

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  $\text{Fe}_3\text{O}_4$ , and known as "bull-dog." The liquated portion is bull-dog slag, and contains most of the impurities.

Exp. 203a. 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.

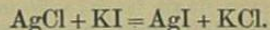
§ 67. The following experiments are given to illustrate wet methods of extraction:—

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.— $\text{Ag}_2\text{SO}_4 + \text{Cu} = \text{CuSO}_4 + \text{Ag}_2$ .

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.— $\text{CuCl}_2 + \text{Fe} = \text{FeCl}_2 + \text{Cu}$

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—



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. 206a. Mix pyrites, salt, and silver sulphide, and roast as before. Warm the residual mass with a 10 per cent. solution of sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ). 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 Patara 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.

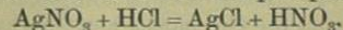
### AMALGAMATION.

§ 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.

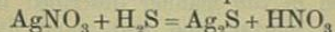
Exp. 211. Weigh out 10 grains of silver, place in a beaker, and dissolve it in dilute nitric acid. Then add a solution of hydrochloric acid, a little at a time, well stir the contents of the beaker with a glass rod, and continue the addition of acid until no further precipitate is formed.



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.



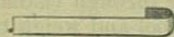
Filter and wash the precipitate, then amalgamate with mercury, and proceed as in the last experiment.

#### 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-

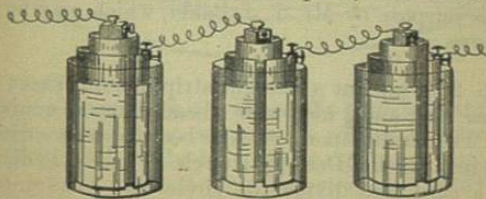


Fig. 48.

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  $90^\circ$ ; 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

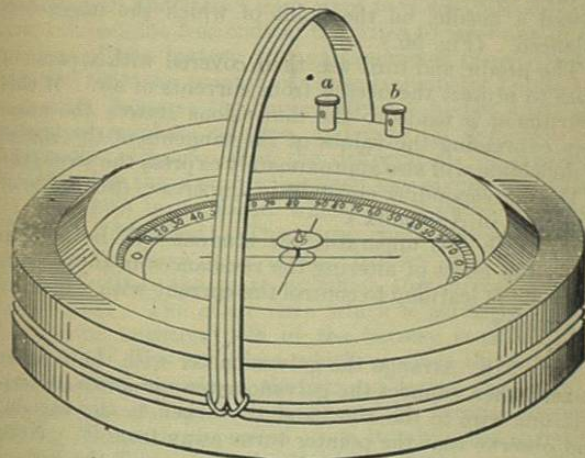


Fig. 49.

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 amperes. (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  $0^\circ$ . 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-immersing 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  $\frac{63.2}{2} = 31.6$ . 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 4½ 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

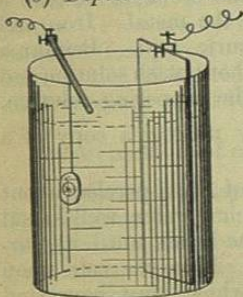


Fig. 51.

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 blacklead. 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 blacklead 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 mould again well blacklead.

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

§ 74. Exp. 221. Beautifully sharp impressions of coins may be obtained in fusible alloy, which may be prepared and used as follows:—Melt together in a small iron ladle,

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 weight of the best glue and let it remain in an excess of "cold" water for several hours. Then put the swollen glue, which has absorbed much water, into a clean tin vessel and place this in a second larger vessel containing water, so that it may be heated like a glue pot. When the glue has melted, pour in one part by weight of treacle and thoroughly stir the mixture until the whole is of uniform composition. Surround the object to be copied with a frame luted outside with clay and oiled to make the entire surface uniformly greasy, avoiding excess of oil. Pour in the 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 consistency 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 indirectly without risk of being injured in the process.

If the student weighs his mould before and after the deposition of copper he will be able to judge of the progress of the operation. An increase in weight of 5000 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, § 71, suspend two stout copper anodes and connect them with the positive pole of the battery. Suspend a very 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  $45^\circ$  is obtained. Examine the anodes from time to time, and observe that they become black and ultimately slimy; while the copper deposited upon the cathode is beautifully clean and of a

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 the 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.

Symbol Ag. Atomic weight 107.6. Chemical equivalent 107.6. Electro-chemical equivalent 0.17243 grains. 1 ampère will deposit 62.0747 grains per hour. Pressure required = .5 to 1 volt. Current density = 1.5 to 4.5 ampères per square foot of cathode.

#### PRELIMINARY EXERCISES.

§ 77. Distilled water free from chloride must be used, except where otherwise stated, and all vessels must be rinsed with distilled 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 ( $\text{AgNO}_3$ ). 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 ( $\text{AgCy}, \text{KCy}$ ). 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 ( $\text{AgCy}$ ). Observe that it is exactly similar in appearance to silver chloride, from which it cannot be distinguished, except by a special test.

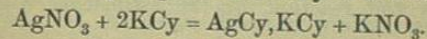
Exp. 232. Decant the liquid from the silver cyanide obtained in the last experiment; wash the precipitate, and add to it a solution of potassium cyanide drop by drop, until the precipitate exactly dissolves. The solution obtained is the double cyanide of silver and potassium.

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 ( $\text{AgCl}$ ), and the latter silver cyanide ( $\text{AgCy}$ ). 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 ( $\text{AgCy}, \text{KCy}$ ) is decomposed and converted into silver chloride ( $\text{AgCl}$ ) by the action of dilute hydrochloric acid; (*b*) that dilute nitric acid decomposes it also, but leaves silver cyanide ( $\text{AgCy}$ ); (*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.

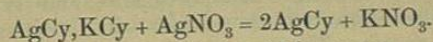
Exp. 234. Make a little silver nitrate (Exp. 225); evaporate to dryness, re-dissolve in distilled water, and add a solution of potassium cyanide drop by drop with brisk shaking until the precipitate formed just re-dissolves.



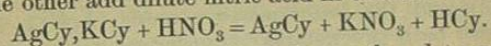
This reaction is employed in estimating the percentage of pure potassium cyanide in a sample of the commercial salt.

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.



To the other add dilute nitric acid in excess.

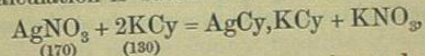


Either of these reactions may be employed to recover silver cyanide when that salt has been re-dissolved by excess of potassium cyanide. (See Exp. 231.)

§ 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:—



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.

$$\begin{array}{l} \text{1 grain contained } \frac{13}{18.9} \\ \text{100 grains } \quad \quad \quad \frac{100 \times 13}{18.9} = 68.78 \text{ per cent.} \end{array}$$

#### PREPARATION OF SILVER PLATING SOLUTION.

§ 79. The preparation of a silver plating solution comprises three distinct operations, viz. :—

- The conversion of silver into silver nitrate.
- The precipitation of the whole of the silver from the above solution as silver cyanide or chloride.
- 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.

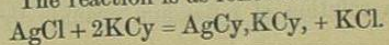
Make a solution of potassium cyanide by dissolving

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:—

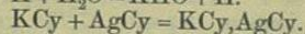
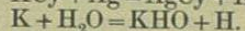
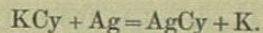


Read off the proportion of cyanide used, and add one-half more for "free cyanide." Make up to 1 quart with water, and filter for use.

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  $\frac{1}{4}$  ounce of silver is dissolved from the anode. The following equations show the action which takes place:



§ 80A. Copper brass and German silver work should be "quicked" immediately before plating. The quickening 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 ( $\text{AuCl}_3$ ) 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 ( $\text{AuCy}$ ) is formed. Well wash the precipitate, and then add just sufficient potassium cyanide ( $\text{KCy}$ ) 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.