

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 $\frac{1}{3}$ rd or $\frac{2}{3}$ rd 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 CO₂. 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 Fe₂O₃, 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 + CO₂; then the separated iron reacts on more oxide of carbon, thus—Fe + 2CO = CO₂ + 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 CO₂, 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— $2\text{PbO} + \text{C} = \text{CO}_2 + \text{Pb}_2$.*

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—CO₂ + 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— $2\text{PbO} + 2\text{C} = 2\text{CO} + \text{Pb}_2$.

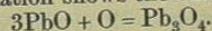
That this is not so, will be illustrated by the next experiment. Having calculated the right amount of carbon to add to 500 grains of litharge, either in form of powdered charcoal, coke, or anthracite; thoroughly mix the oxide and reducing agent on a sheet of glazed paper; carefully brush the whole into a clay crucible (Fig. 35b); 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:—



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

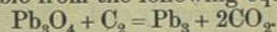
oxide thus reduced melting to a liquid. Pour into a half-round mould and allow to cool. Weigh the button of litharge. The amount possible may be calculated from the following equation:— $\text{Pb}_3\text{O}_4 = 3\text{PbO} + \text{O}$.

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.

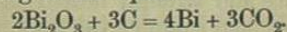
In the reduction of red lead in the manner explained above, care must be taken not to raise the temperature too high, or the litharge will form a silicate with the clay of the pot.

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:—



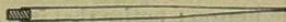
This experiment is carried out precisely as with litharge (Exp. 127).

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



This metal is similar to lead in some respects; thus on heating metallic bismuth after fusion in a muffle, a pale yellow oxide forms at first, which becomes darker in colour as the temperature is raised, fusing at a red heat to a glass which is of a deeper tint than the unfused oxide. Like fused litharge, it readily corrodes a clay 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— $\text{HgO} = \text{Hg} + \text{O}$.

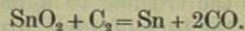
Exp. 134. Take 200 grains of oxide of zinc, mix with excess of carbon, which may be calculated from the equation— $\text{ZnO} + \text{C} = \text{CO} + \text{Zn}$.

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 some 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.

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

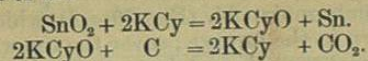
mix it with 100 grains of anthracite or coke dust which has been passed through a fine sieve; place the mixture in a plumbago crucible (Fig. 39 *a, b*), which must be put well down in the furnace; cover the top with a piece of coke, and heat strongly for twenty minutes; then remove the coke covering, 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.



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.



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.— $2\text{Sb}_2\text{O}_3 + 3\text{C} = 4\text{Sb} + 3\text{CO}_2$.

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.— $\text{NiO} + \text{C} = \text{CO} + \text{Ni}$.

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.— $\text{Fe}_2\text{O}_3 + 3\text{C} = 3\text{CO} + \text{Fe}_2$.

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:— $\text{Pb} + \text{S} = \text{PbS}$.

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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

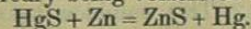
nature. A good specimen should have a dark bluish grey colour, should be brittle, with a crystalline fracture, and a metallic lustre. If the sample is somewhat malleable with a granular fracture, it is a mixture of lead and lead sulphide. It must then be broken up in an iron mortar and treated over again 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— $\text{Sn} + \text{S} = \text{SnS}$.

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.

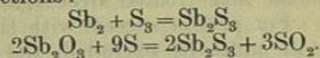
Zinc sulphide is also formed when a mixture of mercury sulphide and zinc is projected into a red hot crucible, the mercury being volatilised thus—



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:—



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. $\text{Ag}_2 + \text{S} = \text{Ag}_2\text{S}$.

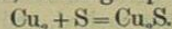
This substance is moderately malleable, of a dark bluish grey colour, with metallic lustre, and a crystalline structure. It is almost as soft as silver.

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— $\text{Fe} + \text{S} = \text{FeS}$.

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. $\text{Ni} + \text{S} = \text{NiS}$.

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:—



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 ($\text{Cu}_2\text{S}, 3\text{FeS}$). 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 ($2\text{Cu}_2\text{S}, \text{FeS}$). 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— $\text{Hg} + \text{S} = \text{HgS}$.

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."

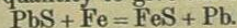
Or melt sulphur in excess in a crucible just sufficiently hot to keep the sulphur melted, and add 200 grains of mercury drop by drop, when a mixture of HgS and Hg_2S will be formed. Now add more sulphur; allow it to combine, and pour into a dry mould, or on to an iron plate if it is desired to sublime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



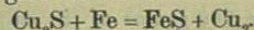
Heat for about fifteen to twenty minutes, or until all action ceases, and pour into a half-round mould; allow to cool, and remove the layer of sulphide of iron by

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:—

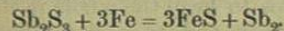


Pour into mould when complete; allow to cool, and examine the product, which is an alloy of copper and iron, with a double sulphide of iron and copper on the top, showing that the reduction is imperfect by this method.

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— $\text{Ag}_2\text{S} + \text{Fe} = \text{FeS} + \text{Ag}_2$.

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

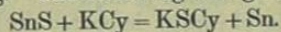


Care must be taken not to have the temperature too

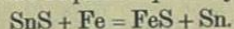
high, or some of the antimony and unreduced antimony sulphide will volatilise. If excess of iron is used, it will form an alloy with the reduced antimony, part of which passes into the regulus. The sulphide of iron has a density very nearly equal to that of antimony, so that, unless the mass is kept 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:—



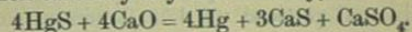
Exp. 162. Take 200 grains of tin sulphide, and reduce with iron in just the requisite quantity.



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.



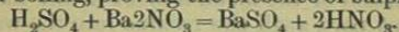
In the above process, it is necessary that all the materials should be dry or the moisture will crack the hot glass.

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.



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.— $ZnS + FeO = ZnO + FeS$.

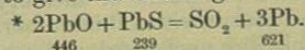
(b) Litharge is an energetic oxidiser for some sulphides; thus, when sulphide and oxide of lead are heated together the sulphur is oxidised and the lead isolated.

(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:—



* 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.

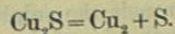
Exp. 174. Take 500 grains of lead sulphide and sufficient lead sulphate to reduce the whole of the lead; thus— $PbS + PbSO_4 = 2SO_2 + 2Pb$.

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

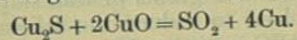
Exp. 175. Break up some sulphide of lead into pieces about the size of peas, or a little less; weigh out 500 grains and roast at moderate temperature for an hour. The product will consist of oxide, sulphate, and unaltered sulphide. Place the whole in a crucible, and fuse till all action ceases, taking 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:—



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



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. $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} = 6\text{Cu} + \text{SO}_2$.
2. $\text{Cu}_2\text{S} + 2\text{CuO} = 4\text{Cu} + \text{SO}_2$.
3. $\text{Cu}_2\text{S} + 3\text{CuO} = 3\text{Cu} + \text{SO}_2 + \text{Cu}_2\text{O}$.
4. $\text{Cu}_2\text{S} + 6\text{CuO} = \text{SO}_2 + 4\text{Cu}_2\text{O}$.
5. $\text{Cu}_2\text{S} + \text{CuSO}_4 = 3\text{Cu} + 2\text{SO}_2$.
6. $\text{Cu}_2\text{S} + 2\text{CuSO}_4 = 3\text{SO}_2 + 2\text{Cu}_2\text{O}$.
7. $\text{Cu}_2\text{S} + 4\text{CuSO}_4 = 5\text{SO}_2 + 6\text{CuO}$.
8. $2\text{Cu}_2\text{S} + 2\text{CuO} = 2\text{Cu} + \text{SO}_2 + \text{Cu}_2\text{S}$.
9. $2\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} = 6\text{Cu} + \text{SO}_2 + \text{Cu}_2\text{S}$.

EXAMPLE.

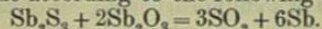
In No. 1 the molecular weight of Cu_2S is 158,* and the weight of two molecules of Cu_2O is 284; then the amount of oxide required for 200 grains of sulphide is calculated by simple proportion,

$$\text{As } 158 : 200 :: 284 : x.$$

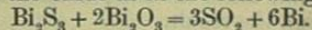
The amount of copper is computed in the same way,

$$\text{As } 158 : 200 :: 378 : x.$$

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



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



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—

○ ○
○ ○
○ ○

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.