acid; then filtering off and washing the insoluble residue, which contains the silica and graphite. Wash the residue into a platinum crucible; evaporate the wash water and add four times the quantity of pure carbonates of soda and potash; well mix with a platinum wire. Heat gently at first so as to cause the mass to clot together, then gradually raise the temperature to a high degree and maintain at this point until no more bubbles of gas are given off and the whole is in a state of tranquil fusion.

The materials should not more than half fill the crucible which should be covered with a lid. Put the crucible and contents, when cool, into a beaker, cover with clock glass, boil first with water, then add hydrochloric acid and boil. Remove the well washed crucible and, if the solution is complete, the liquid will be clear, except for a few flakes of silica and the graphite. (If a heavy powder subsides, the decomposition has been incomplete, and the residue must be again fused with alkali.) Evaporate the whole to dryness, when the silica and graphite, being insoluble in hydrochloric acid, may be well washed and treated as before by ignition to remove graphite. Weigh the residual silica. (See § 292.)

§ 298. An excellent method proposed by Drown is preferable to evaporation with hydrochloric acid, but is not applicable when it is desired to estimate sulphur as well as silica in the same sample Weigh 25 to 50 grains of iron, which need not be very finely divided, place in an evaporating dish, and very cautiously add 10 to 15 c.c. of nitric acid drop by drop, keeping the dish covered with a clock glass. When the action has ceased, add 3 to 4 c.c. of strong sulphuric acid and digest until the metal has dissolved. Evaporate nearly to dryness; add water; boil and filter hot. Wash the residue with strong hydrochloric acid; then with water; dry; ignite

and weigh. This method, like the preceding simple processes cannot be employed for iron containing a high percentage of silicon and manganese on account of the impurity of the residue, as well as the length of time taken in dissolving.

§ 299. The following methods are reliable, and recommended for adoption in iron and steel works:—

Take 150 grains of steel, or
100 grains of white pig iron, or
50 grains of grey or mottled pig iron.

First reduce a considerable portion to a small state of division, select a typical sample, and weigh out the required quantity; place in a No. 5 Berlin porcelain dish and cover with a clock glass having a hole at the edge through which a pipette may be introduced; then cautiously add 15 to 25 c.c. of nitric acid, specific gravity 1·2, by means of the pipette, and when the first violence of the action has subsided, heat gently until the metal has dissolved. Wash the cover with acid and water; evaporate the solution carefully to dryness, avoiding loss by rapidly stirring with a glass rod until all the acid has evaporated. Now gradually increase the heat over a ring burner till all nitrous fumes are expelled; cool; add 10, 25, or 35 c.c. of hydrochloric acid, according to the quantity of metal present and allow to stand for an hour. Warm gently until all iron compounds seem to be dissolved, then boil for five minutes; rinse the deposit on the cover into basin and evaporate to a syrup; dilute with boiling dilute hydrochloric acid (1 to 20); boil for a few minutes; allow to settle for ten minutes and filter through a thick English or Rhenish filter previously exhausted with acid and water. (The usual way is to drop hydrochloric acid round the filter until thoroughly wetted, then to remove acid with boiling water.) Wash precipitate on to filter with hot dilute

hydrochloric acid (1 to 20), rinse out basin with strong hydrochloric acid, and finally rub any residue adhering to sides of basin with a "finger tip" (which acts better than rubber on glass rod) or a feather; rinse into filter; drop concentrated acid round edge of filter after the water has drained off; then wash with boiling distilled water until all traces of iron and acid are removed. (Test for iron in the washings with sulphocyanide of potassium and for acid with litmus paper.) It is better to wash the silica, etc., into the cone of the filter, so as to facilitate subsequent operations.

Now dry the precipitate and filter in a water oven or a hot air bath; then open the dried filter paper; transfer the silica to a clock glass placed on glazed paper and cover with a funnel; then burn the paper in a weighed platinum crucible and cover; add the silica; cover with lid and heat very gently at first, as silica is carried away by rapid burning; then ignite strongly, preferably in a muffle or with a blowpipe, until the mass is perfectly white, stirring several times with a platinum wire when much carbon is present to assist in its combustion. Allow to cool, and weigh the SiO_2.

§ 300. As stated on a previous page, the silica obtained from common irons is often impure, so that a further examination of the residue becomes necessary when an accurate result is required. The most reliable process known for this purpose is the "hydrofluoric acid" method. A store of re-distilled hydrofluoric acid should be kept in gutta-percha bottles where a number of silicon assays are frequently being made; but as this acid generally leaves a residue on evaporation, the amount must be determined for each portion, which is done as follows :—

As a measure, the lid of a platinum crucible may be used or a small platinum capsule, always using the same

measure in subsequent assays. Take one measure of hydrofluoric acid, pour into a weighed platinum crucible, add 2 c.c. of sulphuric acid (1 to 1) and carefully evaporate to dryness to avoid spitting, gently ignite, weigh, and note the amount of residue in one measure of the acid.

Now add one measure of the hydrofluoric acid to the before-mentioned ignited silica residue and 2 c.c. of sulphuric acid (1 to 1), evaporate most carefully to dryness, ignite as before and weigh. The loss in weight is due to silica removed as gas, and after making allowance for the residue introduced by the hydrofluoric acid, the quantity of pure silica is ascertained. The following result will show the mode of calculation :—

	Grains.
Weight of crucible, cover, and siliceous residue - - -	= 173·56
Weight of crucible - - -	= 172·10
Weight of siliceous residue -	= 1·46
Less residue in one measure of acid	= ·04
Weight of siliceous residue from iron	= 1·42
Weight of residue after treating with hydrofluoric acid - -	= ·21
Weight of pure SiO_2 - -	1·21

As 100 grains of iron were taken and $\frac{7}{15}$ or ·4667 of SiO_2 is silicon, then 1·21 × ·4667 gives the percentage. The evaporation must be conducted in a fume chamber with a good draught.

The bodies most likely to be present in silica obtained by evaporation with hydrochloric or sulphuric acid are oxide of iron, phosphorus compounds, titanic acid, oxide of vanadium (rather rare), and sand.

Care must be taken in working with hydrofluoric acid, as it is highly poisonous, and the operation should be performed in a fume chamber.

§ 301. Mr. Turner performed a series of experiments on a sample of Northampton pig iron with a view to test the value of the various methods of estimating silicon, and found that it was practically almost impossible to obtain a white residue by treatment with aqua regia, evaporating, and extracting with hydrochloric acid; for although the residue was boiled four times with strong hydrochloric and four times with water, filtered, well washed and ignited, a distinct colour was observed. The sample contained 1·84 per cent. of phosphorus. In the case of other acids it is very difficult to obtain a pure residue, but the colour is not so marked. The same iron was dissolved in sulphuric acid, and evaporated to dryness when a white residue was obtained, but was too heavy, showing the presence of impurities. On fusion with acid potassium sulphate, both iron and phosphorus were extracted, leaving a snow-white silica, whose weight was lower than with the aqua regia or sulphuric acid methods. The latter method must always be employed with caution, as there is nothing in the colour of the residue or solution to indicate when iron has been removed, so that the washings should always be tested until quite free from iron.

The following conclusions may be inferred from the foregoing:—

1. That with cast irons of specially good quality the silicon can be correctly estimated by evaporation with dilute sulphuric acid.

2. With phosphoric irons the residue obtained, though white, is often impure and should be further treated in order to obtain accurate results.

3. With phosphoric irons containing titanium, the silica is contaminated not only with iron, but also with titanic

acid and phosphoric acid. The residue may be very nearly white and still contain 20 per cent. of substances other than silica.

4. On treatment with aqua regia, the colour of the residue is usually an indication of its purity.

Any vanadium there may be in the iron shows itself in the silica residue. It may be detected by adding hydrochloric acid and gently warming, when a deep brownish green colour is produced with evolution of chlorine.

Nearly all the sand in the residue will be left after acting on the mass with hydrofluoric acid, for, owing to the rapidity of its action on amorphous silica, the acid is weakened to such an extent that sand is not appreciably attacked.

In irons containing more than half a per cent. of phosphorus or any titanium, the fluorine method is invaluable where anything like accuracy is desired.

ESTIMATION OF COPPER IN IRON.

§ 302. This is a substance often present in iron and diminishes the malleability and ductility when over ·1 per cent.; the usual amount is about ·03 per cent. According to C. Rump, the purest iron of commerce is not free from copper. This is especially the case with iron smelted with coke, since coal almost always contains copper pyrites. Swedish iron generally contains only a trace of this element.

Dissolve 200 grains of iron borings or turnings in hydrochloric acid (1 to 1); filter; wash residue; dry and ignite in a porcelain crucible. Allow to cool; moisten with nitric acid; evaporate again to dryness and ignite. Now extract with hydrochloric acid, filter and add filtrate to the main solution of iron. Pass a rapid stream of sulphuretted hydrogen through the solution for ten minutes; allow to settle in a warm place until nearly all

odour of sulphuretted hydrogen has disappeared and the precipitate has settled to the bottom. Filter; wash thoroughly with hot water; dry; burn paper and heat precipitate in a weighed porcelain crucible in a muffle until the sulphide is completely roasted to oxide; ignite more strongly, and weigh the CuO.

79 parts of CuO contain 63 parts of copper.

ESTIMATION OF SULPHUR IN IRON AND STEEL.

§ 303. Sulphur is generally oxidised to sulphuric acid by means of nitric acid, chlorine, bromine, or other oxidising agents and the amount of sulphuric acid determined by means of a solution of barium chloride. It is of course essential that the body employed for bringing the iron into solution as well as the agent used to effect the oxidation should be free from sulphur. The amount of metal taken for assay will also vary with the relative amount of sulphur in the iron. In the case of common iron 50 grains will suffice, in other cases 200 grains will be required.

Weigh out the sample; place in a large beaker; add 20 to 50 c.c. of pure hydrochloric acid and 10 to 25 c.c. of pure nitric acid; cover with clock glass and heat gently on a sand bath or hot plate. Drop in 2 or 3 crystals of potassium chlorate and slowly evaporate to dryness; then heat carefully to expel the nitric acid. Remove; allow to cool; add sufficient hydrochloric acid to dissolve all the iron and evaporate to the consistence of syrup. Now add a few drops of hydrochloric acid to dissolve the crust formed on the surface; dilute with water; boil and filter through cotton wool, which separates the silica and graphite. The filtrate contains the sulphuric acid and should be free from excess of hydrochloric acid, as acid solutions of ferric chloride dis-

solve small quantities of barium sulphate. Now add 2 to 5 c.c. of barium chloride solution (containing 1 part of $BaCl_2$ to 10 parts water) and allow to stand for a few hours in a warm place. After the precipitate has settled, add a drop or two of the re-agent to ascertain if all the salt is thrown down, then filter through an ashless filter paper without disturbing the precipitate; then wash precipitate on to filter; well wash with distilled water; dry; burn paper in a weighed platinum crucible; then add precipitate; ignite at a moderate heat; allow to cool and weigh the $BaSO_4$. The result multiplied by ·13734 (the coefficient for sulphur) gives the amount of sulphur present in the sample of iron taken.

§ 304. The above method of estimating sulphur is not applicable in all cases, especially in iron and steel containing small quantities of sulphur, as some of the sulphur is probably evolved in the form of sulphuretted hydrogen; so that the following excellent method is to be preferred, except in the case of white iron, which is not easily acted on by hydrochloric acid.

Take 200 grains of iron or steel, or 100 grains of ordinary grey pig iron; but, as some grey forge pigs contain little sulphur, 200 grains should be employed in such cases. The operation must be conducted so as to exclude the air as much as possible. The apparatus shown in the accompanying figure may be employed for the purpose. The iron is placed in the flask E; hydrochloric acid introduced from bulb tube B, and the gas passed through the empty bottle F, in which any solid matter mechanically carried over may be deposited; then into the U-tube G, which contains a solution of bromine and potassium bromide, and from thence through a vessel H containing distilled water. The action is based on the fact that when iron containing sulphur is heated with hydrochloric acid, the sulphur is evolved as sulphuretted hydrogen. By passing this

gas through a solution of bromine it is completely absorbed and oxidised to sulphuric acid which is subsequently precipitated with barium chloride.

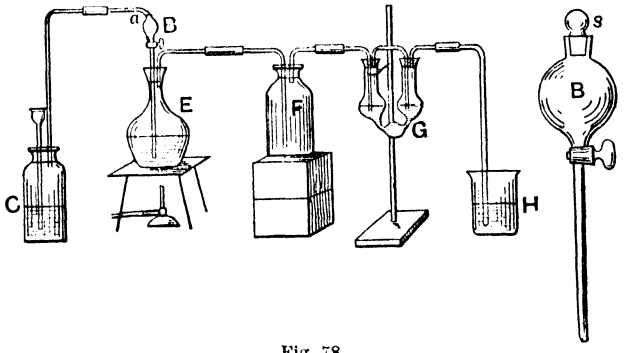


Fig. 78.

To conduct an assay, place the finely divided iron in the flask E, fill the bulb tube B with hydrochloric acid, and to the U-tube G add 2 c.c. bromine, 15 grains of potassium bromide and 20 c.c. water, which should about two thirds fill the two upper bulbs; in this U-tube, the glass tubes are so arranged as to cause the gas to pass twice through the bromine solution. When the whole apparatus is fitted together, run into the flask a little hydrochloric acid and gently heat, continuing to add fresh acid as required until the iron is completely dissolved. Then boil for two or three minutes; replace stopper S by the cork *a*, which is connected with the bottle C, in which are placed bits of marble, for generating a current of carbonic acid by the action of dilute hydrochloric acid. The carbonic acid passing through the flask sweeps the last remnants of sulphuretted hydrogen through the bromine solution. Transfer the bromine solution to a beaker; carefully evaporate to dryness; take up with water and a little hydrochloric acid; then precipitate the sulphuric acid by means of a solution of

barium chloride, as in the former method. It is also advisable to test the iron solution for sulphuric acid by evaporating to a small bulk and adding 1 c.c. of barium chloride. Any insoluble residue in the flask may also contain sulphur and should be dried and fused with fusion mixture and treated as in § 297. If copper be present to any extent in the iron, free sulphur will be found in the residue, which sulphur must be collected, dried and weighed.

Instead of bromine solution, some chemists use a dilute solution of potash or soda to absorb the sulphuretted hydrogen, and afterwards oxidise with bromine in a beaker. In all cases it is very advisable to test the re-agents and absorbents by making a blank experiment to ascertain whether they contain sulphur, so as to allow for this in the final result. (See method, § 278 (*b*). Also volumetric method, § 372.)

§ 305. *Eggertz' method for small quantities of Sulphur.*

Two grains of finely divided pig iron are placed in a stoppered bottle with 16 grains of water and 8 grains of sulphuric acid. A clean plate of silver, $\frac{3}{4} \times \frac{3}{8}$ inch, is suspended by a wire in the upper part of the bottle for fifteen minutes when the discoloration will be proportional to the amount of sulphuretted hydrogen evolved. The plate is then compared with a series of standard colours, each of which corresponds to a definite quantity of sulphur as determined by experiment on samples whose composition is known. Thus plates are obtained of coppery yellow, bronze, brown, blue, and so on, corresponding to ·02, ·04, ·06, etc., per cent. of sulphur. Full particulars of this process will be found in Crookes' Select Methods in Chemical Analysis, pages 160-164.

ESTIMATION OF MANGANESE IN IRON AND STEEL.

§ 306. The usual method of assay for manganese is as follows :—

Take 50 grains of steel or 15 to 20 grains of pig iron, containing upwards of ·5 per cent. of manganese ; place in an evaporating basin ; add strong hydrochloric acid in sufficient quantity to well cover the finely divided metal ; cover with a clock glass and heat gently. When the action ceases, add nitric acid in equal quantity ; dilute with water and again heat until the iron is dissolved, adding fresh nitric acid if necessary. Evaporate cautiously to dryness and heat the residue strongly to destroy all organic matter. Re-dissolve in hydrochloric acid and a little nitric ; add water and boil until all is dissolved, except silica and graphite. Filter, if the residue is large, through cotton wool or filter paper ; if small, this filtration may be neglected, as it will be removed in the next stage with the iron. Transfer solution to a quart beaker ; make up to a pint with boiling water and add cautiously a dilute solution of ammonium hydrate, until a permanent precipitate is obtained, without any odour of free ammonia, showing that the liquid is nearly neutral. Now add 15 to 20 c.c. of a concentrated solution of sodium acetate, or better, ammonium acetate ; raise the liquid to the boiling point and keep at that temperature for two or three minutes ; allow the precipitate of basic acetate of iron to settle, which should be of a brick red colour ; if it be dark red, an insufficient amount of ammonium acetate has been added and more of that salt must be introduced. Wash two or three times with dilute acetate of ammonium by combined decantation and filtration into a 30-ounce flask, when the filtrate should be quite clear and colourless ; well wash the precipitate, after transferring it to filter, with hot

water. If pig iron is being assayed, the precipitate will contain manganese. This must be re-dissolved and the iron re-precipitated as before with acetate of ammonia. If steel is being assayed, one precipitation will be sufficient. The two filtrates are then concentrated by evaporation, transferred to a flask, cooled, and 10 c.c. of bromine added, a little at a time, with frequent shaking, when the solution should be of a deep red colour. Then cautiously add strong ammonia in excess, well shaking after each addition, and gradually raise the liquid to boiling. In half an hour the black oxide will completely separate out. Allow precipitate to settle; filter and wash with hot water: any particles of precipitate which adhere to sides of flask may be removed by rubbing with scraps of ashless filter paper and glass rod. Dry; burn paper in a weighed platinum or porcelain crucible; ignite precipitate strongly, finishing with five minutes over blowpipe flame, when the black MnO_2, changes to the coffee coloured Mn_3O_4; cool in desiccator, and weigh the Mn_3O_4.

This precipitate may contain silica, especially if a new glass flask has been used. Also when copper is present in the iron, that metal will be present in the manganese precipitate. The copper in such case may be precipitated before the iron and manganese with sulphuretted hydrogen, as described in § 302. The filtrate from the manganese precipitate retains a little manganese. Evaporate to dryness; re-dissolve in water and test for manganese with bromine and ammonia as before; add the result to the main portion; ignite and re-weigh. The weight of the Mn_3O_4 obtained, multiplied by ·7205, gives the weight of metallic manganese in the portion assayed.

Volumetric methods for estimating manganese are given in § 371.

§ 307. The estimation of small quantities of manganese in the presence of much iron by converting the

latter into ferric acetate is troublesome on account of the large volume of liquid to be boiled and filtered; an operation which must be repeated where accuracy is desired, as some of the manganese is carried down with this precipitate. Moreover, a student frequently fails to effect complete precipitation of the iron, or obtains it in such a condition that filtration is very difficult.

Mr. Chas. L. Bloxam has devised the following process to simplify the estimation :—"The metal is dissolved in hydrochloric acid in a beaker; the solution evaporated to dryness; the residue taken up with hydrochloric acid and water as usual, and the graphite and silica filtered off. The filtrate is then heated, and a few crystals of potassium chlorate added to oxidise the iron, etc.; then cooled and carefully neutralised with ammonia; an excess of acetic acid added to convert the whole of the iron into acetate; then an excess of sodium phosphate is introduced, by which the iron is precipitated as ferric phosphate. Filter and re-dissolve in hydrochloric acid without washing and re-precipitate as above. The two filtrates are mixed; an excess of ammonia added and the solution boiled, when the manganese is precipitated as the crystalline very insoluble ammonium phosphate, which is filtered off and washed. As soon as the washings leave no residue on evaporation, the wet precipitate with the filter is placed in a weighed platinum crucible, covered with lid and ignited. It then has the formula $Mn_2P_2O_7$. It is well to keep the ammoniacal solution near the boiling point for an hour and allow to stand some hours before filtering. The ignited precipitate should be re-dissolved in hydrochloric acid and the solution mixed with ammonium acetate to detect any ferric phosphate, which may be ignited, weighed, and deducted from the manganese precipitate."

§ 308. *Estimation of Manganese by Electrolysis.*

"The manganese solution, after removing all iron salts,

is placed in a platinum crucible, which serves as the negative electrode, the positive being formed by a spiral of platinum wire. The manganese is deposited on the crucible in the form of dioxide. The accuracy of the result is not impaired by the presence of copper, cobalt, nickel, zinc, magnesium, aluminium, alkalies, or alkaline earths. By this method ·0005 grm. of MnO_2 can be easily estimated, and ·000025 grm. detected by the rose coloration which it exhibits." (*A. Riche.*)

ESTIMATION OF PHOSPHORUS IN IRON AND STEEL.

§309. Two methods are in common use for the estimation of phosphorus in iron and steel, each of which possesses advantages in particular cases. One is known as the magnesia method and the other as the molybdate method. The general opinion seems to be, that a combination of the two methods yields the most correct results. The magnesia process gives results a little below the truth, the precipitate being sensibly soluble in its mother-liquor; while the phospho-molybdate precipitate is liable to retain a little molybdic acid. The latter method, however, yields a comparatively large and heavy precipitate, containing only a small percentage of phosphorus and is 17 times heavier than the corresponding magnesia precipitate and therefore more suitable for the determination of small quantities of phosphorus; it also has the great advantage of being quicker.

§ 310. *Phospho-Magnesia Method.*

Take 25 grains of phosphoric pig iron or 50 grains of steel. If the phosphorus is very small, 200 grains will be necessary. Dissolve in 20 to 30 c.c. of hydrochloric and 10 to 15 c.c. of nitric acid in a 20 oz. beaker; first adding the acid, then the metal a little at a time, as the

action is somewhat violent at first; cover with a clock glass and heat gently until the iron is dissolved. Evaporate to dryness; heat strongly to destroy organic matter and take up with hydrochloric acid and water; filter off any silica and graphite; dilute considerably with cold water and add sufficient sodium sulphite to reduce the whole of the iron to the ferrous condition. Boil to remove all excess of sulphurous acid; add a little ferric chloride and cautiously neutralise with ammonium carbonate. The ferric chloride causes a precipitate of basic salt to separate on boiling, which contains all the phosphorus, if sufficient ferric chloride has been added. The iron salt, which has been reduced to the ferrous condition by the sodium sulphite, remains in solution. The precipitated iron phosphate is white if no ferric salt is in excess; but it is best to have a little excess of the ferric chloride, so as to insure the complete precipitation of the phosphoric acid. The precipitate will be of a red colour. Filter; wash once and re-dissolve the precipitate in hydrochloric acid; filter the liquid and to the filtrate add half an ounce of citric acid. Now add strong ammonia until the liquid smells strongly of the gas; then add 2 c.c. of the magnesia mixture (described in § 104, *d*) and allow to stand several hours, occasionally stirring with a glass rod; filter; wash with ammonia containing four times its volume of water; dry; ignite in a weighed platinum crucible; allow to cool and weigh the $P_2O_7Mg_2$. The weight multiplied by ·2793 gives the phosphorus.

The precipitate may contain arsenic, if it is present in the iron. Re-dissolve in hydrochloric acid; dilute; warm to 60° C. and pass a current of sulphuretted hydrogen, when the presence of arsenic is indicated by a yellow precipitate; allow to stand several hours. Filter on to weighed paper; dry, and add bisulphide of carbon to dissolve any free sulphur; dry at 100° C. and weigh. The precipitate multiplied by ·610 gives the arsenic.

This is not the whole of the arsenic contained in the iron.

If arsenic is suspected in the sample to be assayed, it should be tested for and removed by sulphuretted hydrogen in the hydrochloric acid solution obtained by re-dissolving the iron precipitate, then the sulphuretted hydrogen boiled off before adding the magnesia mixture. When hydrochloric acid is employed to dissolve the iron, some of the arsenic is volatilised as chloride during evaporation. (See § 179.)

§ 311. *Method of Estimating Phosphorus by the Magnesia and Molybdate Methods Combined.*

Take the same quantity of iron as in the previous method; dissolve in 5 c.c. hydrochloric and 10 c.c. nitric acids in a covered beaker; wash down the sides; evaporate to dryness; cool and take up with 10 c.c. hydrochloric acid; boil; dilute; boil again and filter off silica, etc., through cotton wool; wash thoroughly with hot water; carefully neutralise with ammonia, using very dilute ammonia at the close of the operation. Now add 3 c.c. of nitric acid; boil and add 10 to 15 c.c. of the ammonium molybdate solution (described in § 313, *a*); well shake the contents until the solution becomes turbid from the separation of phospho-molybdate of ammonium $\{Am_2O,5(H_2OMoO_3) + Am_2PO_4\}$; gently boil for a short time, when the whole of the phosphorus will be precipitated; allow to stand a few hours to settle; filter and well wash precipitate down to the apex of the filter with a solution of ammonium nitrate, containing nitric acid. Dissolve the precipitate in the smallest quantity of ammonia and wash the filter paper with dilute ammonia. Now add hydrochloric acid until the precipitate formed at first re-dissolves with difficulty; add 2 or 3 c.c. of magnesia mixture; shake as before; allow to stand some time; then add one third of its bulk of ammonia; allow to stand a few hours; filter; wash

with dilute ammonia; dry; ignite cautiously in a platinum crucible; cool and weigh the $Mg_2P_2O_7$.

§ 312. The following can be recommended as a reliable method for estimating phosphorus in pig iron :—

Take sufficient iron in the form of fine turnings to yield about 15 grains of phospho-molybdate of ammonium. For Cleveland or Northampton pig iron containing 1 to 2 per cent. of phosphorus use 10 to 15 grains and increase the amount in proportion as the phosphorus is less.

Place the iron in a large beaker, add cautiously 10 c.c. of nitric acid of specific gravity 1·40, and when the action has subsided add 20 c.c. hydrochloric acid free from sulphur; evaporate nearly to dryness; then add another 20 c.c. of hydrochloric acid and again evaporate until nearly all acid is removed. Dilute to 50 c.c., filter and thoroughly wash. If the solution exceeds 90 c.c. then evaporate down to that amount and transfer to a 150 c.c. flask. Heat to boiling; add 15 c.c. of ammoniacal solution of ammonium molybdate, then nitric acid of specific gravity 1·20 (free from nitrous acid) drop by drop until the precipitate becomes yellow and granular. Allow to stand half an hour and filter through double weighed filter papers; wash with water containing ammonium nitrate; then with distilled water; dry for three hours at a temperature of 110° C. and weigh, transferring outer filter to the scale-pan containing the weights. Precipitate contains 1·63 per cent. of phosphorus. Or weight multiplied by ·0163 gives the phosphorus in the sample taken.

The ammoniacal solution of ammonium molybdate is prepared as follows :—Dissolve 200 grammes of ammonium molybdate in weak ammonia (300 c.c. ammonia of specific gravity ·880 in 700 c.c. of water) and make up to 1 litre. Then add 2 grammes of magnesium chloride and allow the solution to settle for a week. Syphon off the clear liquor for use.

The filter papers are prepared as follows :—Take two Swedish filter papers as nearly equal in weight as possible; fold one and cut off apex (Fig. 79); then trim the other with scissors until they exactly counterpoise and arrange in funnel so that there are four thicknesses of paper all round; the inner one contains the precipitate, the outer one with apex cut out is placed on the same scale-pan as the weights.

Fig. 79.

§ 313. Mr. E. F. Wood of Pittsburg has described in the Chemical News a modification of the molybdate method of estimating phosphorus in steel :—

"A series of experiments were undertaken with the view of discovering a rapid method of estimating phosphorus which resulted in the adoption of the following chromic acid process :—

"It is well known that phosphorus cannot be estimated in steel by the molybdate process without evaporation and ignition to destroy some interfering substances. The modified method is conducted as follows :—Place in a 200 c.c. beaker, 1·63 grammes steel, add 30 c.c. nitric acid (specific gravity 1·2); when violent action has ceased, boil till the residue is dissolved and the solution concentrated to 15 c.c.; add 15 to 18 c.c. of a solution of 50 grammes of chromic acid in 1 litre of nitric acid (specific gravity 1·42), boil down to 15 c.c.; rinse into a beaker using as little water as possible; so as not to exceed 8 c.c.; cool to 40° C. or less; add 70 to 80 c.c. of ammonium molybdate solution warmed to 30° or 40° C.; shake violently for several minutes, then set aside for 15 minutes. Prepare a No. 1 Swedish filter paper 6 c.m. in diameter; dry in water oven for 30 minutes at 100° C. and weigh rapidly to within 1 milligramme. Remove most of the supernatant liquid with a syphon; gather precipitate on to filter; wash with water containing

2 per cent. of nitric acid four to six times; dry precipitate for 50 minutes at 100° and rapidly weigh. The precipitate contains 1·63 per cent. of phosphorus, and, as 1·63 grammes of steel were taken, each milligramme of the precipitate is equivalent to ·001 per cent. of phosphorus."

(*a*) The molybdate solution is prepared by placing in a beaker 1200 c.c. water; then 1 lb. of molybdic acid is stirred in; then 700 c.c. of ammonia (specific gravity ·9) is stirred in until the acid is dissolved; 400 c.c. of nitric acid (specific gravity 1·42) are then added and the solution cooled. Place in another beaker 715 c.c. of water; add 6·15 c.c. of nitric acid; then 600 c.c. of first solution and well mix the whole. Let it stand 24 hours, then filter for use. The process is not applicable to pig iron, as strong nitric acid precipitates silica in a form difficult to free from phosphorus.

ESTIMATION OF CHROMIUM IN IRON AND STEEL.

§ 314. Take 20 to 50 grains according to the amount of chromium present; dissolve in strong hydrochloric acid; add a little nitric acid and evaporate to dryness to remove silica, graphite, etc. Heat strongly to destroy organic matter. Take up with hydrochloric acid; dilute and pass a current of sulphuretted hydrogen to remove any copper, arsenic, etc.; boil to remove sulphuretted hydrogen and precipitate iron, chromium and aluminium with ammonia. Separate chromium by fusion and estimate it as lead chromate as described in § 194.

§ 315. Mr. J. O. Arnold adopts the following excellent plan:—

"Dissolve in hydrochloric acid; evaporate slowly to dryness; transfer to platinum dish; crush to a powder

with glass rod and fuse with one part sodium carbonate and one part potassium nitrate. When the fusion is complete, allow to cool; transfer to beaker; boil with water, occasionally stirring with a glass rod; remove dish, well washing with boiling water; cool; add a few drops of alcohol to decompose any manganate, and allow the oxides of iron and manganese to settle. Decant clear liquid; wash by decantation; filter the residue and well wash. The clear filtrate contains the silicon and chromium; add 20 c.c. of hydrochloric acid a little at a time till the solution is acid, keeping the beaker covered with clock glass. Boil to remove all nitrous fumes and carbonic acid; add dilute ammonia till alkaline and again heat nearly to boiling. Filter off precipitate which contains the chromium; well wash; dissolve in hydrochloric acid; evaporate to dryness to remove silica; take up with hydrochloric acid; dilute largely with hot water; filter off silica; well wash and precipitate the chromium as before with ammonia in the least possible excess. The precipitate is now free from silica and alkalies. Filter; wash; dry and ignite in a weighed platinum crucible, when the resulting Cr_2O_3 multiplied by ·6862 gives the amount of chromium present in the sample taken."

ESTIMATION OF TITANIUM IN IRON AND STEEL.

§ 316. When iron or steel containing titanium is dissolved in acid and the solution evaporated for silica in the usual way, part of the titanium remains with the silica and part goes into the solution with the iron. One of the best methods yet devised is Riley's, although this is far from perfect. Place 25 grains of the iron in a conical beaker and digest with fuming nitric acid, add hydrochloric acid occasionally and boil. Evaporate to dryness; heat strongly; take up with hydrochloric acid

and water; filter off the insoluble silica which retains some titanic acid; dry and fuse with potassium bisulphate; grind the fused mass to a fine powder and treat with cold water, when the titanium passes into solution. Mix this solution with the above acid filtrate; treat with sodium thiosulphate; boil until the excess of sulphurous acid is driven off and the higher oxides of iron and titanium are reduced to the lower oxides; then nearly neutralise with ammonia; add sodium acetate and a few drops of nitric acid so that the precipitate is distinctly red; boil and filter. Drive off the nitric acid from the precipitate with sulphuric acid. Fuse the residue with potassium bisulphate; dissolve in cold water as before; boil for some hours and allow to stand for several hours; filter off the titanic acid; wash with dilute sulphuric acid; dry; ignite and weigh the TiO_2.

Titanium may be estimated in pig iron by boiling a comparatively large quantity in hydrochloric acid, adding fresh acid from time to time so as to thoroughly extract all the iron. The solution is then thrown on dried counterpoised filters encircling each other (Fig. 79), and the filters well washed to remove all the iron. The residue is then treated with solution of potash until the whole of the silica is removed. Well wash and dry at 118° C. until the weight is constant. This gives the graphite and titanium oxide; ignite; fuse residue with potassium bisulphate, and digest with cold water to extract the titanium as above. (For further particulars see Crooke's Select Methods, page 191.)

ANALYSIS OF IRON ORES, SLAGS.

§ 317. The following tables give the composition of different ores of iron; also slags from various furnaces, and are intended as a general guide to know what to

look for. Occasionally, other elements, such as chromium and titanium, are present :—

	Magnetic Iron Ore.	Red Hematite	Brown Iron Ore.	Spathic Ore.	Clay Ironstones.		Cleveland
	Dannemora.	Ulverstone.	Dean Forest.	Brendon, Somersetshire.	Blackband, Lowmoor	Dudley.	Eston.
Ferric oxide (Fe_2O_3)	27·55	93·23	90·05	·81	1·45	·40	3·60
Ferrous ,, (FeO),	58·03	—	—	43·04	36·14	45·86	39·92
Manganese oxide (MnO),	·10	·23	·08	12·64	1·38	·96	·95
Alumina (Al_2O_3),	·29	·63	·14	·01	6·74	5·56	7·86
Lime (CaO),	·38	·05	·06	·28	2·70	1·37	7·44
Magnesia (MgO),	·61	—	·20	3·63	2·17	1·85	3·82
Potash (K_2O),	—	—	—	—	·65	—	·27
Silica (SiO_2),	12·54	4·90	·92	·07	17·37	10·68	8·76
Carbon dioxide (CO_2),	·12	—	—	38·86	26·57	31·02	22·85
Phosphorous pentoxide (P_2O_5),	—	—	·09	—	·34	·21	1·86
Sulphuric acid (SO_3)	—	·09	—	—	—	—	—
Sulphur,	·04	—	—	—	—	—	·11
Iron pyrites (FeS_2),	—	·03	—	—	·10	·10	—
Water,	·11	·56	8·22	·18	1·77	1·08	2·77
Organic matter,	—	—	—	—	2·40	·90	—

Composition of Blast Furnace Slags.

Silica,	43·07	31·46	27·48	42·96
Alumina,	14·85	8·50	22·28	20·20
Lime,	29·00	52·00	40·12	10·19
Ferrous oxide,	2·53	·79	·80	19·80
Manganous oxide,	1·37	2·38	·20	1·53
Magnesia,	5·87	1·38	7·07	2·90
Calcium sulphide,	1·90	2·96	2·00	1·32
Alkalies,	1·84	—	—	1·10

Composition of Refining Slag, etc.

	From a Refinery.	From a Puddling Furnace.	From a Re-heating Furnace.
Ferric oxide, - -	—	8·27	—
Ferrous oxide, - -	65·52	66·32	76·73
Silica, - - -	25·77	7·71	15·15
Manganous oxide, -	1·57	1·29	1·51
Alumina, - - -	3·60	1·63	1·95
Lime, - - -	·45	3·91	trace
Magnesia, - - -	1·28	·34	trace
Sulphur, - - -	0·23	1·78	1·36
Phosphorus, - -	1·37	—	—
Phosphoric acid, -	—	8·07	2·22

All ores, slags and products to be subjected to analysis, must first be properly sampled, crushed to a fine powder and passed through a sieve with at least eighty meshes to the linear inch, then dried at 100° C. If the amount of moisture is desired, the analysis must be made on the sample without previous drying.

§ 318. (*a*) *Determination of Moisture and Combined Water.* Take 100 to 200 grains of the substance; place in porcelain dish and heat at 100° C. in a water oven until the mass ceases to lose weight. This gives the hygroscopic moisture. For combined water, as in case of brown hematites, 25 grains are placed in a bulb tube of hard glass (B), one end of which is connected with a U-tube containing chloride of calcium, to dry the air passed through, and the other end with a similar weighed tube to absorb the water driven off from the ore. The bulb is heated by a Bunsen burner. The increase in weight gives the amount of water present in the sample taken. The tube and corks must be perfectly dried before the

experiment (Fig. 80). A is drying tube for air, containing calcium chloride; B the bulb tube; C the absorption

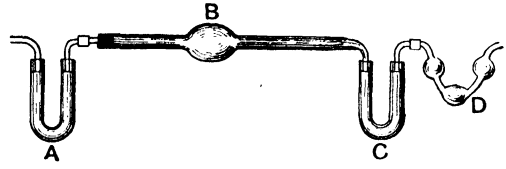


Fig. 80.

tube containing calcium chloride; D contains sulphuric acid to indicate the rate the air passes and to prevent moisture passing into the calcium chloride tube. The delivery tube of D is attached to an aspirator in order to produce the required current of air. In the absence of much carbonic acid a weighed portion is sometimes heated to redness in a porcelain crucible and the loss stated as organic matter and water. In this case the carbonic acid, if any, is deducted, and also the amount of oxygen absorbed in converting protoxide of iron into trioxide, after estimating the amount of carbonic acid and protoxide of iron in the ore.

(*b*) *Estimation of Carbonic Acid.* For this purpose the apparatus in Fig. 69 or 72 is employed. Twenty to twenty-five grains of ore are treated with hydrochloric acid and the carbonic acid absorbed by soda lime. The presence of carbonic acid in an ore may be ascertained by adding dilute hydrochloric acid to a portion in a test-tube and observing whether any effervescence occurs and whether the gas evolved turns lime water milky. Slags do not contain carbonic acid.

(*c*) *Insoluble Matter.* If it is found that a moderate portion of the substance is insoluble in strong hydrochloric acid; treat 200 grains with strong hydrochloric acid, add a little nitric acid, boil for an hour, evaporate

to dryness, take up with hydrochloric acid, dilute, filter and well wash the residue with hot water. Transfer residue to a platinum crucible; ignite and weigh. This residue may contain silica, titanium oxide, alumina, oxide of iron, lime and magnesia. Reserve for further treatment.

(*d*) *Hydrochloric Acid Filtrate from* (*c*). Add strong nitric acid, or a few crystals of potassium chlorate and boil till chlorine ceases to come off; carefully nearly neutralise with ammonium carbonate; add two ounces of a strong solution of pure ammonium acetate and boil for two or three minutes. Allow precipitate to settle; decant liquid through filter and wash precipitate two or three times by decantation; filter off the precipitate and well wash. This precipitate consists of basic acetates of iron and aluminium and phosphoric acid. Reserve for further treatment.

Make filtrate alkaline with ammonia; cool; add 10 c.c. of bromine; shake; cork up and allow to stand some time. Add ammonia in excess, boil, filter off the hydrated oxide of manganese and estimate as Mn_3O_4 as in § 306.

The filtrate from the manganese oxide contains lime and magnesia. Concentrate by evaporation; add ammonia, then ammonium oxalate in excess; allow to stand for several hours; filter; wash; dry; burn paper; gently heat at first and strongly ignite at finish to convert the oxalate into CaO.

The filtrate from the lime precipitate contains magnesia and potash. Add ammonia in excess, then a solution of ammonium sodium phosphate; heat gently and well stir with a glass rod. Allow to stand several hours; filter; well wash with water containing ammonia; dry; transfer to a weighed platinum crucible; ignite gently at first, then strongly, and weigh the $Mg_2P_2O_7$; this multiplied by ·36 gives the amount of MgO in the sample taken.

Acidify filtrate with hydrochloric acid; evaporate to

dryness; dissolve in water; add a little hydrochloric acid; then to the clear liquid add a concentrated solution of platinum chloride in slight excess; evaporate to small bulk on water bath; add an equal bulk of alcohol; allow to stand some time; filter through weighed paper; dry at 100° C. and weigh the ($PtCl_4$,2KCl); this multiplied by ·19 gives the amount of K_2O in the portion analysed.

It would be preferable to determine the alkalies in a separate portion as in § 276 (*f*).

(*e*) *Treatment of the first Precipitate from the Hydrochloric Acid Solution containing Iron, Alumina, etc.* Dissolve in hydrochloric acid and make up the solution to 500 c.c. Take 250 c.c., which represent half the amount of ore taken for analysis, and proceed to estimate phosphorus as described in § 311.

The remaining 250 c.c. are then boiled in a platinum basin with the addition of caustic soda in excess, which precipitates the iron as oxide. Filter; wash; dry; ignite and weigh the Fe_2O_3; this gives the total amount of iron in the ore.

The filtrate contains alumina and phosphoric acid. Acidify with hydrochloric acid; boil; add a few crystals of potassium chlorate to destroy organic matter; nearly neutralise with ammonia; then add ammonium carbonate in excess; allow to stand several hours in a warm place; filter; wash; dry and ignite. Weigh the Al_2O_3. This precipitate and the ignited residue contain some phosphoric acid. Dissolve in aqua regia; estimate the phosphoric acid by ammonium molybdate as described in § 311. After deducting the P_2O_5, the difference gives the true amount of alumina.

(*f*) *Treatment of the insoluble residue.* Fuse in a platinum dish, with four to six times the amount of potassium and sodium carbonates; dissolve in dilute hydrochloric acid; evaporate to dryness; well moisten

with hydrochloric acid; allow to stand for an hour; add water; boil and filter off silica; wash; dry; ignite and weigh the SiO_2.

The filtrate containing alumina, iron, lime, etc., is then treated as already described and the total amounts of the various oxides thus ascertained.

For method of determining the amounts of ferrous and ferric oxides see § 285.

A method of effecting the solution of difficultly soluble ores and slags is given in § 286.

ANALYSIS OF FURNACE GASES.

§ 319. It is not the intention in the present chapter to deal with refined methods of gas analysis, such being beyond the scope of this work. In many cases such methods cannot render the best service, and it will often be possible to learn all that is desired by simple means. Particulars of various suitable apparatus contrived by Bünté, Elliot, Hempel, Orsat and Stead may be found in technical periodicals and modern text-books.

§ 320. The following description of Bünté's apparatus (Fig. 81) and the directions for its use will, it is hoped, assist those who, in special cases, wish to use the other arrangements.

A is a burette capable of holding about 110 c.c., and graduated into fifths of a cubic centimetre; *a* communicates with the gas to be tested; *x* leads either to a water supply C, or to an aspirator D; the three way cock *k* places A either in communication with the sample of gas or with the funnel *d*. The use of the burette B will be explained afterwards.

§ 321. The principal solutions required are caustic potash, cuprous chloride, and pyrogallic acid. Commercial

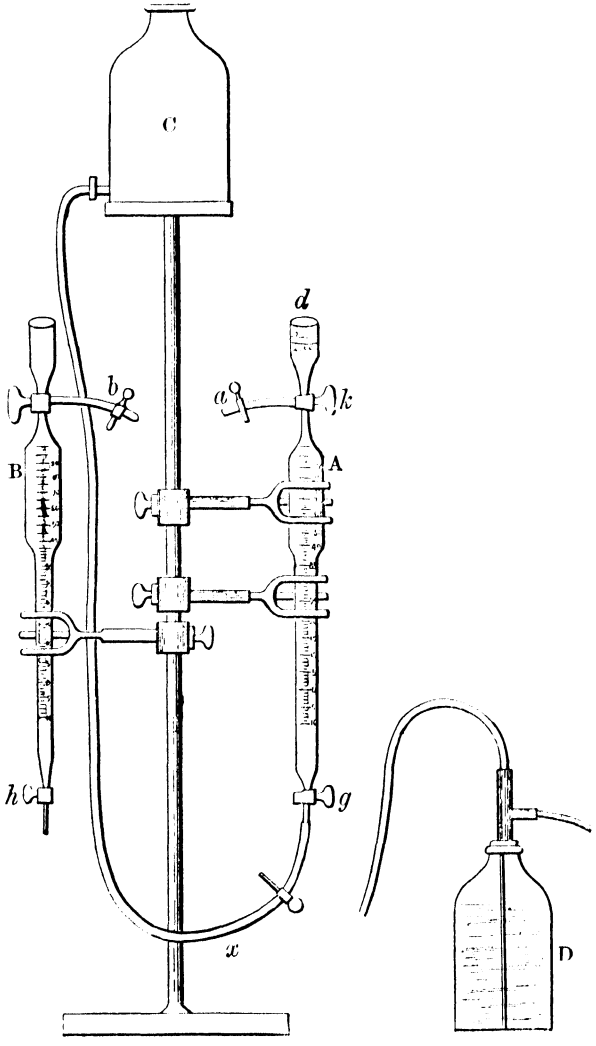


Fig. 81.

potash is sufficiently pure for such determinations as are here contemplated. A saturated solution may be diluted with from two to five times its bulk of water, so as to have a specific gravity of 1·2 to 1·1, according to the quantity of carbonic acid present in the gas. Cuprous chloride may be prepared by dissolving 4 parts of finely-divided copper and 5 parts of the black oxide of copper in strong hydrochloric acid, then adding one fourth its volume of water to the decanted solution and also about 5 c.c. of stannous chloride to 2 litres of solution, neglecting the white precipitate which will dissolve in hydrochloric acid (specific gravity 1·1) when required to form more solution. If a coil of copper wire is put into the solution and the bottle kept well stoppered, it will remain of a brown colour.

Another mode of preparation is to well mix 2 parts of powdered copper oxide with one of common zinc powder (obtained from zinc condensers) and then to add the mixture very gradually to crude concentrated hydrochloric with constant stirring, dissolving the white sediment as it forms by adding more acid. Let the yellowish brown liquid settle for a few seconds, then pour the clear liquid into a flask capable of holding several times the volume of the solution; fill up with recently boiled water and close air-tight. White cuprous chloride separates, which should be well washed with distilled water, and nearly all dissolved in hydrochloric acid (specific gravity 1·1); stannous chloride and copper wire being added as in the preceding case.

Pyrogallic acid is dissolved as required in from four to six times its weight of water, and rendered alkaline in the burette, into which has been put about fifteen times the quantity of potassium hydrate in solution.

§ 322. If the gas to be examined is to be taken from a flue or other place where it has not been at rest long enough to mix thoroughly, it should be withdrawn by

means of a tube with fine slit reaching along the side of the tube. The size of the aspirator and the rate of flow will depend in each case upon the period over which it is proposed each examination shall extend. In most cases it will be advisable to draw the gas through a plug of asbestos to prevent soot and dust reaching the receiver.

§ 323. In addition to the burette, re-agents, and means of collecting the gas, there will be required a supply of water free from excess of air, and of fairly constant temperature (a gallon will be ample for one analysis), an aspirator D (Fig. 81), and one or two beakers. If the hydrogen and hydrocarbons have to be determined, the burette B (Fig. 81), a porcelain tube and copper oxide and a hard glass tube containing palladium black are required.

§ 324. (*a*) To conduct an analysis, attach the water supply *c* to burette A, as in Fig. 81 ; open the pinchtap and taps *g* and *k*, and let the water rise steadily until it has filled the tap *k* and reaches about half way up the funnel *d*. Close the taps ; detach the water supply, and attach in its place the aspirator D ; connect the tube delivering the gas with *a*, and turn the tap *k*, so that the gas may enter the body of the burette ; turn the tap *g*, and draw in enough gas to occupy 100 c.c. Close taps *k*, *g*, *a* ; place glass cup over *a*, and adjust the temperature by turning the water supply over the outside of the burette for a short time ; then adjust the pressure by turning tap *k* so that some gas may escape if its pressure is in excess, or some water from funnel *d*, if the internal pressure is less than that of the atmosphere, taking care that sufficient water is quietly supplied to the funnel to prevent any risk of air entering. Read off the volume of gas, and if the under side of meniscus is exactly at zero, no calculation for the volumes of carbonic

oxide, oxygen and carbonic acid will be required, as the subsequent readings will give the percentages of each constituent; if there is a difference, it must be recorded and the results corrected accordingly.

(*b*) Attach the aspirator; open tap *g* and withdraw most of the water; then close tap *g*; detach the aspirator; put potash solution in a beaker, and immerse in the potash the point of the burette A; turn the tap *g*, when some of the potash will be drawn up; close the tap; detach burette from its stand and well shake, keeping one hand over the funnel *d*; add more potash, shake and repeat the operation until the volume of gas does not diminish; adjust for temperature and pressure and note the volume; this gives the percentage of carbonic acid or data for calculating it. It is obvious that the absorbents may be introduced through the funnel *d* when the use of an aspirator is inadmissible.

(*c*) Remove some of the potash solution by means of the aspirator; replace it by pyrogallic acid and determine the percentage of oxygen in the same way as that of the carbonic acid.

(*d*) Before the carbonic oxide can be determined, the burette must be thoroughly washed out, to remove every trace of the pyrogallic solution. This is done by opening the taps *g* and *k*, keeping *d* constantly full by means of a stream of water so conveyed as to prevent the formation of air bubbles. If the gas cannot be subjected to the washing without altering its composition, the tube B must be connected with A by means of the taps *a* and *b*, and the gas transferred thus:—Fill the burette B with water by connecting *h* with C; then detach; connect with aspirator; open *a* and *b*, when the gas will be drawn from A to B, and in the same way transferred back again when A has been thoroughly washed.

(*e*) The carbonic oxide is now absorbed by means of the cuprous chloride solution which may be introduced to the gas while in the burette B, so that when it is transferred to the clean burette the volume may be at once determined, after adding a little potash to absorb any acid vapours which have been evolved, taking precautions as usual to ensure uniformity of temperature and pressure.

§ 325. The hydrogen and hydrocarbons may be estimated together in the gas from which the carbonic acid, oxygen and carbonic oxide have been abstracted, by passing the mixed gases, after being measured, slowly to and fro over copper oxide in a porcelain tube heated to redness and arranged between the taps *a* and *b* (Fig. 81). Cool the gases to the proper temperature; measure; absorb the carbonic acid by potash and measure again; the difference between the first and last measurements will give the total volume of hydrocarbons and hydrogen. As furnace gases seldom contain a notable quantity of any hydrocarbon except marsh gas (CH_4), and as marsh gas yields its own volume of carbonic acid, the absorption by potash may usually be taken to represent the marsh gas present. The residual gas is nitrogen.

§ 326. Suppose the gas taken for analysis to have the following composition :—

Carbonic acid (CO_2),	9·51
Oxygen (O_2),	—
Carbonic oxide (CO),	19·53
Hydrogen (H_2),	3·20
Marsh gas (CH_4),	6·69
Nitrogen (N_2),	61·07
	100·00

The results would be stated in the note-book thus:—

	Indicated Volume.	Difference in c.c.	Percentage.
Volume taken, - -	+ 3·00 cc.		
,, after potash,	- 6·8	9·8	9·51 CO_2.
,, after pyrogallic acid,	- 6·8	0·0	0·00 O_2.
,, after cuprous chloride,	-26·9	20·1	19·53 CO.
,, after passing over oxide,	-30·2	3·3	3·20 H_2.
,, after potash, -	-37·1	6·9	6·69 CH_4.
,, of residual gas, 100 - 37·1,	—	62·9	61·07 N_2.
	—	103·0	100·00

§ 327. (*a*) To determine free hydrogen, measure about 25 c.c. of gas in the burette A from which carbonic acid, oxygen and carbonic oxide have been abstracted and estimated; mix with two or three times its volume of air and note the total volume. Now place 20 grains of palladium black, or an equivalent quantity of asbestos coated with 30 per cent. of palladium sponge, in a U-tube, and connect with the taps *a* and *b* (Fig. 81); then pass the gas forwards and backwards over the palladium, which is kept heated to about 90° C.; by this means the hydrogen unites with the oxygen of the air, forming water. Allow to cool, then measure; two thirds of the contraction in volume is due to hydrogen.

(*b*) Working with the above sample, and taking, say 24·82 c.c., the contraction would be 1·68, for 29·04 per

cent. is carbonic acid and carbonic oxide; so that 3·2 parts hydrogen are contained in 100 – 29·04 = 70·96; therefore 24·82 parts will contain $\frac{24{\cdot}82 \times 3{\cdot}2}{70{\cdot}96} = 1{\cdot}12$; and 1·12 plus one third = 1·68.

Having read off the amount of the contraction, which in the present supposition is 1·68, and from this deducted one third for oxygen, it is found that 24·82 parts of gas contain 1·12 parts hydrogen, and as 70·96 parts of the residual gases contain the whole of the hydrogen in 100 parts of the original sample, the percentage of hydrogen is $\frac{70{\cdot}96 \times 1{\cdot}12}{24{\cdot}82} = 3{\cdot}20$.

(*c*) If, after careful working, it is found that the quantity of hydrogen does not agree by the two methods, the difference is probably due to the presence of heavier hydrocarbons, the analysis of which is very difficult to perform successfully without considerable experience.

The palladium must be dried and revivified by passing a current of heated air occasionally through the tube; always doing so before laying it aside for any length of time.

VOLUMETRIC ANALYSIS; OR DETERMINATION BY VOLUME.

§ 328. By this method, the estimation of the amount of a given body is effected by using re-agents of known strength called "Standard Solutions." The process is generally rapidly performed, and in many cases is as exact as the "Gravimetric way." It is essential that the termination of the re-action should be recognised with certainty (which somewhat limits the application of the

method), and that all experiments should be conducted under identical conditions as to time, temperature, etc.

In this work it is only proposed to deal with those processes which the ordinary metallurgist is likely to require.

§ 329. Volumetric methods may be conveniently classified under three heads, viz. :—

1. Where the determination is effected by saturation of another substance of opposite properties; used for acids, alkalies, etc.

2. Where the determination is effected by a reducing or oxidising agent of known power; such as bichromate of potash, which is used to oxidise, and sodium thiosulphate, which is used for reduction.

3. Where the determination is effected by precipitating a definite compound; such as silver chloride by a solution of common salt.

§ 330. The measuring vessels employed in this system are flasks, pipettes, burettes and tubes.

(*a*) Measuring flasks having a large body and long neck, with one mark, which indicates that the vessel, when filled exactly to the mark with a liquid, such as water, contains a definite and known quantity at a given temperature. The neck should be moderately wide and fitted accurately with a ground glass stopper. The mark should occupy about the middle of the neck.

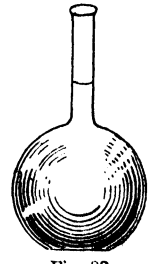


Fig. 82.

In some cases, it is necessary to have a stoppered vessel, with several graduations, the flask then

takes the form of a cylinder, generally called a test mixer.

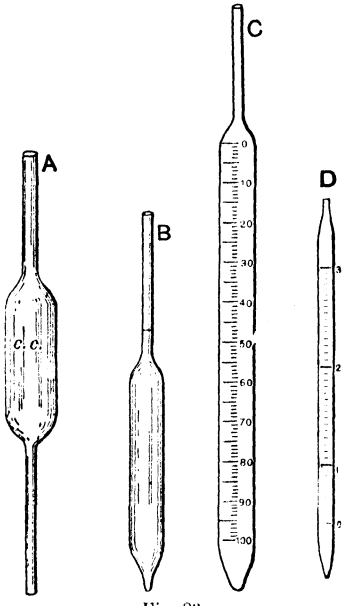


Fig. 83.

(*b*) Pipettes are glass vessels of the shape shown in the accompanying (Fig. 83, A–D), with one mark on the neck for delivering a definite volume of liquid, the most common being the 50 c.c. and 10 c.c. pipettes. They are filled by suction, until the liquid rises a little above the graduation line, then closed with the thumb, and the liquid allowed to run out until it stands just level with the mark.

Graduated pipettes divided throughout their whole length are also employed for small quantities, so that 1 c.c. or a fraction of this may be delivered.

(*c*) The burette (Fig. 84) is most generally employed for measuring the liquids used in an assay. This useful vessel was invented by Gay-Lussac, and after passing through various modifications, has arrived at great perfection. It is a narrow cylindrical tube, generally graduated into cubic centimeters; the 50 c.c. and 100 c.c. burettes being most commonly used, although some experimenters prefer the grain divisions. The narrow portion at the bottom is connected with a glass jet by means of a piece of caoutchouc tubing, which permits of the burette being closed by means of a pinch-tap. But this is objectionable in some cases, as caout-

chouc is acted on by the liquids employed. At the present time, burettes are made with glass stop-cocks, which, when properly fitted, leave nothing to be desired.

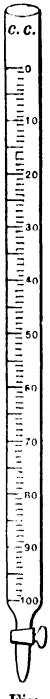


Fig 84.

To charge a burette, a small glass funnel placed in the top is convenient, and the liquid poured in until it reaches above the zero. Then open the tap cautiously, and allow the liquid to run out, drop by drop, till it sinks to the zero mark.

(*d*) The proper reading off is of great importance. The eye must be on a level with the fluid, and the reading taken from the bottom of the curve which most liquids make on the surface in narrow glass tubes. All uncertainty in reading off is removed by the use of Erdmann's float (Fig. 85). It consists of an elongated glass bulb, narrower than the burette and weighted at the lower end with mercury. The top part of the float contains a small glass ring, by which it can be lifted in or out by a bent wire; a line is scratched round its centre, and the coincidence of this line with the graduation mark on the burette is accepted as the true reading.

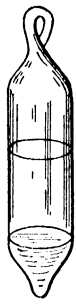


Fig. 85.

(*e*) The correctness of the graduation of a burette may be tested by filling the instrument with water at 15°·5 C., then running 10 c.c. into a weighed flask and weighing; then repeating with another 10 c.c., and so on for the rest. If correct, 10 c.c. will weigh 10 grammes, but differences of ·01 gramme may be disregarded.

It should be mentioned that the volume of every body varies with the temperature, and that the divisions on a measure for liquids, as well as the strength of a standard solution, are applicable for one temperature only. Stan-

dard solutions are called "normal" when 1 litre contains an atomic proportion of a univalent substance such as silver, sodium, etc., or, in the case of salts of univalent substances, a molecular proportion; thus in the normal caustic soda solution (§ 331, *b*), 1 litre contains 40 grammes of sodium hydrate. In the case of bivalent substances, one half the atomic weight of an element, or one half the molecular weight of its salts is contained in 1 litre of solution. In the case of trivalent substances, one third the atomic proportion to the litre is employed. Deci-normal solutions are made one tenth the normal strength.

ALKALIMETRY (ANALYSIS BY SATURATION).

§ 331. Methods based on this principle depend on the fact that potash, soda, ammonia, baryta, strontia and lime combine easily and directly with acids, and that the corresponding carbonates are fully decomposed in contact with stronger acids, giving off carbonic acid. Neutral salts of the above bases do not affect litmus, while the smallest excess of acid or alkali is immediately detected by its turning litmus either red or blue.

(*a*) *Litmus Solution.* This is prepared by digesting half an ounce of litmus with half a pint of distilled water for a few hours and decanting the clear liquid. A few drops of nitric acid are then added, so as to produce a violet colour. It is best preserved in a bottle with an open glass tube through the cork. This tube has a mark scratched on, by which means a uniform volume may be used in each case. To test the indicating power of the litmus solution take 5 c.c. and dilute to 100 c.c.; divide into two parts. To one part add one drop of standard acid, to the other add one drop of standard

alkali, when the solution should be turned red and blue respectively.

(*b*) *Normal Caustic Soda Solution.* Dissolve 40 grammes of pure sodium hydrate in 1 litre of water, which will then contain 31 grammes of Na_2O. One cubic centimetre of such a solution therefore contains ·031 gramme of Na_2O. Sodium hydrate generally contains a little water, so that it is better to take about 43 grammes dissolved in 800 c.c. of water, titrate with normal acid and litmus, then dilute to normal strength.

(*c*) *Deci-normal Caustic Soda Solution.* Take 100 c.c. of the normal solution and make up to a litre with water. This will then contain about 3·1 grammes of soda, Na_2O, per litre.

(*d*) *Deci-normal Sodium Carbonate Solution.* Take about 10 grammes of pure sodium bicarbonate, heat strongly in a platinum dish until no more carbonic acid is given off. When cold weigh out 5·3 grammes of the sodium carbonate, Na_2CO_3, obtained. Dissolve in water and make up to a litre.

(*e*) *Normal Sulphuric Acid.* Take 30 c.c. of pure sulphuric acid of specific gravity 1·840; mix with three or four times its volume of water; allow to cool; then make up to a litre with water. This solution will contain rather more than 49 grammes of H_2SO_4 per litre.

Place 10 c.c. of deci-normal sodium carbonate solution in a beaker; add one measure of litmus solution; then run in a few c.c. of the acid and boil; continue the addition of acid, boiling each time to expel carbonate acid until the colour is exactly neutralised. Suppose 8·9 c.c. of acid are required, then 890 c.c. of acid will be required for one litre of the standard; remove excess of acid from the burette and dilute to 1 litre; 10 c.c. of each solution should exactly neutralise each other.

The strength may also be tested by precipitating with barium chloride.

(*f*) *Normal Oxalic Acid* ($C_2H_2O_4,2OH_2$).

This solution may be obtained by dissolving a weighed portion of pure oxalic acid in distilled water; 63 grammes of pure re-crystallised oxalic acid is dissolved in 1 litre of water; therefore 1 c.c. contains ·063 gramme, and will neutralise 1 c.c. of the standard alkali. As deci-normal solutions are chiefly used it will be convenient to take one tenth the above quantity and make up to a litre with water.

§ 332. *Mode of Conducting an Analysis.*

Weigh 1 gramme of commercial carbonate of soda; dissolve in water; filter off and well wash any insoluble matter. Add one measure of litmus solution, and run in from a graduated burette, standard sulphuric acid, until a claret tinge begins to appear. Boil, to expel carbonic acid, which helps the neutralisation of the alkali, when the blue colour again appears. Continue to add the sulphuric acid, a drop at a time, until the claret tinge again begins to appear.

Suppose 1 gramme of carbonate of soda required 18 c.c. of sulphuric acid, then as 1 c.c. of standard acid neutralises 1 c.c. of Na_2O, which equals ·031 gramme, and $18 \times ·031 = ·558$ gramme of Na_2O, which is equivalent to ·954 gramme of carbonate of soda. The sample then contains 95·4 per cent. of carbonate of soda.

ACIDIMETRY.

§ 333. To determine the amount of acid in a solution or metallic salt, the principles involved are the same as those already described under the head of Alkalimetry.

§ 334. *Estimation of Free Sulphuric Acid in a Copper Sulphate Solution.*

Take half a pint of solution; dilute to a quart; add 1 measure of litmus solution; then run in standard soda solution from a graduated tube until the red colour of the litmus begins to change; take the reading and add one drop more, which, if the right point has been reached, should produce a decidedly blue tint. From the number of c.c. of soda solution required the amount of free acid per gallon is easily computed.

§ 335. *Estimation of Combined Carbon-Dioxide.*

(*a*) The carbonate is soluble in water. Dissolve 1 gramme of the substance in water; filter off any insoluble residue; add about 25 c.c. of standard sulphuric acid and boil until all the CO_2 is expelled. Now add a measure of litmus solution and run in from a burette a portion of standard soda solution until the blue colour is restored. By this process an excess of sulphuric acid is added above that required to displace the carbon-dioxide, and this excess is determined by the soda solution as above.

Suppose that 1 gramme of the carbonate to which 25 c.c. of sulphuric acid have been added, requires 10 c.c. of soda solution, and as 10 c.c. of soda are equivalent to 10 c.c. of sulphuric acid, the amount of acid required to replace the CO_2 is 15 c.c., which indicates 33 per cent. of carbon-dioxide, assuming the base to be present entirely as carbonate. For 1 c.c. of sulphuric acid is equivalent to ·022 gramme of CO_2.

(*b*) *The Carbonate is Insoluble.* Weigh out 1 gramme; place in flask A (Fig. 86) and add a little water. This flask is fitted with an india-rubber bung perforated with two holes. Through one passes the pipette C, which contains strong hydrochloric acid, and is closed at top by a pinchtap. A is connected with the flask B by means of a bent glass tube, which flask contains 15 c.c. of am

monia solution; the wider tube D is partially filled with broken glass, moistened with dilute ammonia. To conduct the operation, warm the flask B so as to fill the whole with ammonia vapours; then run a little acid from C on to the carbonate, which is decomposed, liberating carbonic acid; the latter traverses the bent tube, which must not dip beneath the surface of the ammonia, and is absorbed by the ammonia vapours forming carbonate. When all effervescence ceases on dropping in more hydrochloric acid, heat the liquid in flask A to boiling, so as to expel the last traces of carbonic acid and allow the whole apparatus to cool. Detach the tubes; wash any carbonate of ammonia from them into B; then add sufficient calcium chloride to completely precipitate the carbonic acid as calcium carbonate; boil; filter and wash as quickly as possible, since the ammoniacal liquid absorbs carbonic acid from the atmosphere; then proceed with the precipitate as in § 335 (*a*).

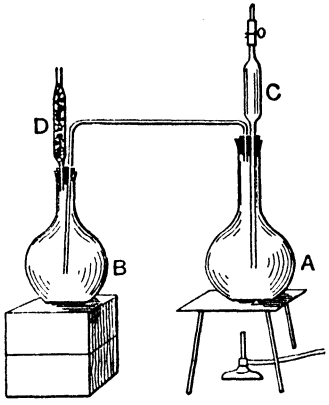


Fig. 86.

EMPLOYMENT OF IODINE AND SODIUM THIOSULPHATE (ANALYSIS BY OXIDATION AND REDUCTION).

§ 336. Sodium hyposulphite, or thiosulphate as it is more properly termed, is a powerful reducing agent; while iodine has an opposite character, being indirectly an oxidising agent. These two bodies, when present in

a solution made alkaline with sodium carbonate, re-act according to the following equation :—

$$2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6,$$

sodium iodide and sodium tetrathionate being formed. If then some substance is present to indicate the point when the free iodine is completely combined with sodium, we have a means of estimating an unknown quantity of that element. The substance thus employed is starch solution, which produces with iodine a blue compound (composition unknown).

(*a*) *Starch Solution.* Take 2 or 3 grains of starch and make into a paste with cold water; then add half a pint of water; boil; allow to settle and decant the clear liquid into a stoppered bottle. A fresh solution should be made every three days.

(*b*) *Standard Sodium Thiosulphate* ($Na_2S_2O_3,5H_2O$). To prepare a deci-normal solution, dissolve 24·8 grammes of the pure re-crystallised salt in water and make up to litre: 1 c.c. therefore contains ·0248 gramme.

(*c*) *Iodine Solution.* A deci-normal solution of pure iodine must contain 12·7 grammes of iodine per litre, or ·0127 gramme per c.c. Weigh the iodine; place it in a litre flask with 18 grammes of pure potassium iodide; add water perfectly cold and place the stopper in flask. When dissolved, add water to make the solution up to a litre. Where iodine solution is added from a burette, the latter must have a glass tap. It is often more convenient to add excess of iodine by a pipette and then to determine the excess by standard sodium thiosulphate.

§ 337. The standard thiosulphate solution may be tested to ascertain its exact strength by means of a standard deci-normal solution of potassium bichromate.

Two hundred and ninety-four parts of bichromate in presence of hydrochloric acid will liberate 762 parts of iodine—

$$K_2Cr_2O_7 + 6KI + 14HCl = 6I + 8KCl + Cr_2Cl_6 + 7OH_2.$$

Therefore 1 c.c. of deci-normal bichromate solution, containing 4·90 grammes per litre, will liberate ·0127 gramme of iodine. A given quantity (say 20 c.c.) of bichromate solution is measured into a small flask, diluted with water till one third full, and 8 to 10 c.c. of a solution of pure potassium iodide and 5 c.c. hydrochloric acid added. Now run in the standard thiosulphate from a burette drop by drop; well shake the flask each time until the iodine has nearly disappeared; then add a few drops of starch solution and continue to run in until the blue colour disappears. Twenty c.c. of bichromate liberate 20 × ·0127 gramme of iodine, and 1 c.c. of thiosulphate, if correct, will convert ·0127 gramme of iodine into iodide, as seen by equation in § 336.

If care be taken in the preparation of the standard iodine solution, it may be used for standardising the thiosulphate. Take 25 c.c. of the thiosulphate solution, add water and a little starch solution, run in iodine solution from a burette until a permanent blue colour persists. Then the quantity of standard iodine solution measures the strength of the thiosulphate.

§ 338. *Estimation of Antimony.*

The metal must exist entirely in the form of trioxide, as the principle on which its estimation is based is its complete oxidation to antimonic acid.

Dissolve ½ gramme of the compound in tartaric acid and water in a flask; neutralise with carbonate of soda; add 20 c.c. of a saturated solution of sodium bicarbonate, then a little starch solution, and run in standard iodine solution until the liquid remains blue for five minutes. One equivalent of antimony requires 2 equivalents of

iodine, so that 1 c.c. of deci-normal iodine solution = ·0061 gramme of antimony.

§ 339. *Estimation of Arsenic.*

This operation is similar to that of antimony. One c.c. of deci-normal iodine = ·00375 gramme of arsenic.

In the case of arseniates the metal partly exists in the state of pentoxide, but some trioxide is generally present. Take 2 grammes; dissolve in water or acid as the case may be; neutralise the acid with carbonate of soda; add a little sodium acetate and acetic acid; boil for some minutes to decompose nitrites and make up the solution to 500 c.c. with water.

Take 50 c.c.; add 20 c.c. of carbonate of soda; then starch solution and potassium iodide as with antimony. The result gives the amount present as As_2O_3 (1 c.c. = ·00495 gramme As_2O_3).

Now pass a current of sulphur dioxide to reduce the pentoxide to trioxide; boil till all SO_2 is expelled; cool and make up solution to 500 c.c. Take 50 c.c. and proceed as before (1 c.c. = ·00575 gramme of As_2O_5). From the second determination the amount of arsenic present as pentoxide is ascertained.

§ 340. *Estimation of Tin.*

Metallic tin or a stannous compound is dissolved in strong hydrochloric acid, a moderately large quantity of a solution of Rochelle salt added, then sodium bicarbonate in excess. If enough of the tartrate solution is present, the solution will be clear; a little starch solution is then added, and deci-normal iodine solution run in until the blue colour is permanent on well shaking the flask. Metallic tin is best dissolved in hydrochloric acid in contact with platinum foil, which forms with it a galvanic couple. A stream of carbon dioxide should also be passed into the vessel while solution is taking place. 254 parts of iodine are equivalent to 118 parts of tin. 1 c.c. of iodine solution = ·0059 gramme of tin.

§ 341. *Estimation of Chlorine in Aqueous Solution of the Gas.*

Take a measured quantity of the water containing chlorine; add a solution of potassium iodide; then run in deci-normal solution of sodium thiosulphate until the iodine has nearly disappeared; add a little starch solution, and continue to run in thiosulphate until the liquid is just colourless.

1 c.c. = ·00355 gramme of chlorine.

§ 342. *Estimation of Hydrocyanic Acid.*

Potassium cyanide when mixed with a solution of iodine removes the colour of the latter as long as any undecomposed cyanide is present, thus—

$$KCy + 2I = KI + CyI.$$

Two equivalents therefore of iodine represent one of cyanogen, *i.e.*, 254I = 26Cy or 65KCy or 27HCy.

Commercial alkaline cyanides are contaminated with oxides and carbonates, which also removes the colour of iodine solution. These must be converted into bicarbonates by adding a saturated solution of carbon dioxide in water.

Weigh 5 grammes of the salt; dissolve in water; make solution up to 500 c.c.; take 10 c.c., which equal ·1 gramme, by means of a pipette; transfer to a flask; dilute to 250 c.c.; add 2 ounces of soda solution and run in from a burette deci-normal iodine solution until the solution just acquires a permanent yellow colour. Suppose 20 c.c. are required, then 20 × ·00325 gives ·0065 gramme, or 65 per cent. of real KCy.

In the case of free hydrocyanic acid, add a slight excess of sodic hydrate, then soda solution as above and proceed in the same way.

ESTIMATION OF CYANOGEN AND CHLORINE BY PRECIPITATION.

§ 343. When silver nitrate is added to an alkaline solution containing cyanogen and well agitated, no precipitation of silver cyanide occurs until all the cyanogen has combined with alkali and silver to form the soluble double cyanide (AgCy, KCy); any further excess of silver nitrate at once produces a permanent precipitate of AgCy, the double compound being destroyed. 108 parts of silver are equivalent to 52 parts of cyanogen—

$$AgNO_3 + 2KCy + KHO = AgCy,KCy + KNO_3 + KHO.$$

This re-action takes place in the presence of sodium chloride, as no precipitate of silver chloride occurs until the silver required to form the above double compound is exceeded.

When no alkali is present the double compound is not formed and the whole of the cyanide is precipitated. In this case 108 parts of silver will be required for 26 parts of cyanogen. The former method is, however, preferable.

§ 344. *Deci-normal Silver Solution.*

10·8 grammes of silver are dissolved in dilute nitric acid placed in a conical beaker, the mouth of which is closed with a funnel to prevent spurting. When solution is complete, wash down funnel and sides of beaker; transfer to litre flask and fill up to mark with water. Instead of using metallic silver, 17 grammes of pure re-crystallised silver nitrate may be dissolved in a litre of water.

The above silver solution may also be used for the estimation of chlorine, the standard liquid being cautiously run in until a precipitate ceases to form. The termination may be very accurately noted by

means of a small quantity of a solution of potassium chromate added to the salt solution. As soon as the whole of the chloride is precipitated, one drop more of silver solution produces a permanent red precipitate of silver chromate which does not disappear on shaking the liquid as before. It is necessary, however, that the free acid should be neutralised by an alkali, such as carbonate of soda, when using potassium chromate as an indicator.

ESTIMATION OF PHOSPHORIC ACID (P_2O_5).

§ 345. Phosphoric acid may be estimated by precipitation as uranium phosphate, using potassium ferrocyanide as indicator. (Atomic weight of Ur = 240.)

This method is based on the fact that when nitrate or acetate of uranium is added to a solution of tribasic phosphoric acid containing ammonium acetate and free acetic acid, the whole of the phosphoric acid is thrown down as double phosphate of uranium and ammonia, which has a light yellow colour. When this precipitate is washed with hot water, dried and burned, the ammonia is volatilised, leaving uranium phosphate $2(UrO_3)P_2O_5$, which contains 80·22 per cent. of uranium oxide UrO_3 and 19·78 of phosphoric acid P_2O_5, therefore $\frac{1}{5}$th of the precipitate may be taken as phosphoric acid. In the presence of fixed alkalies instead of ammonia, the precipitate consists simply of uranium phosphate. By this method, phosphoric acid may be completely removed from the alkalies and alkaline earths; also, with a slight modification, from iron, but not easily from alumina.

Preparation of Standard Solutions.

(*a*) *Sodium Phosphate.* 50·218 grammes of pure crystallised sodium phosphate (which has been freed from moisture by pressing between sheets of filtering paper)

are dissolved in water, and the solution diluted to a litre. 1 c.c. therefore represents ·01 gramme of phosphoric acid.

(*b*) *Uranium Nitrate.* Dissolve sufficient crystallised uranic nitrate, which contains 43·7 per cent. of uranic oxide, so as to obtain a solution with 22 grammes of uranium oxide UrO_3 to a litre. The solution is made at first a little stronger than necessary; its value is then determined, and it is diluted accordingly, thus—50 c.c. of standard sodium phosphate are measured into a beaker, 3 or 4 c.c. of ammonia added, then acetic acid in excess and the mixture gently warmed. The beaker is then brought under a burette containing the uranium solution and portions of it delivered in from time to time, with constant stirring, until a drop taken out with a glass rod and placed on another drop of a solution of potassium ferrocyanide (1 to 20) on a white plate, produces a faint chocolate brown colour. A few moments should be allowed to elapse on the addition of each portion of uranium solution before testing, as the decomposition is not very rapid unless the fluid is considerably heated. Suppose the re-action has been produced with 18 c.c. of uranium solution, that quantity is equivalent to ·50 gramme of P_2O_5. To save calculation, dilute the uranium solution to the same strength as the sodium phosphate, which is done by measuring 180 c.c. and adding water to 500 c.c., or 360 c.c. to one litre. In case the point of saturation in an analysis is overstepped, a portion of the phosphate solution may be added and the analysis corrected.

In order to produce the above-mentioned brown colour a certain excess of uranium is necessary, and this excess varies with the quantity of liquid; for if the uranium solution is titrated so that the amount of fluid is about 4 ounces, it would require a few drops less of the standard solution to produce the same shade of colour than when

the same quantity of phosphoric acid was contained in only 2 ounces.

(*c*) When greater accuracy is required the following plan should be adopted—The uranium solution is put into a burette graduated to $\frac{1}{10}$th c.c.; 20 c.c. of the phosphate solution are measured into a beaker together with the requisite quantities of ammonia and acetic acid, the quantities of which in any analysis should always be as near as possible the same as used in the original titration; the rest of the manipulation is conducted as above described. When a sufficient quantity of uranium solution has been added to produce the distinct colour with a drop of ferrocyanide, the height of the total fluid in the beaker is marked by a slip of gummed paper, the contents emptied, and the glass again filled to the same height with water containing the same quantities of ammonia and acetic acid as were added to the phosphate. The uranium solution is then added, drop by drop, until a drop of the mixture produces the same amount of colour with ferrocyanide as in the previous case; the quantity of uranium so required is deducted from that used for the phosphate, and thus the proportion found which was absolutely required to precipitate the phosphoric acid. If the same plan is pursued in all analyses, great accuracy will be obtained, however variable the amount of fluid. In ordinary cases the difference of the two methods is slight. (Sutton's Volumetric Analyses, p. 219.)

The process is applicable to alkaline and alkaline earthy phosphates, but not to phosphates of sesquioxides, nor is it available in the presence of arsenic acid or any metals giving coloured precipitates with ferrocyanide of potassium, such as copper.

VOLUMETRIC ESTIMATION OF SILVER.

§ 346. This method is based on the powerful affinity of silver for chlorine, and when these bodies are in solution together, they form an insoluble chloride of silver which readily separates from the solution in which it is suspended. For the purposes of assay three solutions of known strength are required.

(*a*) *Standard Solution.* Take a quantity of pure sodium chloride; crush to a fine powder and heat for half an hour to remove every trace of moisture; allow to cool in a desiccator and weigh a sufficient number of grains of salt to precipitate 10 grains of silver, or if the French system of weights be used, a sufficient amount of salt for 1 gramme of silver. This quantity is calculated from the equation

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

As 108 : 10 : : 58·5 : 5·416 grains;

Or as 108 : 1 : : 58·5 : ·542 grammes.

The 5·416 grains of salt are then dissolved in pure distilled water, and the solution diluted to 1000 grains by means of a measuring flask, at 15°·5 C., or the ·542 gramme to 500 cubic centimetres. These quantities may be then multiplied to any convenient extent, thus—30,000 grains of water would contain 30 × 5·416 grains of salt, which should be kept in a half gallon stoppered bottle.

(*b*) *Deci-normal Solution of Salt.* For the purpose of attaining a greater degree of accuracy in the results, 1000 grains of the normal solution are removed and diluted with water to 10,000 grains in a quart bottle by means of a measuring flask. This should be kept stoppered when not in use and labelled "deci-normal solution," to prevent mistakes. This solution contains

$\frac{1}{10}$th as much salt as the standard solution, 1000 grains will therefore precipitate ·542 grain of silver.

In case of gramme weights, 100 c.c. is diluted to 1 litre, which = 1000 c.c. to form a deci-normal solution; 1 c.c. will precipitate ·001 gramme of silver.

(*c*) *Deci-normal Solution of Silver.* Dissolve 10 grains of pure silver in a small quantity of pure nitric acid diluted with twice its volume of water. The solution is very conveniently effected in a conical beaker. When the silver is dissolved, blow out the nitrous fumes; add water; transfer to the 1000 grains measuring flask and fill up to the mark with water. Place this solution in a quart bottle and make it up to 10,000 grains with distilled water, so that 1000 grains of the solution contain 1 grain of silver. Keep it from the light.

This solution is used when too much salt solution has been added to an assay, then, knowing the number of liquid grains of silver solution which has been necessary to precipitate the excess of salt, the true amount of salt for the silver present is ascertained. It is also used in standardising the standard salt solution, to which, if too strong, the necessary amount of water to be added is thereby ascertained. For example, if one thousandth of the deci-normal silver solution is required, then one thousandth of its weight of water would have to be added to the total amount of solution.

With the gramme system 1 gramme of pure silver is dissolved and the solution diluted to 1 litre. Each c.c. contains ·001 gramme of silver.

§ 347. *Testing of Standard Solution.*

As the exact strength of this solution cannot absolutely be relied on, the real working power must be determined by experiment. Take a little over 10 grains of pure silver, say 10·02; place in an assay bottle which holds about 12 ounces; add nitric acid, 1 : 2; put the bottle in

a vessel containing water and boil the water gently until the silver in the bottle is dissolved; then dilute till the bottle is one third full. This method of heating the bottle keeps it at a uniform temperature and prevents it cracking, which would be the case with a higher temperature and unequal heating of the parts.

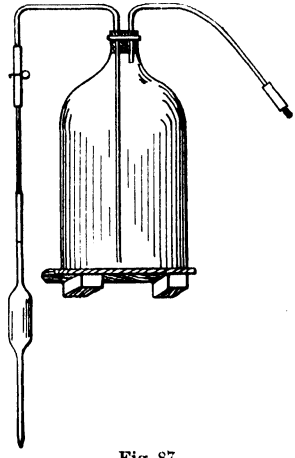


Fig. 87.

(*a*) It will be convenient to fix an india-rubber bung with two holes in the mouth of the bottle (Fig. 87). Through the bung pass two glass tubes, one reaching to the bottom and the other only just through the bung. The latter tube may have a piece of india-rubber tubing on its outer end, which may be fitted with a bit of glass rod, so as to open or close it at will. The outer end of the longer tube should be bent and drawn out to a point, so as easily to pass inside the mouth of the pipette which is used for measuring the quantity of liquid employed.

(*b*) To fill the pipette, stop the bottom up with one finger; remove the glass rod stopper, and blow into the tube until the liquid begins to run into the pipette; then re-place stopper and the liquid will continue to flow into the pipette. When the solution just reaches the mark the flow is discontinued, and the contents, which may be 1000 grains or 100 c.c., run into the assay bottle. Now close with stopper and shake vigorously, giving the bottle at the same time a rotatory motion, by which means the particles of precipitated

silver chloride clot together and quickly subside. When the liquid is clear, add 10 grains of the deci-normal solution from a small pipette; shake as before if a precipitate forms and allow to stand till clear. This must be repeated until no further precipitate is perceived.

(*c*) Suppose that the 10·02 grains of silver required 1000 grains of the normal solution, and that 30 grains of the deci-normal solution were also added, the last 10 grains of which produced no precipitate, then we may assume that only 5 of the last 10 grains were required, so that 1002·5 grains of the normal solution satisfy 10·02 grains of silver, then

10·02 silver : 1002·5 salt : : 10 silver : x = 1000·5 salt, which is near enough for practical purposes.

§ 348. *Assay of Silver Alloys.*

For the sake of practising this method it is well to operate on alloys of known composition, such as the silver coinage. Roll out very thin a clean shilling without annealing, so as to get three or four pieces of about 11 grains each, having the same composition. It is advisable to take in all cases such a quantity of an alloy as contains at least 10 grains of silver, which in the case of our standard coin is 10·83 grains.

(*a*) Suppose 10·88 grains of the alloy have been taken, dissolved in nitric acid as before, and diluted to the same bulk. Now run in 1000 grains of the normal solution, and when clear, add the decimal solution, 10 grains at a time, until the silver is completely precipitated. The amount added may be noted thus—

1000	grains	normal	solution.
10	,,	deci-normal	solution.
10	,,	,,	,,
10	,,	,,	,,
10	,,	,,	,,
10	,,	,,	,,
10	,,	,,	,,
10	,,	,,	,,
10	,,	,,	,,

1008·0 grains of normal solution.

Assuming that the last 10 grains of solution produced no precipitate, this cannot be included. Also we do not know how much of the previous 10 grains were required, so that 5 grains may be considered the requisite quantity, which gives 1006·5 grains of normal solution as the quantity required for 10·88 grains of the alloy.

As 1000 salt : 10 silver : : 1006·5 : $x = 10{\cdot}065$.
As 10·88 alloy : 10·065 solution : : 1000 : $x = 925$.

(*b*) Before an estimation can be made of alloys of unknown composition by this method, it is necessary to know approximately the quantity of the contained silver. For this purpose weigh about 5 grains of the alloy; dissolve in nitric acid and dilute as before; then run in the standard solution cautiously from a graduated 1000 grains burette until only a feeble turbidity is produced, then add a drop at a time until no turbidity is perceived. The bottle must be shaken each time and the liquid allowed to clear itself as usual. The last drops are not reckoned. Suppose 5 grains required 408 grains of normal solution, its amount of silver is computed thus—

$$1000 : 408 : : 10 : x = 4{\cdot}08,$$

the amount required for a correct assay thus—

$$4{\cdot}08 : 10{\cdot}02 : : 5 : x = 12{\cdot}28.$$

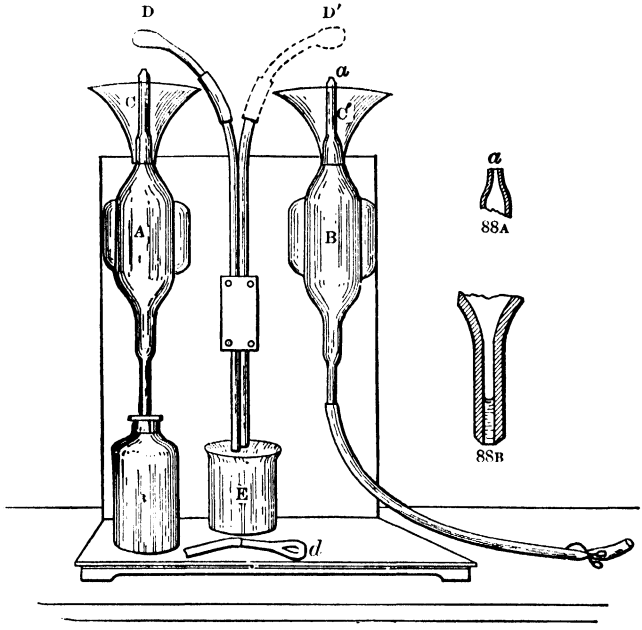
(*c*) With alloys of silver which contain lead, tin, antimony and gold, the portion taken for assay is digested with the smallest quantity of nitric acid as long as red vapours are formed; then boiled with concentrated sulphuric acid till the gold has well settled together; then diluted and the normal solution run in. In the presence of mercury, mercurous chloride may be carried down with the silver and vitiate the result. When the quantity of mercury is small, Levol recommends the addition of 25 c.c. of ammonia and 20 c.c. of acetic acid, which decompose mercury chloride and prevent its precipitation. When much mercury is present the ammonium acetate is not effective, and Debray recommends to drive off the mercury by igniting in a muffle for four hours, in a small crucible made of gas carbon.

§ 349. In mints and assay offices, where a large number of assays are daily made, the apparatus is constructed so as to allow several estimations to be rapidly made. A large glass or stoneware vessel containing the normal solution is placed on a shelf at a convenient height and provided with a tap near the bottom by which any quantity may be run off and measured by the pipette.

(*a*) *The "Stas" double Pipette* (Fig. 88), as used in the Royal Mint, is filled from the large vessel some 6 feet above the level of B. The salt solution introduced from below, rises into A or B (according as the tube is attached), but any overflow is caught by the platinum caps or tubes D D′ (shown in section at *d*), and flows down into the beaker E, which is a receptacle for the waste solution. When the pipette is full, the orifice at the top is covered with the finger and the salt solution is then run into the assay bottle.

Each pipette contains 100 c.c. The platinum caps are attached by india-rubber tubing to glass tubes which pass into the beaker below; these caps are so arranged as to

catch any normal solution which under pressure would be spurted up. If they were not provided the operator



would have to watch the pipette constantly. The glass funnels C C' are merely to retain any solution which the caps fail to catch and would otherwise run down the pipette into the assay bottle. The orifice (*a*) at the top of the pipette to be closed with the finger must be small, and the tube at the lower end of the pipette must be carefully ground and adjusted so as to always retain a drop of the same size. These are shown one-third the actual size in Figs. 88A and 88B. The pipettes are adjusted as nearly as possible to each other, but the assays made by each are kept separate and each is corrected with a separate proof of fine silver.

(*b*) When the normal salt solution has been run into the assay bottles, the latter are stoppered and the con-

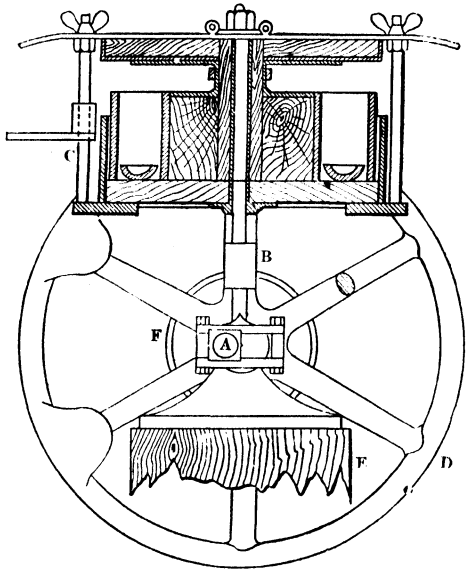


Fig. 89.

tents agitated in an apparatus called a "shaker," which causes the precipitated silver chloride rapidly to subside.

A very perfect form of "shaker" worked by power or by hand is shown in Figs. 89 to 91. It is an American adaptation, as arranged in the Royal Mint and used in conjunction with the "Stas" pipette for rapidly conducting a large number of assays. The general arrangement of the appliance is shown by a plan and by two elevations, both partly in section, from which it will be evident that the block bearing the driving shaft and pulleys is firmly secured to a wooden base E. A circular wooden frame or receptacle for ten bottles is supported by one end of a central vertical rod, which passes through

the guiding block B, while the other end of the rod is provided with a cross-head. The end A of a short crank

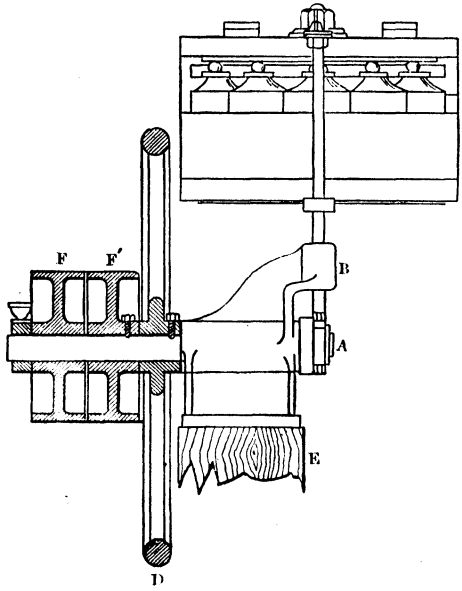


Fig. 90.

fixed to the driving shaft enters a slot in this cross-head, and the revolution of the crank thus imparts a rapid up-and-down movement to the vertical rod and therefore to the bottle frame it supports. Additional steadiness is afforded by the block C through which a rod on the bottle-frame passes. Each bottle is protected by a vulcanite cell and rests on an india-rubber cup, and each set of bottles is retained in position by a padded lid in two portions, only one of which is shown in the plan. This lid is secured by thumb screws. The motion is imparted by shifting a band from the loose pulley F to the fast pulley F'. There is a fly wheel D, and it is usual to

drive the shaker at the rate of about 300 revolutions a minute.

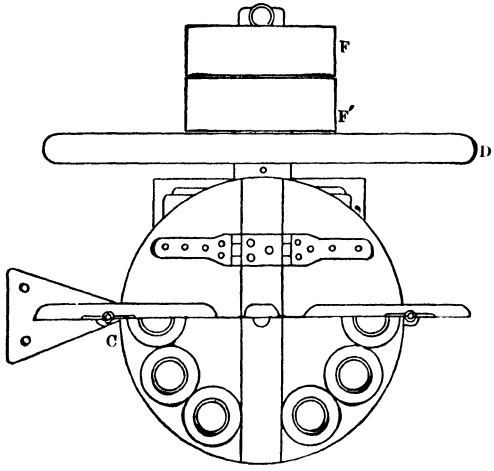


Fig. 91.

Description of Figs. 89 to 91.—A, End of crank. B, Guide block for rod which supports the bottle frame. C, Guide block to steady the frame. D, Fly wheel. E, Beam to which the appliance is fixed. F, Loose pulley. F', Driving pulley.

In practice the normal solution is made from common salt, and the amount of water necessary to make a solution of the requisite strength, assuming the salt to be pure, is added and the exact amount of NaCl determined by experiment. When this is known it is easy to calculate the amount of water or salt to be added so as to obtain a correct standard. It is then again tested to verify its correctness.

INDIAN METHOD OF SILVER ASSAYING.

§ 350. Although this is a gravimetric method it will be more convenient to introduce it here. The cupellation

assay is not considered correct enough, and the volumetric method is not suitable because the high temperature of the climate causes evaporation of the salt solution.

To illustrate this process weigh two portions of pure silver about 20 grains each; place each in a stoppered bottle and dissolve in nitric acid, 1 : 2, by heating the bottles in hot water; blow out fumes; dilute with water; add sufficient hydrochloric acid to precipitate the silver, and shake as usual to collect the precipitate and clear the liquid. Then add one drop more to see if any further silver chloride separates. When the precipitation is considered complete, allow the liquid to remain until quite clear. Siphon off the supernatant liquid; wash two or three times with distilled water, siphoning off each time when clear. Then fill the bottles with distilled water; invert each into a small French crucible full of water and allow to stand in that position until all the precipitate has fallen to the bottom of the crucible. Then remove bottle; pour off as much as possible of the water without disturbing the precipitate; carefully dry the latter at 100° C. and weigh.

$$AgNO_3 + HCl = AgCl + HNO_3.$$

As 143·5 : 108 : : Wt. of ppt. : amount of silver.

The amount of silver thus found will be short of the true quantity present. An experiment performed with 20 grains of fine silver gave 19·962 grains, so that to the result of each assay of standard silver containing 20 grains of silver ·038 grain must be added for loss.

VOLUMETRIC ESTIMATION OF LEAD.

§ 351. The following simple process was invented by Dr. H. Schwarz. Dissolve 14·730 grammes of pure potassium bichromate in sufficient water to form 1 litre. One cubic centimetre of this solution precipitates ·0207 gramme of lead.

(*a*) The solution of the lead should be effected with the smallest quantity of nitric acid; then diluted with water; carefully neutralised with ammonia, or sodium carbonate, and an excess of sodium acetate added; then the standard bichromate solution run in from a burette, by which means the lead is precipitated as lead chromate. When the precipitation is nearly completed and commences readily to subside, place a few drops of a neutral solution of silver nitrate on a porcelain plate and touch the silver solution with a glass rod which has been dipped in the assay liquid. As soon as the bichromate is in excess the drop is coloured red, while the precipitate has no effect on the silver nitrate. Should the solution form a yellow colour before the silver re-action has commenced, it indicates that an insufficient quantity of sodium acetate has been added, more of which must now be introduced, and also a c.c. of normal lead solution containing ·0207 gramme of lead as nitrate. The slight turbidity which occurs soon passes off, and the operation may be proceeded with. One c.c. of the bichromate solution must be deducted from the final result on account of the extra addition of lead.

(*b*) Bismuth is the only metal which interferes with the above re-action. Silver, if present, may be precipitated as chloride with sodium chloride, which, if the latter is not added in excess, may be left in the solution, lead chromate not being decomposed by sodium chloride. Mercurous compounds when present would interfere, but the mercury may be precipitated as chloride with hydrochloric acid, and the precipitate boiled till it is converted into mercuric chloride.

Lead sulphate must be boiled with sodium carbonate to decompose it, and the carbonate dissolved with nitric acid.

(*c*) Salts of lead, such as phosphate, arsenite, etc., which are insoluble in acetic acid, should be dissolved in nitric acid and estimated by gravimetric methods.

VOLUMETRIC ESTIMATION OF COPPER.

§ 352. *Parkes' method by Potassium Cyanide.* This method is well adapted for the estimation of copper in ores and slags free from manganese, nickel, cobalt, silver, mercury, and zinc, which metals interfere with the re-action and require to be removed before proceeding with the assay. The re-action is based on the fact that when potassium cyanide is slowly added to a copper solution which has been rendered blue by ammonia, the copper solution gradually loses its colour and finally becomes colourless. By ascertaining the amount of a solution of cyanide required to decolourise a solution of copper containing a known quantity of pure copper, the amount of copper in a given ore may be easily determined. The re-action (which is not absolutely uniform with variable quantities of ammonia) is such that a double cyanide of copper and ammonia is formed, cyanogen being liberated; this re-acts on the free ammonia, producing urea, oxalate of urea, cyanide and formate of ammonium. It is, therefore, necessary that the solution analysed should contain about the same quantity of ammonia as that with which the cyanide was originally titrated.

§ 353. Messrs. J. & C. Beringer have performed an exhaustive series of experiments on this subject and have arrived at the following conclusions :—

(*a*) The accuracy depends on the speed at which the last two or three c.c. are run in.

(*b*) With an increase of temperature, less cyanide is required.

10° C.	20° C.	35° C.	47° C.
23·5 c.c.	23·3 c.c.	23·05 c.c.	22·85 c.c.

(*c*) Ammonium nitrate interferes more than ammonia, requiring more cyanide. The same remark applies to

the sulphate, chloride and carbonate of ammonium. Also with an increase of ammonia, an increase of cyanide is required.

If an acid solution is just neutralised with sodium hydrate and then ammonia added, it is an advantage.

(*d*) *Conditions for Proportional Results.* Ammonium salts being absent, the temperature and mode of working the same, and only a slight excess of soda present, then, when the copper, the ammonia, and the bulk of the solution vary in relative proportions, the cyanide will be proportional to the copper present.

If the copper and bulk of solution remain constant and the ammonia is increased, then more cyanide is required; but if the copper and ammonia remain constant and the bulk of solution is increased, then less cyanide is required. Therefore an increase in bulk may neutralise the excess of cyanide required for an increase of ammonia.

There is a certain strength of ammonia with which proportional results can be obtained. With a slightly alkaline solution this strength is 15 c.c. of strong ammonia to each 300 c.c. of solution.

§ 354. *Standard Solution.*

(*a*) Dissolve 2000 grains of pure potassium cyanide in 4 pints of water, or 60 grammes in 1 litre of water. If common cyanide be used, half as much again as this may be requisite. It should be of such strength that 1000 liquid grains equal 10 grains of copper, or 50 c.c. equal half a gramme of copper, a stronger solution than this not being advisable. This solution decomposes somewhat in a few days, causing it to become discoloured, so that when a large quantity is made, it should be re-standardised every five or six days. Dr. Percy kept a solution for two years, and obtained from it the following standards:—

October, 1858, 1000 grains = 10·06 grains of copper.
July, 1859, 1000 „ = 9·84 „ „
March, 1860, 1000 „ = 9·45 „ „
June, 1860, 1000 „ = 8·92 „ „

From which it will be seen that it requires considerable time to make any considerable alteration in the strength of pure solutions.

(*b*) To standardise a cyanide solution; weigh 3 pieces of pure electrotype copper, or best conductivity copper wire (which has been perfectly cleansed in nitric acid), about 5 grains each, and obtain their exact weights on a delicate balance. Put each piece in a 30 ounce flask, and dissolve in a measured quantity of dilute nitric acid ; boil to expel nitrous fumes and dilute till the flask is about one third full; then add sufficient ammonia from a measuring glass to render the solution a deep blue colour. Observe the quantity added, so that the same amount may be used in each case. Allow to cool.

(*c*) Fill the burette, and carefully run off until the liquid stands at zero, which is the uppermost division on the scale. Now place the flask containing the copper solution, which must be quite cold,* under the point of the burette, and run into it a quantity of standard solution ; then well shake so as to thoroughly mix the contents and continue until the colour becomes very pale; then add the liquid, drop by drop, with frequent shaking until only a faint trace of colour is perceived after standing a few minutes; then take the reading of the burette scale. Proceed in the same way with the other two samples.

(*d*) Suppose 5, 6, and 7 grains have been employed with the result that 32 c.c., 38·5 c.c., and 45 c.c., respectively are required, then—

* Some assayers employ a uniform temperature of 15° C.

As 32 : 50 : : 5 : 7·81.
38·5 : 50 : : 6 : 7·79.
45 : 50 : : 7 : 7·77.

The mean of these numbers is taken as the standard, which is found to be 7·79. That is, 50 c.c. of the cyanide solution will just decolourise a solution containing 7·79 grains of copper.

§ 355. *Mode of Conducting an Assay.*

It is assumed that the ore is properly sampled, crushed and passed through a sieve with 80 meshes to the linear inch. *The ore is a carbonate.* Then weigh 15 and 17 grains respectively; place in 2 conical beakers; add a small quantity of hydrochloric acid, and digest at a gentle heat for half an hour; then add a little nitric acid, and heat for another ten minutes until nitrous fumes cease to be given off. Dilute with water; heat; and if the ore is dissolved, transfer to a 30 ounce flask; dilute until one third full as before; cool and add a measured quantity of ammonia till blue; then run in cyanide cautiously to decolourise. Ammonia first precipitates the iron, which may be disregarded, and the colour is observed between the top of the precipitate and the surface of the liquid. When quite cold, cautiously add the cyanide solution, shaking each time, and allowing the precipitate to settle. Great care is required in the finishing stages of the operation which are necessarily slow. About half an hour is required for each decolourisation.

Suppose 15 grains of ore require 40 c.c. of cyanide—

50 : 40 : : 7·79 : x = 6·232.
15 : 100 : : 6·232 : x = 41·55.

The ore then contains 41·55 per cent. of copper.

§ 356. *Copper Pyrites.*

(*a*) Weigh 20 and 25 grains of the finely sifted ore, place each portion in a conical beaker, moisten with

strong sulphuric acid; then add strong nitric acid and digest for an hour, adding a little fresh nitric acid from time to time as the other evaporates, and when all soluble matter is dissolved proceed as before. In oxidising sulphur ores with nitric acid, globules of free sulphur may form, enclosing some of the ore. These may be easily picked out of the diluted solution, ignited, and the residue dissolved in nitric acid. This must be added to the main portion.

(*b*) Oxide of iron imparts a greenish colour to the ammoniacal solution and it requires a little experience to detect the proper tint. If any uncertainty arises it is better to filter off the precipitate towards the completion. When the assay is finished, the oxide of iron will be free from copper, but if the iron is removed first, it retains a considerable portion of copper, which cannot be entirely removed by washing with ammonia. After the copper has been determined, the iron precipitate may be filtered off; washed; dissolved in hydrochloric acid, and the iron estimated by a standard solution of potassium bichromate as explained in the volumetric iron assay.

(*c*) Another way of treating pyritic ores is to roast the weighed assay portions in order to remove sulphur and convert them into oxides. Powder the roasted ore in an agate mortar; treat with nitric acid and proceed as with carbonates, as described in § 355. This plan, when proper care is exercised, yields better results than by solution direct.

(*d*) Grey ores (Cu_2S) are treated in the same way as pyrites, with or without previous roasting.

§ 357. *Interfering Metals.*

As stated at the commencement, some metals interfere with the accuracy of the copper assay by potassium cyanide.

Manganese may be removed by precipitating its oxide with ammonium carbonate and bromine, heating and allowing to stand some time.

The presence of nickel and cobalt is generally detected by the yellowish tinge of the solution after the blue colour has been removed. In such a case precipitate the copper first by sulphuretted hydrogen in an acid solution and re-dissolve the precipitate after filtering and washing.

Copper containing zinc must be treated in the same way. Silver may be precipitated with hydrochloric acid and filtered off before adding ammonia to the copper solution. Dr. Percy investigated this subject. His results are embodied in the table on following page, 5 grains at least of the foreign metal being present.

§ 358. *Colouration Test for Copper Slags.*

This method is adopted for approximately determining the amount of copper in slags and products containing only a small portion of copper. A series of white glass bottles of exactly the same capacity, preferably square in section, are filled with dilute solutions of copper, coloured blue by ammonia. Each contains a known quantity of copper, say $\frac{1}{10}$th, $\frac{2}{10}$th, $\frac{3}{10}$th of a grain and so on, the intensity of the blue colour being proportional to the amount of copper present. These are kept as standards, for comparison. Fresh standards are required from time to time, as the colour alters slightly on standing.

The slag to be examined is pounded fine and sifted; then a portion, say 25 grains, weighed and dissolved in aqua regia by boiling gently for half an hour until decomposed. Then evaporate to dryness; add hydrochloric acid and a little nitric acid to oxidise the iron, and gently warm to dissolve the metallic matter; add water and warm again for about fifteen minutes; then filter off the insoluble silica and wash. Transfer the filtrate to one of the empty test bottles; add ammonia

and fill up with water, so that the volume may be the same as that of the standards. This solution is then

Weight of Electro-type Copper taken.	Estimation made in presence of	Remarks.	Grains of Cyanide required.	Calculated Amount of Copper 1000 grains of solution is equal to
5·345	- - -	- - - - - - -	910	5·873
5·675	- - -	- - - - - - -	960	5·910
6·305	Sesquioxide of iron,	Added as sesquichloride before addition of ammonia, - - - -	1070	5·89
8·150	Lead, antimony, tin & bismuth,	Added as chlorides before ammonia, - - -	1350	5·96
6·645	Nickel,	Added as sulphate before addition of ammonia; there was no precipitate formed on adding cyanide, and the solution was not decolourised, but remained yellow after adding 1630 grains.		
6·41	Cobalt,	Added as chloride, and the solution was not decolourised by 2000 grains of the cyanide.		
6·90	Antimony, -	Added as chloride, - -	1160	5·948
5·30	Bismuth, -	Added as chloride, - -	910	5·810
5·95	Lead, - -	Added as chloride, - -	1020	5·838
5·335	Tin, - -	Added as chloride, - -	910	5·863
4·70	Arsenic, -	Added as arsenic acid, -	790	5·974
5·450	Silver, -	Added as chloride. The cyanide acts on it during decolourisation.		
3·955	Silver, -	Added as nitrate. Action as with chloride.		
3·895	Zinc, -	Added as chloride; solution became turbid at close, - - - -	1300	

compared with those in the test bottles, and that with which it most closely agrees, noted. Suppose it agrees with that containing $\frac{9}{10}$th of a grain of copper, then the percentage is easily computed—

$$25 : 100 : : \tfrac{9}{10} : x = 3{\cdot}6 \text{ per cent.}$$

The presence of oxides of nickel, cobalt, etc., which dissolve in ammonia, producing coloured solutions, render this method inaccurate.

SODIUM THIOSULPHATE METHOD.

§ 359. (*a*) This method is well adapted to the estimation of copper in alloys of that metal when lead and iron are not present in large quantity. The process is based on the re-action between iodine and thiosulphuric acid, the completion being determined by the bleaching effect produced upon a solution of starch added during the experiment.

(*b*) The re-agents required are—1. A solution of sodium thiosulphate, made by dissolving 700 grains of the pure crystallised salt in 2 pints of water. 2. Crystals of potassium iodide free from iodate. 3. Solution of starch (§ 336, *a*). 4. Pure acetic acid. 5. Crystals of pure sodium carbonate.

§ 360. *To Standardise the Solution.* (*a*) Weigh three pieces of electrotype copper, about 5 or 6 grs. each, and dissolve in nitric acid diluted with double its volume of water, using the smallest possible quantity to effect solution. Blow out the red fumes; dilute with water and transfer to a 12 ounce flask; add water till the flask is one third full; then add sodium carbonate in crystals, well shake and continue the addition until the liquid is neutral, which can be ascertained by the copper beginning

to be precipitated. Now add acetic acid in slight excess, and when quite cold, add crystals of potassium iodide equal to about six times the weight of the copper present. When the iodide has dissolved, run in the standard solution until the solution acquires a yellow colour, taking care to frequently shake the contents. A little starch solution (about 3 c.c.) must now be added and the standard solution added a drop at a time until the liquid after shaking is completely bleached. The number of divisions on the burette must now be read off and the strength computed.

(*b*) When iron is present, the red colour of the acetate renders it difficult to observe the re-action of the thiosulphate.

(*c*) In case of ores containing iron it is necessary to precipitate the copper by sodium thiosulphate; to filter and dissolve the precipitated copper sulphide in nitric acid, when the assay may be proceeded with as before.

(*d*) When potassium iodide is added to the acetic acid solution, cuprous iodide is formed and free iodine liberated, which dissolves in the excess of potassium iodide present, the potash uniting with the acetic acid. By the addition of sodium thiosulphate the free iodine is converted into sodium iodide, with the formation of tetrathionate of soda. The starch solution is used to render the termination manifest, the blue iodide of starch being gradually bleached. The following equations show the change which takes place :—

$$2Cu\bar{A}_2 + 4KI = Cu_2I_2 + I_2 + 4K\bar{A}.$$
$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

Suppose that 50 c.c. of standard solution to be equal to 9·85 grains of copper and that 10 grains of a sample of Muntz's metal required 30·5 grains of the standard,

Then 50 : 30·5 : : 9·85 : 6·008.

The metal contains 60·08 per cent. of copper.

(*e*) In the case of alloys containing a little lead, a few drops of sulphuric acid should be added after dissolving in nitric acid to precipitate the lead as sulphate.

VOLUMETRIC ESTIMATION OF ZINC.

§ 361. *By a Standard Solution of Sodium Sulphide.*

(*a*) When a solution of sodium sulphide is added to a solution of zinc containing oxide of iron which has been made alkaline with ammonia, the zinc is precipitated as sulphide first; then the iron, which is at once recognised by the dark colour of iron sulphide, sulphide of zinc being white. By ascertaining the amount of sodium sulphide necessary to exactly precipitate a known weight of zinc, we have a means of determining the amount of zinc in any given compound.

Iron, manganese, copper and silver, when present in a zinc compound in notable quantity, interfere with the re-action and should be previously removed. Cadmium does not interfere.

(*b*) *Standard Solution.* Counterpoise a dry beaker and weigh in it 700 grains of crystallised sodium sulphide ($Na_2S,9OH_2$); dissolve in water and make up the solution to 2 pints. The solution should be clear and colourless; any residue must be filtered off. This solution slowly decomposes and requires standardising every three days. It should be kept in bottles of glass free from lead.

Instead of the above method, 500 grains of caustic soda may be dissolved in ½ pint of water, then saturated with sulphuretted hydrogen; then ½ pint of water in which another 500 grains of caustic soda has been dissolved added to the first to remove the smell of the free gas. The solution is then ready for standardising.

(*c*) *Iron Solution.* Dissolve 50 grains of ferric oxide in hydrochloric acid, or 35 grains of iron wire in nitro-hydrochloric acid, and dilute the solution to 1 pint.

§ 362. *To Standardise.* Weigh accurately three or four pieces of pure zinc, about 5 grains each; dissolve in hydrochloric acid; add a little nitric acid; dilute with water; place each quantity in a 30 oz. flask; add water until half full, then 3 c.c. of the iron solution; then add ammonia until the liquid is alkaline. When cold, run in the standard solution from a burette (keeping the liquid in the flask well agitated), until the oxide of iron just begins to turn black. The number of divisions is then read off and the mean of three or four results taken as the standard. Suppose 5·84 grains of zinc required 29 c.c., then 50 c.c. of standard would equal 10·06.

§ 363. *Assay of Zinc Ores.*

(*a*) The ore to be examined must be crushed fine and passed through No. 80 sieve as usual. Take 20 and 25 grains respectively; place in conical beakers; add hydrochloric acid and a little nitric, using the minimum quantity of acid to effect solution; then heat for about thirty minutes until the ore is completely decomposed. Dilute with water and filter into a 30 ounce flask to remove insoluble matter, which must be washed with warm ammoniacal water. Assuming interfering metals to be absent from the filtrate, dilute till the flask is half full; add 3 c.c. of iron solution, cool, and proceed as in standardising. Take reading of burette and calculate the percentage of zinc in the following way :—

50 c.c. of standard equals 10·06 grains of zinc.
25 grains of calamine in an assay required 62·5 c.c.
20 „ „ „ „ 50 „

As 50 : 62·5 : : 10·06 : 12·57.
50 : 50 : : 10·06 : 10·06.

Multiplying these results by 4 and 5 respectively 50·28 and 50·30 per cent. of zinc is obtained.

(*b*) It is desirable to have the oxide of iron present in the flocculent condition, so that it is better to add ammonia to the 3 c.c. of ferric chloride before mixing it with the ammoniacal solution of zinc. As before remarked the solution must be constantly agitated while running in the standard, otherwise the oxide of iron may be blackened before the complete precipitation of zinc sulphide. When the change from reddish brown to black takes place the standard solution must only be added one drop at a time.

§ 364. *Estimation of Zinc by a Standard Solution of Potassium Bichromate.*

This process depends on the fact that when zinc sulphide is mixed with ferric chloride and hydrochloric acid, ferrous chloride, zinc chloride and free sulphur are produced.

$$Fe_2Cl_6 + ZnS = 2FeCl_2 + S + ZnCl_2.$$

The amount of ferrous chloride is then estimated by a standard solution of potassium bichromate, and the proportional quantity of zinc ascertained; for 2 atoms of iron which equal 112, represent 1 atom of zinc which equals 65.

20 or 25 grains of ore are dissolved as before, evaporated, precipitated with ammonia and ammonium carbonate; digested until the zinc precipitate is re-dissolved, then filtered, and washed. The filtrate and washings contain the zinc, which is precipitated with sodium sulphide or ammonium sulphide, then filtered and washed with warm ammonia water. The filter and its contents are transferred to a beaker, a slightly acid dilute solution of ferric chloride added, the beaker covered and the whole digested for ten to fifteen minutes; sulphuric acid is then poured in and a gentle heat con-

tinued until the free sulphur coagulates. The solution is then filtered, well washed with hot water, and the amount of ferrous chloride in the filtrate determined. This process is described under the head of Iron Assays, § 366. Suppose 50 c.c. of bichromate solution indicate 10 grains of iron,

	iron.	iron.	zinc.	zinc.
Then	112	: 10	:: 65	: 5·80.

VOLUMETRIC ESTIMATION OF IRON.

§ 365. Two principal methods are in use; one is due to Marguérite and known as the Permanganate method, the other to Dr. Penny, known as the Bichromate method. These depend on the circumstance that, when iron is in solution as ferrous chloride, it may be oxidised to ferric chloride by means of an oxidising agent, the amount of which is proportional to the quantity of iron present. The above two methods differ in the nature of the oxidising agent employed and the mode of judging the completion.

§ 366. *Potassium Bichromate Method.*

(*a*) For general work this method is preferable to the permanganate process, for the following reasons.

1. Bichromate solution is less liable to decomposition by long keeping than permanganate, and requires less frequent standardising.

2. The result obtained is more reliable, not being subject to error through evolution of chlorine.

3. In some cases it occupies less time, as filtration is necessary with the permanganate method when carbonaceous or organic matter is present, and the solution need not be cooled.

On the other hand, an external indicator is required, and the completion somewhat prolonged.

(*b*) When potassium bichromate solution is added to a solution of a proto-salt of iron, the latter is oxidised into a sesqui-salt with the production of a potash salt and a sesquisalt of chromium. The following re-action occurs when the iron dissolved in hydrochloric acid is treated with bichromate—$6FeCl_2 + 14HCl + Cr_2O_7K_2 = 3Fe_2Cl_6 + 2KCl + 7OH_2 + Cr_2Cl_6$. To indicate the completion, a very weak, nearly colourless, solution of potassium ferricyanide is used, which produces a greenish blue tint when mixed with proto-salts, but is unaltered by sesquisalts of iron. An excess of acid must be present.

§ 367. *Standard Solution.*

(*a*) Crush up a quantity of pure crystals of potassium bichromate; weigh 305 grains and dissolve in warm water; filter if necessary; then make up the solution to 4 pints.

(*b*) *Indicator.* Dissolve 1 grain of potassium ferricyanide in 4 ounces of water and preserve in a stoppered bottle.

(*c*) *To Standardise.* Place a small quantity of hydrochloric acid and an equal bulk of water in a conical beaker, stopped with a funnel, boil until all air has been expelled and the flask is full of the vapours of the acid. Then add a weighed piece of practically pure and clean iron wire to the boiling acid, and gently boil till it is dissolved. The solution must be colourless.

In the meantime fill up the burette, either a 50 c.c. or a 1000 grain, with the bichromate solution, and level for use. Then dilute the colourless solution of iron; transfer to a large evaporating dish (No. 7); dilute to about half a pint and run in the standard solution, constantly stirring meanwhile.

(*d*) To indicate the progress, a number of spots of the ferricyanide solution are placed on a white tile about

4 inches square, one spot being touched by a drop of liquid carried from the basin by a glass rod, after each addition of the standard solution. As long as any ferrous chloride is unoxidised, the union of the two drops will produce a blue colour which becomes very faint towards the conclusion; the termination of the titration being complete when no colour, or only the faintest tint is observed. The mean of three experiments gave 10·232 grains of iron as equivalent to 1000 liquid grains of the standard bichromate solution.

§ 368. *Estimation of Iron in Ores.*

(*a*) *Hæmatite.* Crush a quantity and pass through a No. 80 sieve. Weigh 10 and 12 grains respectively. Place each in a conical beaker; add strong hydrochloric acid and gently boil until dissolved, or until only insoluble silica remains; then add water until the beaker is one third full. The iron is in solution in the ferric condition, and requires to be completely reduced to the ferrous condition. This may be effected by adding a little zinc free from iron, which generates hydrogen, and this being in the nascent condition gradually reduces the yellow ferric chloride solution to colourless ferrous chloride, thus—

$$Fe_2Cl_6 + H_2 = 2FeCl_2 + 2HCl.$$

Transfer to an evaporating dish; well swill out the beaker and make up the solution to half a pint as before; then run in the standard solution until the contents cease to produce a faint blue tint with a spot of the ferricyanide on the white tile.

Suppose 624 and 748 thousandths are required, then—

As 1000 : 624 : : 10·232 : $x = 6·385$.
„ 1000 : 748 : : 10·232 : $x = 7·653$.
10 : 100 : : 6·385 : 63·85.
12 : 100 : : 7·653 : 63·97.

For Spathic, Northampton, and clay iron ore, take 20 and 25 grains.

(*b*) *Northampton Ore.* Dissolve 20 and 25 grains in strong hydrochloric acid; dilute and transfer to a pint flask; dilute until half full. Then add 30 grains of sodium sulphite (Na_2SO_3) in crystals, and keep in a warm place till nearly decolourised, which takes about fifteen minutes; then boil until all odour of sulphurous acid ceases, and pour into dish for titration with the standard solution as before.

(*c*) *Blackband.* Take 20 and 25 grains and calcine in muffle for fifteen minutes, then dissolve in hydrochloric acid, decolourise with zinc and proceed as usual.

(*d*) *Tap Cinder.* Take 10 and 12 grains and dissolve in hydrochloric acid. It is well in this case to add a few bits of glass to prevent gelatinous silica from sticking to the ore. Titrate as usual.

(*e*) *Titaniferous Iron Ore.* Take 20 and 25 grains of the finely divided ore and boil with strong hydrochloric acid for an hour until decomposed, then add water and reduce with sodium sulphite as in (*b*). Two experiments gave 37·20 and 37·108 per cent. respectively

Now, when zinc is used, incorrect results are obtained, so that zinc cannot be used in the reduction of solutions obtained from ores containing titanic acid, because it converts the tetrachloride of titanium ($TiCl_4$) into sesquichloride (Ti_2Cl_6), so that sulphite of soda must be used as described with the Northampton ore. When zinc is employed, the ferric chloride is reduced first, and if quickly poured off when the solution becomes colourless, the iron might be approximately estimated; but if left too long the solution turns violet and afterwards blue.

20 and 25 grains of ore were treated with zinc instead

of with sodium sulphite as above, and gave 44·75 and 42·68 per cent. of iron respectively. Compare these results with the former when sodium sulphite was used as the reducing agent.

§ 369. In the case of mixed ores like magnetite, and compounds containing both ferrous and ferric oxides, it is often required to know the amount of each oxide present. This may be done as follows :—

1. Dissolve 10 to 20 grains in hydrochloric acid or aqua regia if necessary ; dilute ; decolourise with zinc, and estimate the total amount of iron present by the standard solution.

2. Weigh another portion and dissolve with sulphuric acid in a flask through which a stream of carbonic acid is constantly passing ; dilute ; transfer to dish, and titrate with standard solution as before ; or use the method in § 201 (*c*). The result gives the amount of iron present as ferrous oxide. The difference between this and the former result gives the amount of iron present as ferric oxide. (See § 201.)

(*a*) When sodium sulphite is used as the reducing agent, care must be taken to add it in sufficient quantity, and that the iron solution contains free acid. The completeness of the reduction may be ascertained by adding a drop of the iron solution to a drop of potassium sulphocyanide, which should impart merely a rose pink colour ; then the sulphurous acid may be boiled off. If any unreduced ferric salt is present, the sulphocyanide will give a blood red colour.

(*b*) Some magnetites and hæmatites are difficultly soluble in hydrochloric acid. They may be reduced to the metallic state by heating a weighed portion—say 10 grains—in a porcelain crucible having a hole through the lid through which a stream of coal gas is constantly

passing (Fig. 69). The reduced metal is then readily soluble in hydrochloric acid.

§ 370. *Potassium Permanganate Method.*

(*a*) The permanganate solution, even when very weak, has a decidedly purple colour, which is immediately discharged as long as any ferrous salt remains unoxidised; but immediately this is accomplished, a single drop of permanganate in excess gives a characteristic rose tint to the solution, so that the exact termination is easily recognised.

(*b*) *Standard Solution.* Dissolve 197 grains of pure potassic permanganate in 4 pints of water. As this solution is affected by the presence of organic matter, it must be kept in a stoppered glass bottle.

(*c*) *To Standardise.* Dissolve about 5 grains of pure iron wire, accurately weighed, in hydrochloric acid, using the precautions given in § 367 (*c*); transfer the diluted colourless solution to a 20 ounce flask, and carefully run in the standard solution, with frequent shaking, until the rose tint appears and remains permanent; then take the reading of the burette, perform three experiments, and take the mean as the correct standard. The ores are dissolved, then reduced by zinc or sodium sulphite, as in former method. (See § 368.)

VOLUMETRIC ESTIMATION OF MANGANESE.

§ 371. (*a*) The following volumetric method, founded on the precipitation of manganese as dioxide, in presence of ferric chloride, is recommended by Mr. J. Pattison. The re-agents employed are—(1) The clear liquid obtained by the decantation from a 1·5 per cent. solution of bleaching powder; (2) light granular calcium carbonate obtained

by precipitating an excess of calcium chloride with sodium carbonate at 180° F.; (3) a 1 per cent. solution of ferrous sulphate in dilute sulphuric acid (1 to 4); (4) a standard solution of potassium bichromate, equivalent to 1 part of iron in 100 of solution.

(*b*) 10 grains of ore dried at 212° F. are dissolved in a 20 ounce beaker in about 100 grains of hydrochloric acid (specific gravity, 1·18). Calcium carbonate is then added until the free acid is neutralised and the liquid turns slightly reddish; 6 or 7 drops of hydrochloric acid are then added, and 1000 grains of the bleaching powder solution, or 500 grains of saturated bromine water; then boiling water is run in until the temperature is raised from 140° to 160° F.; 25 grains of calcium carbonate are then added and the whole well stirred. If the supernatant liquid has a pink colour, the permanganate is reduced by a few drops of alcohol. The precipitated oxides of iron and manganese are filtered off and washed; 1000 grains of the acidified ferrous sulphate solution are measured into the 20 ounce beaker already used, and the filter with its washed contents added. A certain quantity of the ferrous sulphate is oxidised by the MnO_2; this quantity is estimated by the standard bichromate solution, and from it the quantity of MnO_2 is estimated. The iron present must be at least equal in weight to the manganese during precipitation in order to ensure the absence of lower oxides. This method is applicable to the analysis of ferro-manganese, spiegel-eisen and manganese slags. (Watt's Dictionary, 3rd Suppl., page 1264.)

VOLUMETRIC ESTIMATION OF SULPHUR.

§ 372. Mr. C. R. A. Wright recommends the following method for technical purposes:—

"Dissolve a suitable quantity of the mineral, or substance containing sulphur in an evaporating dish by means of nitric acid or other oxidising agent free from sulphuric acid; evaporate to a small bulk to expel excess of acid; dilute with water; boil and nearly neutralise with ammonia.

"Run in a dilute solution of barium chloride of known strength until no further precipitation occurs. The exact point is found by filtering off a small portion into a test tube and adding a drop of the standard. If a precipitate forms, add this filtrate to the original solution, well mix, and repeat the filtering a second time. In case the finishing point is overreached, a solution of sodium sulphate of a strength equal to that of the barium chloride is cautiously added to bring it back to the point where no further precipitation occurs, as determined by means of filtering and testing. In such a case the volume of sodium sulphate used is subtracted from the total volume of barium chloride required.

"For standard solution, instead of having a deci-normal solution of 20·8 grammes to the litre, which corresponds to ·32 of sulphur for 100 c.c., that amount of barium chloride, which is equivalent to ·5 gramme of sulphur, may be dissolved in a litre of water, namely 32·5 grammes; then if 1 gramme of ore be dissolved, each c.c. of standard solution will represent ·5 per cent. of sulphur.

"The standard solution of sodium sulphate must then contain 22·19 grains of anhydrous sodium sulphate. This method will not yield perfectly accurate results. In presence of lead, the method is not applicable in consequence of the formation of insoluble lead sulphate."

APPENDIX.

TABLE I.

TABLE OF ELEMENTS WITH THEIR SYMBOLS, ATOMIC WEIGHTS, AND SPECIFIC GRAVITIES.

METALS.

Names.	Symbols.	Atomic Weights.	Specific Gravity.
Aluminium,	Al	27	2·56
Antimony,	Sb	120	6·72
Arsenic,	As	75	5·67
Barium,	Ba	137	3·75
Bismuth,	Bi	207·5	9·8
Cadmium,	Cd	112	8·6
Caesium,	Cs	133	1·88
Calcium,	Ca	40	1·58
Cerium,	Ce	141	6·68
Chromium,	Cr	52·4	6·8
Cobalt,	Co	58·6	8·5
Copper,	Cu	63·2	8·8
Didymium,	Di	145	6·5
Erbium,	E	112·6	—
Glucinum,	Gl	9	2
Gold,	Au	196·8	19·32
Indium,	In	113·4	7·4
Iridium,	Ir	192·5	22·4
Iron,	Fe	56	7·86
Lanthanium,	La	138·5	6·2
Lead,	Pb	206·4	11·37
Lithium,	Li	7	·58
Magnesium,	Mg	24	1·74
Manganese,	Mn	55	8
Mercury,	Hg	200	13·59
Molybdenum,	Mo	96	8·6
Nickel,	Ni	58·6	8·8
Niobium,	Nb	94	6·27
Osmium,	Os	195	22·48
Palladium,	Pd	106·2	11·5
Platinum,	Pt	194·3	21·5
Potassium,	K	39	·87

METALS—*Continued.*

Names.	Symbols.	Atomic Weights.	Specific Gravity.
Rhodium,	Rh	104	12·1
Rubidium,	Rb	85·2	1·52
Ruthenium,	Ru	103·5	12·26
Silver,	Ag	107·6	10·53
Sodium,	Na	23	·97
Strontium,	Sr	87·2	2·54
Tantalum,	Ta	182	10·8
Thallium,	Tl	203·5	11·9
Thorium,	Th	232	11·1
Tin,	Sn	117·4	7·3
Titanium,	Ti	48	—
Tungsten,	W	184	19·1
Uranium,	U	240	18·7
Vanadium,	V	51	5·5
Yttrium,	Y	61·7	—
Zinc,	Zn	65	7·15
Zirconium,	Zr	90·4	4·15

NON-METALS.

Names.	Symbols.	Atomic Weights.	Specific Gravity.
Boron,	B	11	2·68
Bromine,	Br	79·76	2·96
Carbon (Graphite,	—	—	2·2
Carbon (Diamond,	C	12	—
	—	—	3·5
Chlorine,	Cl	35·5	—
Fluorine,	F	19	—
Hydrogen,	H	1	—
Iodine,	I	126·54	4·95
Nitrogen,	N	14	—
Oxygen,	O	16	—
Phosphorus,	P	31	1·8–2·1
Selenium,	Se	79·5	4·28–4·8
Silicon,	Si	28·3	2·49
Sulphur,	S	32	1·97–2·07
Tellurium,	Te	126·3	6·25

TABLE II.

TABLE OF MELTING AND BOILING POINTS.

	Melting Point.	Boiling Point.
Aluminium,	625° C.	
Antimony,	440°	
Bismuth,	270°	
Bromine,	−7°	59°
Cadmium,	320°	860°
Calcium,	—	1040°
Chlorine,	—	−50°
Cobalt,	1500°	
Copper,	1050°	
Gold,	1045°	
Indium,	176°	
Iodine,	107°	187°
Iron—		
Cast,	1100°–1300°	
Steel,	1300°–1500°	
Wrought,	Above 1600°	
Lead,	325°	1040°
Lithium,	180°	
Magnesium,	750°	
Mercury,	−39°·4	350°
Nickel,	1500°–1600°	
Phosphorus,	44°	
,, Amorphous,	250°	
Potassium,	62°·5	
Platinum,	1775°	
Silver,	945°	
Selenium,	217°	700°
Sodium,	95°	
Sulphur,	115°	440°
Tellurium,	525°	
Thallium,	88°	
Tin,	27°	
Zinc,	415°	1040°

All statements with regard to melting points at very high temperatures must be taken with reserve, as there

is probably no instrument yet invented on which absolute reliance can be placed, so that the temperatures given for iron, nickel, platinum, etc., can only be considered to approximate to the correct degrees.

The following results arrived at by Pouillet may be useful to the student as a general guide:—

Incipient red heat	corresponds to	525° C.	977° F.
Dull red	do.	700°	1292°
Incipient cherry red	do.	800°	1472°
Cherry red	do.	900°	1652°
Clear cherry red	do.	1000°	1832°
Deep orange	do.	1100°	2012°
Clear orange	do.	1200°	2192°
White	do.	1300°	2372°
Bright white	do.	1400°	2552°
Dazzling white	do.	1500°–1600°	2732°–2912°

Some metals readily vapourise when melted, such as zinc, cadmium, and antimony, while arsenic, under ordinary conditions, passes into the state of vapour without melting.

TABLE III.

METALS ARRANGED IN THE ORDER OF THEIR MALLEABILITIES, DUCTILITIES, TENACITIES, AND HARDNESS.

Malleability.	Ductility.	Tenacity.	Hardness.
Gold.	Gold.	Steel.	Manganese.
Silver.	Silver.	Iron.	Cobalt.
Copper.	Platinum.	Nickel.	Nickel.
Tin.	Iron.	Copper.	Iron.
Platinum.	Nickel.	Platinum.	Copper.
Lead.	Copper.	Silver.	Platinum.
Zinc.	Aluminium.	Gold.	Zinc.
Iron.	Zinc.	Zinc.	Silver.
Nickel.	Tin.	Tin.	Gold.
	Lead.	Lead.	Aluminium.
			Magnesium.
			Tin.
			Lead.

TABLE IV.

CONDUCTIVITY OF SUBSTANCES FOR ELECTRICITY.

According to Dr. Matthiessen, the order of conductivity is as follows:—

Silver,	100	Tin,	12·4
Copper,	99·9	Thallium,	9·2
Gold,	77·9	Lead,	8·3
Zinc,	29	Arsenic,	4·8
Cadmium,	23·7	Antimony,	4·6
Palladium,	18·4	Mercury,	1·6
Platinum,	18	Bismuth,	1·2
Cobalt,	17·2	Graphite,	·069
Iron,	16·8	Gas Coke,	·038
Nickel,	13·1	Bunsen's Coke,	·025

TABLE V.

RELATIVE VALUES OF THE FRENCH WITH THE BRITISH SYSTEM OF WEIGHTS AND MEASURES.

METRICAL MEASURES OF LENGTH.

	In English Inches.	In English Feet.	In English Yards.
Millimetre,	·03937	·003281	·0010936
Centimetre,	·39371	·032809	·0109363
Decimetre,	3·93708	·328090	·1093633
Metre,	39·37079	3·280899	1·0936331
Decametre,	393·70790	32·808992	10·9363306
Hectametre,	3937·07900	328·089917	109·3633056
Kilometre,	39370·79000	3280·899167	1093·6330556

1 inch = 2·539954 centimetres. | 1 yard = 0·9143835 metre.
1 foot = 3·0479449 decimetres. | 1 mile = 1·6093149 kilometre.

Metrical Measures of Surface.

	In English Square Feet.	In English Square Yards.	In English Acres.
Centiare, - - - - or sq. metre,	10·764299	1·196033	·0002471
Are, - - - - - or 100 sq. metres,	1076·429934	119·603326	·0247114
Hectare, - - - - or 10,000 sq. metres,	107642·993419	11960·332602	2·4711431

1 square inch = 6·5413669 square centimetres.
1 square foot = 9·2899683 square decimetres.
1 square yard = 0·83609715 square metre.
1 acre = 0·40467102 hectare.
1 square mile = 258·989451 hectares.

Metrical Measures of Weight.

	In Grains.	In Avoirdupois Ounces = 437·5 Grains.	In Avoirdupois Lbs. = 7000. Grains.
Milligramme, -	·015432	·000035	·0000022
Centigramme, -	·154323	·000353	·0000220
Decigramme, -	1·543235	·003527	·0002205
Gramme, - -	15·432349	·035274	·0022046
Decagramme, -	154·323488	·352739	·0220462
Hectagramme, -	1543·234880	3·527394	·2204621
Kilogramme, -	15432·348800	35·273940	2·2046213

1 grain = ·064799 gramme.
1 troy ounce = 31·103496 grammes.
1 lb. avoir. = ·453593 kilogramme.
1 cwt. = 50·802377 kilogrammes.

METRICAL MEASURES OF CAPACITY.

	In Cubic Inches.	In Cubic Feet.	In Pints.
Millilitre, or cubic centimetre,	·06103	·000035	·001761
Litre, or cubic decimetre, - -	61·02705	·035317	1·760770

1 cubic inch = 16·386176 cubic centimetres.
1 cubic foot = 28·315312 cubic decimetres.
1 gallon = 4·543458 litres.

TABLE VI.

METRICAL SYSTEM OF WEIGHTS AND MEASURES.

LENGTH.

1 millimetre = ·001 metre.
1 centimetre = ·01 ,,
1 decimetre = ·1 ,,
1 metre = the ten millionth part of a quarter of the earth's meridian.

CAPACITY.

1 millilitre = 1 cubic centimetre, or the measure of 1 gramme of water
1 centilitre = 10 cubic centimetres.
1 decilitre = 100 ,, ,,
1 litre = 1000 ,, ,,

WEIGHT.

1 milligramme = ·001 gramme.
1 centigramme = ·01 ,,
1 decigramme = ·1 ,,
1 gramme = the weight on 1 cubic centimetre of pure water at 4° C.
1 decagramme = 10 grammes.
1 hectagramme = 100 ,,
1 kilogramme = 1000 ,,

TABLE VII.

TABLE OF CORRESPONDING TEMPERATURES ON THE SCALES OF CENTIGRADE AND FAHRENHEIT THERMOMETERS.

Deg. Cent.	Deg. Fahr.	Deg. Cent.	Deg. Fahr.	Deg. Cent.	Deg. Fahr.
0	32	34	93·2	68	154·4
1	33·8	35	95	69	156·2
2	35·6	36	96·8	70	158
3	37·4	37	98·6	71	159·8
4	39·2	38	100·4	72	161·6
5	41	39	102·2	73	163·4
6	42·8	40	104	74	165·2
7	44·6	41	105·8	75	167
8	46·4	42	107·6	76	168·8
9	48·2	43	109·4	77	170·6
10	50	44	111·2	78	172·4
11	51·8	45	113	79	174·2
12	53·6	46	114·8	80	176
13	55·4	47	116·6	81	177·8
14	57·2	48	118·4	82	179·6
15	59	49	120·2	83	181·4
16	60·8	50	122	84	183·2
17	62·6	51	123·8	85	185
18	64·4	52	125·6	86	186·8
19	66·2	53	127·4	87	188·6
20	68	54	129·2	88	190·4
21	69·8	55	131	89	192·2
22	71·6	56	132·8	90	194
23	73·4	57	134·6	91	195·8
24	75·2	58	136·4	92	197·6
25	77	59	138·2	93	199·4
26	78·8	60	140	94	201·2
27	80·6	61	141·8	95	203
28	82·4	62	143·6	96	204·8
29	84·2	63	145·4	97	206·6
30	86	64	147·2	98	208·4
31	87·8	65	149	99	210·2
32	89·6	66	150·8	100	212
33	91·4	67	152·6		

TABLE VIII.

TABLE OF TANGENTS.

Deg.	Tangent.	Deg.	Tangent.	Deg.	Tangent.
1	·0174	31	·6009	61	1·8040
2	·0349	32	·6249	62	1·8807
3	·0524	33	·6494	63	1·9626
4	·0699	34	·6745	64	2·0503
5	·0875	35	·7002	65	2·1445
6	·1051	36	·7265	66	2·2460
7	·1228	37	·7535	67	2·3558
8	·1405	38	·7813	68	2·4751
9	·1584	39	·8098	69	2·6050
10	·1763	40	·8391	70	2·7475
11	·1944	41	·8693	71	2·9042
12	·2125	42	·9004	72	3·0777
13	·2309	43	·9325	73	3·2708
14	·2493	44	·9657	74	3·4874
15	·2679	45	1·0000	75	3·7320
16	·2867	46	1·0355	76	4·0108
17	·3057	47	1·0724	77	4·3315
18	·3249	48	1·1106	78	4·7046
19	·3443	49	1·1504	79	5·1445
20	·3640	50	1·1917	80	5·6713
21	·3839	51	1·2349	81	6·3137
22	·4040	52	1·2799	82	7·1154
23	·4245	53	1·3270	83	8·1443
24	·4452	54	1·3764	84	9·5144
25	·4663	55	1·4281	85	11·4300
26	·4897	56	1·4826	86	14·3007
27	·5095	57	1·5399	87	19·0811
28	·5317	58	1·6003	88	28·6362
29	·5543	59	1·6643	89	57·2899
30	·5773	60	1·7320	90	X.

TABLE IX.

TABLE OF COEFFICIENTS GIVING THE AMOUNT OF THE BODY SOUGHT BY SIMPLE MULTIPLICATION.

Element.	Found.	Form.	Sought.	Form.	Coefficient
Aluminium,	Alumina,	Al_2O_3	Aluminium,	Al_2	·53398
Ammonium,	Ammonic chloride,	NH_4Cl	Ammonia,	NH_3	·31804
	Ammonio-platinic chloride	$2NH_4Cl,PtCl_4$	,,	$2NH_3$	·07614
Antimony,	Antimonious oxide,	Sb_2O_3	Antimony,	Sb_2	·83562
	,, sulphide,	Sb_2S_3	,,	,,	·71765
	,, ,,	,,	Antimonious oxide,	Sb_2O_3	·85882
	Diantimonic tetroxide,	Sb_2O_4	,, ,,	Sb_2O_3	·94805
Arsenic,	Arsenious anhydride,	As_2O_3	Arsenic,	As_2	·75758
	Arsenic ,,	As_2O_5	,,	,,	·65217
	,, ,,	,,	Arsenious anhydride,	As_2O_3	·86087
	Arsenious sulphide,	As_2S_3	,, ,,	,,	·80488
	,, ,,	,,	Arsenic anhydride,	As_2O_5	·93496
	Ammonic-magnesic arseniate,	$(MgNH_4AsO_4)_2OH_2$	,, ,,	,,	·60526
	,, ,, ,,	,,	Arsenious anhydride,	As_2O_3	·52105
Barium,	Baryta,	BaO	Barium,	Ba	·89542
	Baric sulphate,	$BaSO_4$	Baryta,	BaO	·65665
	,, carbonate,	$BaCO_3$	,,	,,	·77665
	,, silico-fluoride,	BaF_2,SiF_4	,,	,,	·54839
Bismuth,	Bismuthous oxide,	Bi_2O_3	Bismuth,	Bi_2	·89655
Boron,	Boric Anhydride,	B_2O_3	Boron,	B_2	·31429
Bromine,	Silver bromide,	$AgBr$	Bromine,	Br	·42560
Cadmium,	Cadmic oxide,	CdO	Cadmium,	Cd	·8750
Calcium,	Lime,	CaO	Calcium,	Ca	·71429
	Calcic sulphate,	$CaSO_4$	Lime,	CaO	·41176
	,, carbonate,	$CaCO_3$	,,	,,	·5600
Carbon,	Carbon dioxide,	CO_2	Carbon,	C	·27273
	Calcic carbonate,	$CaCO_3$	Carbon dioxide,	CO_2	·440
Chlorine,	Silver chloride,	$AgCl$	Chlorine,	Cl	·24724
	,, ,,	,,	Hydrochloric acid,	HCl	·25421
Chromium,	Chromic oxide,	Cr_2O_3	Chromium,	Cr_2	·68619
	,, ,,	,,	Chromic acid,	$2CrO_3$	1·31381
	Lead chromate,	$PbCrO_4$	,, ,,	,,	·31062
Cobalt,	Cobalt sulphate,	$CoSO_4$	Cobalt,	Co	·37984
	,, tetroxide,	Co_3O_4	,,	Co_3	·73444
Copper,	Cupric oxide,	CuO	Copper,	Cu	·79849
	Cuprous sulphide,	Cu_2S	,,	Cu_2	·79849
Fluorine,	Calcic fluoride,	CaF_2	Fluorine,	F_2	·48718
	Silicic ,,	SiF_4	,,	F_4	·73077
Hydrogen,	Water,	H_2O	Hydrogen,	H_2	·11111
Iodine,	Silver iodide,	AgI	Iodine,	I	·54049
	Palladium iodide,	PdI_2	,,	I_2	·70556
Iron,	Ferric oxide,	Fe_2O_3	Iron,	Fe_2	·700
	,, ,,	,,	Ferrous oxide,	$2FeO$	·900
	Ferrous sulphide,	FeS	Iron,	Fe	·63636
Lead,	Lead oxide,	PbO	Lead,	Pb	·92825
	,, sulphate,	$PbSO_4$	,, oxide,	PbO	·73597
	,, ,,	,,	,,	Pb	·68317
	,, chloride,	$PbCl_2$	,,	,,	·74482
	,, sulphide,	PbS	,,	,,	·86864
Lithium,	Lithium carbonate,	Li_2CO_3	Lithium oxide,	Li_2O	·40541
	,, sulphate,	Li_2SO_4	,, ,,	,,	·27273
	,, phosphate,	Li_3PO_4	,, ,,	,,	·38793

TABLE IX.—*Continued.*

Element.	Found.	Form.	Sought.	Form.	Coefficient
Magnesium,	Magnesium oxide,	MgO	Magnesium,	Mg	·600
	,, sulphate,	$MgSO_4$	,, oxide,	MgO	·33350
	,, pyrophosphate,	$Mg_2P_2O_7$	,, ,,	2MgO	·36036
Manganese,	Manganese tetroxide,	Mn_3O_4	Manganese,	Mn_3	·72052
	,, sulphide,	MnS	,,	Mn	·63218
Mercury,	Mercury,	2Hg	Mercurous oxide,	Hg_2O	1·0400
	,,	Hg	Mercuric ,,	HgO	1·0800
	Mercurous chloride,	Hg_2Cl_2	Mercury,	Hg_2	·84940
	Mercuric sulphide,	HgS	,,	Hg	·86207
Nickel,	Nickel oxide,	NiO	Nickel,	Ni	·78667
Nitrogen,	Ammonio-platinum chloride,	$2NH_4Cl,PtCl_4$	Nitrogen,	N_2	·06271
	Platinum,	Pt	,,	,,	·14155
	Baric sulphate,	$BaSO_4$	Nitric pentoxide,	N_2O_5	·46352
	Silver cyanide,	AgCN	Cyanogen,	CN	·19410
	,, ,,	,,	Hydrocyanic acid,	HCN	·20156
Oxygen,	Alumina,	Al_2O_3	Oxygen,	O_3	·46602
	Antimony oxide,	Sb_2O_3	,,	O_3	·16438
	Arsenious acid,	As_2O_3	,,	O_3	·24242
	Arsenic ,,	As_2O_5	,,	O_5	·34783
	Barium oxide,	BaO	,,	O	·10458
	Bismuth ,,	Bi_2O_3	,,	O_3	·10345
	Cadmium ,,	CdO	,,	O	·12500
	Chromium ,,	Cr_2O_3	,,	O_3	·31381
	Cobalt ,,	CoO	,,	O	·21333
	Copper ,,	CuO	,,	O	·20151
	Ferrous ,,	FeO	,,	O	·22222

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