

monia solution; the wider tube D is partially filled with broken glass, moistened with dilute ammonia. To conduct the operation, warm the flask B so as to fill the whole with ammonia vapours; then run a little acid from C on to the carbonate, which is decomposed, liberating carbonic acid; the latter traverses the bent tube, which must not dip beneath the surface of the ammonia, and is absorbed by the ammonia vapours forming carbonate.

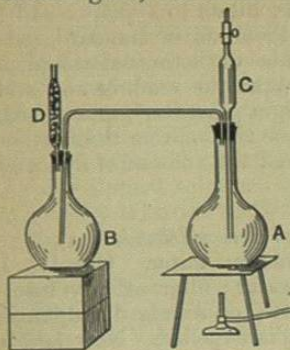


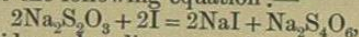
Fig. 86.

When all effervescence ceases on dropping in more hydrochloric acid, heat the liquid in flask A to boiling, so as to expel the last traces of carbonic acid and allow the whole apparatus to cool. Detach the tubes; wash any carbonate of ammonia from them into B; then add sufficient calcium chloride to completely precipitate the carbonic acid as calcium carbonate; boil; filter and wash as quickly as possible, since the ammoniacal liquid absorbs carbonic acid from the atmosphere; then proceed with the precipitate as in § 335 (a).

EMPLOYMENT OF IODINE AND SODIUM THIOSULPHATE (ANALYSIS BY OXIDATION AND REDUCTION).

§ 336. Sodium hyposulphite, or thiosulphate as it is more properly termed, is a powerful reducing agent; while iodine has an opposite character, being indirectly an oxidising agent. These two bodies, when present in

a solution made alkaline with sodium carbonate, re-act according to the following equation:—



sodium iodide and sodium tetrathionate being formed. If then some substance is present to indicate the point when the free iodine is completely combined with sodium, we have a means of estimating an unknown quantity of that element. The substance thus employed is starch solution, which produces with iodine a blue compound (composition unknown).

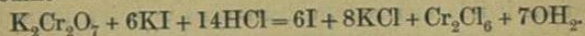
(a) *Starch Solution.* Take 2 or 3 grains of starch and make into a paste with cold water; then add half a pint of water; boil; allow to settle and decant the clear liquid into a stoppered bottle. A fresh solution should be made every three days.

(b) *Standard Sodium Thiosulphate* ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$). To prepare a deci-normal solution, dissolve 24.8 grammes of the pure re-crystallised salt in water and make up to litre: 1 c.c. therefore contains .0248 gramme.

(c) *Iodine Solution.* A deci-normal solution of pure iodine must contain 12.7 grammes of iodine per litre, or .0127 gramme per c.c. Weigh the iodine; place it in a litre flask with 18 grammes of pure potassium iodide; add water perfectly cold and place the stopper in flask. When dissolved, add water to make the solution up to a litre. Where iodine solution is added from a burette, the latter must have a glass tap. It is often more convenient to add excess of iodine by a pipette and then to determine the excess by standard sodium thiosulphate.

§ 337. The standard thiosulphate solution may be tested to ascertain its exact strength by means of a standard deci-normal solution of potassium bichromate.

Two hundred and ninety-four parts of bichromate in presence of hydrochloric acid will liberate 762 parts of iodine—



Therefore 1 c.c. of deci-normal bichromate solution, containing 4.90 grammes per litre, will liberate .0127 gramme of iodine. A given quantity (say 20 c.c.) of bichromate solution is measured into a small flask, diluted with water till one third full and 8 to 10 c.c. of a solution of pure potassium iodide and 5 c.c. hydrochloric acid added. Now run in the standard thiosulphate from a burette drop by drop; well shake the flask each time until the iodine has nearly disappeared; then add a few drops of starch solution and continue to run in until the blue colour disappears. Twenty c.c. of bichromate liberate $20 \times .0127$ gramme of iodine, and 1 c.c. of thiosulphate, if correct, will convert .0127 gramme of iodine into iodide, as seen by equation in § 336.

If care be taken in the preparation of the standard iodine solution, it may be used for standardising the thiosulphate. Take 25 c.c. of the thiosulphate solution, add water and a little starch solution, run in iodine solution from a burette until a permanent blue colour persists. Then the quantity of standard iodine solution measures the strength of the thiosulphate.

§ 338. *Estimation of Antimony.*

The metal must exist entirely in the form of trioxide, as the principle on which its estimation is based is its complete oxidation to antimonic acid.

Dissolve $\frac{1}{2}$ gramme of the compound in tartaric acid and water in a flask; neutralise with carbonate of soda; add 20 c.c. of a saturated solution of sodium bicarbonate, then a little starch solution, and run in standard iodine solution until the liquid remains blue for five minutes. One equivalent of antimony requires 2 equivalents of

iodine, so that 1 c.c. of deci-normal iodine solution = .0061 gramme of antimony.

§ 339. *Estimation of Arsenic.*

This operation is similar to that of antimony. One c.c. of deci-normal iodine = .00375 gramme of arsenic.

In the case of arseniates the metal partly exists in the state of pentoxide, but some trioxide is generally present. Take 2 grammes; dissolve in water or acid as the case may be; neutralise the acid with carbonate of soda; add a little sodium acetate and acetic acid; boil for some minutes to decompose nitrites and make up the solution to 500 c.c. with water.

Take 50 c.c.; add 20 c.c. of carbonate of soda; then starch solution and potassium iodide as with antimony. The result gives the amount present as As_2O_3 (1 c.c. = .00495 gramme As_2O_3).

Now pass a current of sulphur dioxide to reduce the pentoxide to trioxide; boil till all SO_2 is expelled; cool and make up solution to 500 c.c. Take 50 c.c. and proceed as before (1 c.c. = .00575 gramme of As_2O_3). From the second determination the amount of arsenic present as pentoxide is ascertained.

§ 340. *Estimation of Tin.*

Metallic tin or a stannous compound is dissolved in strong hydrochloric acid, a moderately large quantity of a solution of Rochelle salt added, then sodium bicarbonate in excess. If enough of the tartrate solution is present, the solution will be clear; a little starch solution is then added, and deci-normal iodine solution run in until the blue colour is permanent on well shaking the flask. Metallic tin is best dissolved in hydrochloric acid in contact with platinum foil, which forms with it a galvanic couple. A stream of carbon dioxide should also be passed into the vessel while solution is taking place. 254 parts of iodine are equivalent to 118 parts of tin. 1 c.c. of iodine solution = .0059 gramme of tin.

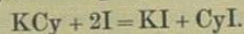
§ 341. *Estimation of Chlorine in Aqueous Solution of the Gas.*

Take a measured quantity of the water containing chlorine; add a solution of potassium iodide; then run in deci-normal solution of sodium thiosulphate until the iodine has nearly disappeared; add a little starch solution, and continue to run in thiosulphate until the liquid is just colourless.

1 c.c. = .00355 gramme of chlorine.

§ 342. *Estimation of Hydrocyanic Acid.*

Potassium cyanide when mixed with a solution of iodine removes the colour of the latter as long as any undecomposed cyanide is present, thus—



Two equivalents therefore of iodine represent one of cyanogen, *i.e.*, $254\text{I} = 26\text{Cy}$ or 65KCy or 27HCy .

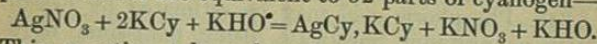
Commercial alkaline cyanides are contaminated with oxides and carbonates, which also removes the colour of iodine solution. These must be converted into bicarbonates by adding a saturated solution of carbon dioxide in water.

Weigh 5 grammes of the salt; dissolve in water; make solution up to 500 c.c.; take 10 c.c., which equal .1 gramme, by means of a pipette; transfer to a flask; dilute to 250 c.c.; add 2 ounces of soda solution and run in from a burette deci-normal iodine solution until the solution just acquires a permanent yellow colour. Suppose 20 c.c. are required, then $20 \times .00325$ gives .0065 gramme, or 65 per cent. of real KCy.

In the case of free hydrocyanic acid, add a slight excess of sodic hydrate, then soda solution as above and proceed in the same way.

ESTIMATION OF CYANOGEN AND CHLORINE BY PRECIPITATION.

§ 343. When silver nitrate is added to an alkaline solution containing cyanogen and well agitated, no precipitation of silver cyanide occurs until all the cyanogen has combined with alkali and silver to form the soluble double cyanide (AgCy , KCy); any further excess of silver nitrate at once produces a permanent precipitate of AgCy , the double compound being destroyed. 108 parts of silver are equivalent to 52 parts of cyanogen—



This re-action takes place in the presence of sodium chloride, as no precipitate of silver chloride occurs until the silver required to form the above double compound is exceeded.

When no alkali is present the double compound is not formed and the whole of the cyanide is precipitated. In this case 108 parts of silver will be required for 26 parts of cyanogen. The former method is, however, preferable.

§ 344. *Deci-normal Silver Solution.*

10.8 grammes of silver are dissolved in dilute nitric acid placed in a conical beaker, the mouth of which is closed with a funnel to prevent spurting. When solution is complete, wash down funnel and sides of beaker; transfer to litre flask and fill up to mark with water. Instead of using metallic silver, 17 grammes of pure re-crystallised silver nitrate may be dissolved in a litre of water.

The above silver solution may also be used for the estimation of chlorine, the standard liquid being cautiously run in until a precipitate ceases to form. The termination may be very accurately noted by

means of a small quantity of a solution of potassium chromate added to the salt solution. As soon as the whole of the chloride is precipitated, one drop more of silver solution produces a permanent red precipitate of silver chromate which does not disappear on shaking the liquid as before. It is necessary, however, that the free acid should be neutralised by an alkali, such as carbonate of soda, when using potassium chromate as an indicator.

ESTIMATION OF PHOSPHORIC ACID (P_2O_5).

§ 345. Phosphoric acid may be estimated by precipitation as uranium phosphate, using potassium ferrocyanide as indicator. (Atomic weight of $Ur = 240$.)

This method is based on the fact that when nitrate or acetate of uranium is added to a solution of tribasic phosphoric acid containing ammonium acetate and free acetic acid, the whole of the phosphoric acid is thrown down as double phosphate of uranium and ammonia, which has a light yellow colour. When this precipitate is washed with hot water, dried and burned, the ammonia is volatilised, leaving uranium phosphate $2(UrO_3)P_2O_5$, which contains 80.22 per cent. of uranium oxide UrO_3 and 19.78 of phosphoric acid P_2O_5 , therefore $\frac{1}{2}$ th of the precipitate may be taken as phosphoric acid. In the presence of fixed alkalies instead of ammonia, the precipitate consists simply of uranium phosphate. By this method, phosphoric acid may be completely removed from the alkalies and alkaline earths; also, with a slight modification, from iron, but not easily from alumina.

Preparation of Standard Solutions.

(a) *Sodium Phosphate.* 50.218 grammes of pure crystallised sodium phosphate (which has been freed from moisture by pressing between sheets of filtering paper)

are dissolved in water, and the solution diluted to a litre. 1 c.c. therefore represents .01 gramme of phosphoric acid.

(b) *Uranium Nitrate.* Dissolve sufficient crystallised uranic nitrate, which contains 43.7 per cent. of uranic oxide, so as to obtain a solution with 22 grammes of uranium oxide UrO_3 to a litre. The solution is made at first a little stronger than necessary; its value is then determined, and it is diluted accordingly, thus—50 c.c. of standard sodium phosphate are measured into a beaker, 3 or 4 c.c. of ammonia added, then acetic acid in excess and the mixture gently warmed. The beaker is then brought under a burette containing the uranium solution and portions of it delivered in from time to time, with constant stirring, until a drop taken out with a glass rod and placed on another drop of a solution of potassium ferrocyanide (1 to 20) on a white plate, produces a faint chocolate brown colour. A few moments should be allowed to elapse on the addition of each portion of uranium solution before testing, as the decomposition is not very rapid unless the fluid is considerably heated. Suppose the re-action has been produced with 18 c.c. of uranium solution, that quantity is equivalent to .50 gramme of P_2O_5 . To save calculation, dilute the uranium solution to the same strength as the sodium phosphate, which is done by measuring 180 c.c. and adding water to 500 c.c., or 360 c.c. to one litre. In case the point of saturation in an analysis is overstepped, a portion of the phosphate solution may be added and the analysis corrected.

In order to produce the above-mentioned brown colour a certain excess of uranium is necessary, and this excess varies with the quantity of liquid; for if the uranium solution is titrated so that the amount of fluid is about 4 ounces, it would require a few drops less of the standard solution to produce the same shade of colour than when

the same quantity of phosphoric acid was contained in only 2 ounces.

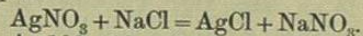
(c) When greater accuracy is required the following plan should be adopted—The uranium solution is put into a burette graduated to $\frac{1}{10}$ th c.c.; 20 c.c. of the phosphate solution are measured into a beaker together with the requisite quantities of ammonia and acetic acid, the quantities of which in any analysis should always be as near as possible the same as used in the original titration; the rest of the manipulation is conducted as above described. When a sufficient quantity of uranium solution has been added to produce the distinct colour with a drop of ferrocyanide, the height of the total fluid in the beaker is marked by a slip of gummed paper, the contents emptied, and the glass again filled to the same height with water containing the same quantities of ammonia and acetic acid as were added to the phosphate. The uranium solution is then added, drop by drop, until a drop of the mixture produces the same amount of colour with ferrocyanide as in the previous case; the quantity of uranium so required is deducted from that used for the phosphate, and thus the proportion found which was absolutely required to precipitate the phosphoric acid. If the same plan is pursued in all analyses, great accuracy will be obtained, however variable the amount of fluid. In ordinary cases the difference of the two methods is slight. (Sutton's Volumetric Analyses, p. 219.)

The process is applicable to alkaline and alkaline earthy phosphates, but not to phosphates of sesquioxides, nor is it available in the presence of arsenic acid or any metals giving coloured precipitates with ferrocyanide of potassium, such as copper.

VOLUMETRIC ESTIMATION OF SILVER.

§ 346. This method is based on the powerful affinity of silver for chlorine, and when these bodies are in solution together, they form an insoluble chloride of silver which readily separates from the solution in which it is suspended. For the purposes of assay three solutions of known strength are required.

(a) *Standard Solution.* Take a quantity of pure sodium chloride; crush to a fine powder and heat for half an hour to remove every trace of moisture; allow to cool in a desiccator and weigh a sufficient number of grains of salt to precipitate 10 grains of silver, or if the French system of weights be used, a sufficient amount of salt for 1 gramme of silver. This quantity is calculated from the equation



As 108 : 10 :: 58.5 : 5.416 grains;

Or as 108 : 1 :: 58.5 : .542 grammes.

The 5.416 grains of salt are then dissolved in pure distilled water, and the solution diluted to 1000 grains by means of a measuring flask, at 15°·5 C., or the .542 gramme to 500 cubic centimetres. These quantities may be then multiplied to any convenient extent, thus—30,000 grains of water would contain 30×5.416 grains of salt, which should be kept in a half gallon stoppered bottle.

(b) *Deci-normal Solution of Salt.* For the purpose of attaining a greater degree of accuracy in the results, 1000 grains of the normal solution are removed and diluted with water to 10,000 grains in a quart bottle by means of a measuring flask. This should be kept stoppered when not in use and labelled "deci-normal solution," to prevent mistakes. This solution contains

$\frac{1}{10}$ th as much salt as the standard solution, 1000 grains will therefore precipitate .542 grain of silver.

In case of gramme weights, 100 c.c. is diluted to 1 litre, which = 1000 c.c. to form a deci-normal solution; 1 c.c. will precipitate .001 gramme of silver.

(c) *Deci-normal Solution of Silver.* Dissolve 10 grains of pure silver in a small quantity of pure nitric acid diluted with twice its volume of water. The solution is very conveniently effected in a conical beaker. When the silver is dissolved, blow out the nitrous fumes; add water; transfer to the 1000 grains measuring flask and fill up to the mark with water. Place this solution in a quart bottle and make it up to 10,000 grains with distilled water, so that 1000 grains of the solution contain 1 grain of silver. Keep it from the light.

This solution is used when too much salt solution has been added to an assay, then, knowing the number of liquid grains of silver solution which has been necessary to precipitate the excess of salt, the true amount of salt for the silver present is ascertained. It is also used in standardising the standard salt solution, to which, if too strong, the necessary amount of water to be added is thereby ascertained. For example, if one thousandth of the deci-normal silver solution is required, then one thousandth of its weight of water would have to be added to the total amount of solution.

With the gramme system 1 gramme of pure silver is dissolved and the solution diluted to 1 litre. Each c.c. contains .001 gramme of silver.

§ 347. *Testing of Standard Solution.*

As the exact strength of this solution cannot absolutely be relied on, the real working power must be determined by experiment. Take a little over 10 grains of pure silver, say 10.02; place in an assay bottle which holds about 12 ounces; add nitric acid, 1 : 2; put the bottle in

a vessel containing water and boil the water gently until the silver in the bottle is dissolved; then dilute till the bottle is one third full. This method of heating the bottle keeps it at a uniform temperature and prevents it cracking, which would be the case with a higher temperature and unequal heating of the parts.

(a) It will be convenient to fix an india-rubber bung with two holes in the mouth of the bottle (Fig. 87). Through the bung pass two glass tubes, one reaching to the bottom and the other only just through the bung. The latter tube may have a piece of india-rubber tubing on its outer end, which may be fitted with a bit of glass rod, so as to open or close it at will. The outer end of the longer tube should be bent and drawn out to a point, so as easily to pass inside the mouth of the pipette which is used for measuring the quantity of liquid employed.

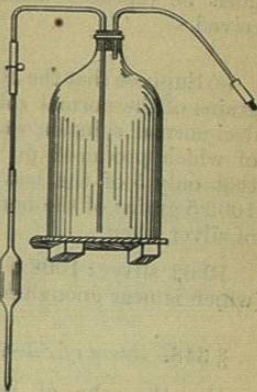


Fig. 87.

(b) To fill the pipette, stop the bottom up with one finger; remove the glass rod stopper, and blow into the tube until the liquid begins to run into the pipette; then re-place stopper and the liquid will continue to flow into the pipette. When the solution just reaches the mark the flow is discontinued, and the contents, which may be 1000 grains or 100 c.c., run into the assay bottle. Now close with stopper and shake vigorously, giving the bottle at the same time a rotatory motion, by which means the particles of precipitated

silver chloride clot together and quickly subside. When the liquid is clear, add 10 grains of the deci-normal solution from a small pipette; shake as before if a precipitate forms and allow to stand till clear. This must be repeated until no further precipitate is perceived.

(c) Suppose that the 10.02 grains of silver required 1000 grains of the normal solution, and that 30 grains of the deci-normal solution were also added, the last 10 grains of which produced no precipitate, then we may assume that only 5 of the last 10 grains were required, so that 1002.5 grains of the normal solution satisfy 10.02 grains of silver, then

10.02 silver : 1002.5 salt : : 10 silver : $x = 1000.5$ salt,
which is near enough for practical purposes.

§ 348. *Assay of Silver Alloys.*

For the sake of practising this method it is well to operate on alloys of known composition, such as the silver coinage. Roll out very thin a clean shilling without annealing, so as to get three or four pieces of about 11 grains each, having the same composition. It is advisable to take in all cases such a quantity of an alloy as contains at least 10 grains of silver, which in the case of our standard coin is 10.83 grains.

(a) Suppose 10.88 grains of the alloy have been taken, dissolved in nitric acid as before, and diluted to the same bulk. Now run in 1000 grains of the normal solution, and when clear, add the decimal solution, 10 grains at a time, until the silver is completely precipitated. The amount added may be noted thus—

1000	grains	normal	solution.
10	"	deci-normal	solution.
10	"	"	"
10	"	"	"
10	"	"	"
10	"	"	"
10	"	"	"
10	"	"	"
10	"	"	"

1008.0 grains of normal solution.

Assuming that the last 10 grains of solution produced no precipitate, this cannot be included. Also we do not know how much of the previous 10 grains were required, so that 5 grains may be considered the requisite quantity, which gives 1006.5 grains of normal solution as the quantity required for 10.88 grains of the alloy.

As 1000 salt : 10 silver : : 1006.5 : $x = 10.065$.

As 10.88 alloy : 10.065 solution : : 1000 : $x = 925$.

(b) Before an estimation can be made of alloys of unknown composition by this method, it is necessary to know approximately the quantity of the contained silver. For this purpose weigh about 5 grains of the alloy; dissolve in nitric acid and dilute as before; then run in the standard solution cautiously from a graduated 1000 grains burette until only a feeble turbidity is produced, then add a drop at a time until no turbidity is perceived. The bottle must be shaken each time and the liquid allowed to clear itself as usual. The last drops are not reckoned. Suppose 5 grains required 408 grains of normal solution, its amount of silver is computed thus—

1000 : 408 : : 10 : $x = 4.08$,

the amount required for a correct assay thus—

4.08 : 10.02 : : 5 : $x = 12.28$.

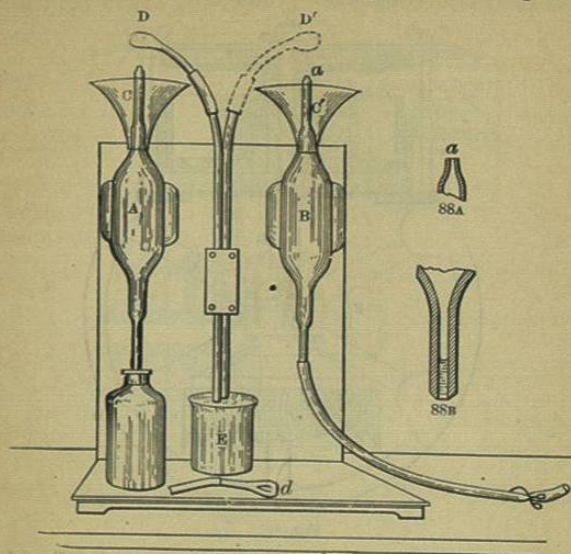
(c) With alloys of silver which contain lead, tin, antimony and gold, the portion taken for assay is digested with the smallest quantity of nitric acid as long as red vapours are formed; then boiled with concentrated sulphuric acid till the gold has well settled together; then diluted and the normal solution run in. In the presence of mercury, mercurous chloride may be carried down with the silver and vitiate the result. When the quantity of mercury is small, Levöl recommends the addition of 25 c.c. of ammonia and 20 c.c. of acetic acid, which decompose mercury chloride and prevent its precipitation. When much mercury is present the ammonium acetate is not effective, and Debray recommends to drive off the mercury by igniting in a muffle for four hours, in a small crucible made of gas carbon.

§ 349. In mints and assay offices, where a large number of assays are daily made, the apparatus is constructed so as to allow several estimations to be rapidly made. A large glass or stoneware vessel containing the normal solution is placed on a shelf at a convenient height and provided with a tap near the bottom by which any quantity may be run off and measured by the pipette.

(a) The "Stas" double Pipette (Fig. 88), as used in the Royal Mint, is filled from the large vessel some 6 feet above the level of B. The salt solution introduced from below, rises into A or B (according as the tube is attached), but any overflow is caught by the platinum caps or tubes D D' (shown in section at *d*), and flows down into the beaker E, which is a receptacle for the waste solution. When the pipette is full, the orifice at the top is covered with the finger and the salt solution is then run into the assay bottle.

Each pipette contains 100 c.c. The platinum caps are attached by india-rubber tubing to glass tubes which pass into the beaker below; these caps are so arranged as to

catch any normal solution which under pressure would be spurted up. If they were not provided the operator



would have to watch the pipette constantly. The glass funnels C C' are merely to retain any solution which the caps fail to catch and would otherwise run down the pipette into the assay bottle. The orifice (*a*) at the top of the pipette to be closed with the finger must be small, and the tube at the lower end of the pipette must be carefully ground and adjusted so as to always retain a drop of the same size. These are shown one-third the actual size in Figs. 88A and 88B. The pipettes are adjusted as nearly as possible to each other, but the assays made by each are kept separate and each is corrected with a separate proof of fine silver.

(b) When the normal salt solution has been run into the assay bottles, the latter are stoppered and the con-

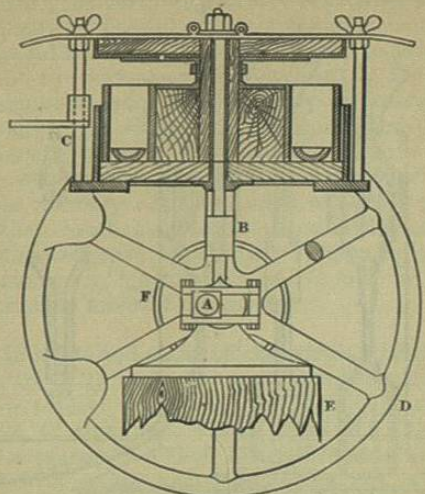


Fig. 89.

tents agitated in an apparatus called a "shaker," which causes the precipitated silver chloride rapidly to subside.

A very perfect form of "shaker" worked by power or by hand is shown in Figs. 89 to 91. It is an American adaptation, as arranged in the Royal Mint and used in conjunction with the "Stas" pipette for rapidly conducting a large number of assays. The general arrangement of the appliance is shown by a plan and by two elevations, both partly in section, from which it will be evident that the block bearing the driving shaft and pulleys is firmly secured to a wooden base E. A circular wooden frame or receptacle for ten bottles is supported by one end of a central vertical rod, which passes through

the guiding block B, while the other end of the rod is provided with a cross-head. The end A of a short crank

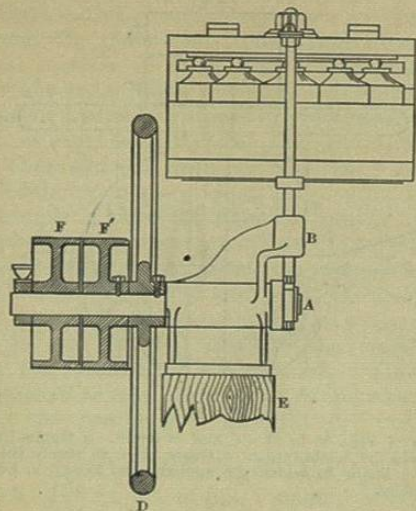


Fig. 90.

fixed to the driving shaft enters a slot in this cross-head, and the revolution of the crank thus imparts a rapid up-and-down movement to the vertical rod and therefore to the bottle frame it supports. Additional steadiness is afforded by the block C through which a rod on the bottle-frame passes. Each bottle is protected by a vulcanite cell and rests on an india-rubber cup, and each set of bottles is retained in position by a padded lid in two portions, only one of which is shown in the plan. This lid is secured by thumb screws. The motion is imparted by shifting a band from the loose pulley F to the fast pulley F'. There is a fly wheel D, and it is usual to

drive the shaker at the rate of about 300 revolutions a minute.

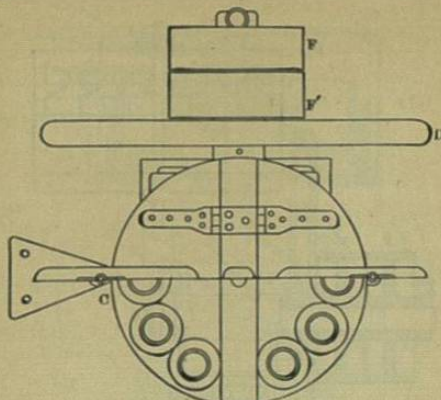


Fig. 91.

Description of Figs. 89 to 91.—A, End of crank. B, Guide block for rod which supports the bottle frame. C, Guide block to steady the frame. D, Fly wheel. E, Beam to which the appliance is fixed. F, Loose pulley. F', Driving pulley.

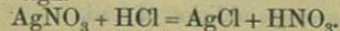
In practice the normal solution is made from common salt, and the amount of water necessary to make a solution of the requisite strength, assuming the salt to be pure, is added and the exact amount of NaCl determined by experiment. When this is known it is easy to calculate the amount of water or salt to be added so as to obtain a correct standard. It is then again tested to verify its correctness.

INDIAN METHOD OF SILVER ASSAYING.

§ 350. Although this is a gravimetric method it will be more convenient to introduce it here. The cupellation

assay is not considered correct enough, and the volumetric method is not suitable because the high temperature of the climate causes evaporation of the salt solution.

To illustrate this process weigh two portions of pure silver about 20 grains each; place each in a stoppered bottle and dissolve in nitric acid, 1 : 2, by heating the bottles in hot water; blow out fumes; dilute with water; add sufficient hydrochloric acid to precipitate the silver, and shake as usual to collect the precipitate and clear the liquid. Then add one drop more to see if any further silver chloride separates. When the precipitation is considered complete, allow the liquid to remain until quite clear. Siphon off the supernatant liquid; wash two or three times with distilled water, siphoning off each time when clear. Then fill the bottles with distilled water; invert each into a small French crucible full of water and allow to stand in that position until all the precipitate has fallen to the bottom of the crucible. Then remove bottle; pour off as much as possible of the water without disturbing the precipitate; carefully dry the latter at 100° C. and weigh.



As 143.5 : 108 :: Wt. of ppt. : amount of silver.

The amount of silver thus found will be short of the true quantity present. An experiment performed with 20 grains of fine silver gave 19.962 grains, so that to the result of each assay of standard silver containing 20 grains of silver .038 grain must be added for loss.

VOLUMETRIC ESTIMATION OF LEAD

§ 351. The following simple process was invented by Dr. H. Schwarz. Dissolve 14.730 grammes of pure potassium bichromate in sufficient water to form 1 litre. One cubic centimetre of this solution precipitates .0207 gramme of lead.

(a) The solution of the lead should be effected with the smallest quantity of nitric acid; then diluted with water; carefully neutralised with ammonia, or sodium carbonate, and an excess of sodium acetate added; then the standard bichromate solution run in from a burette, by which means the lead is precipitated as lead chromate. When the precipitation is nearly completed and commences readily to subside, place a few drops of a neutral solution of silver nitrate on a porcelain plate and touch the silver solution with a glass rod which has been dipped in the assay liquid. As soon as the bichromate is in excess the drop is coloured red, while the precipitate has no effect on the silver nitrate. Should the solution form a yellow colour before the silver re-action has commenced, it indicates that an insufficient quantity of sodium acetate has been added, more of which must now be introduced, and also a c.c. of normal lead solution containing 0.207 gramme of lead as nitrate. The slight turbidity which occurs soon passes off, and the operation may be proceeded with. One c.c. of the bichromate solution must be deducted from the final result on account of the extra addition of lead.

(b) Bismuth is the only metal which interferes with the above re-action. Silver, if present, may be precipitated as chloride with sodium chloride, which, if the latter is not added in excess, may be left in the solution, lead chromate not being decomposed by sodium chloride. Mercurous compounds when present would interfere, but the mercury may be precipitated as chloride with hydrochloric acid, and the precipitate boiled till it is converted into mercuric chloride.

Lead sulphate must be boiled with sodium carbonate to decompose it, and the carbonate dissolved with nitric acid.

(c) Salts of lead, such as phosphate, arsenite, etc., which are insoluble in acetic acid, should be dissolved in nitric acid and estimated by gravimetric methods.

VOLUMETRIC ESTIMATION OF COPPER.

§ 352. *Parke's method by Potassium Cyanide.* This method is well adapted for the estimation of copper in ores and slags free from manganese, nickel, cobalt, silver, mercury, and zinc, which metals interfere with the re-action and require to be removed before proceeding with the assay. The re-action is based on the fact that when potassium cyanide is slowly added to a copper solution which has been rendered blue by ammonia, the copper solution gradually loses its colour and finally becomes colourless. By ascertaining the amount of a solution of cyanide required to decolourise a solution of copper containing a known quantity of pure copper, the amount of copper in a given ore may be easily determined. The re-action (which is not absolutely uniform with variable quantities of ammonia) is such that a double cyanide of copper and ammonia is formed, cyanogen being liberated; this re-acts on the free ammonia, producing urea, oxalate of urea, cyanide and formate of ammonium. It is, therefore, necessary that the solution analysed should contain about the same quantity of ammonia as that with which the cyanide was originally titrated.

§ 353. Messrs. J. & C. Beringer have performed an exhaustive series of experiments on this subject and have arrived at the following conclusions:—

(a) The accuracy depends on the speed at which the last two or three c.c. are run in.

(b) With an increase of temperature, less cyanide is required.

10° C.	20° C.	35° C.	47° C.
23.5 c.c.	23.3 c.c.	23.05 c.c.	22.85 c.c.

(c) Ammonium nitrate interferes more than ammonia, requiring more cyanide. The same remark applies to

the sulphate, chloride and carbonate of ammonium. Also with an increase of ammonia, an increase of cyanide is required.

If an acid solution is just neutralised with sodium hydrate and then ammonia added, it is an advantage.

(d) *Conditions for Proportional Results.* Ammonium salts being absent, the temperature and mode of working the same, and only a slight excess of soda present, then, when the copper, the ammonia, and the bulk of the solution vary in relative proportions, the cyanide will be proportional to the copper present.

If the copper and bulk of solution remain constant and the ammonia is increased, then more cyanide is required; but if the copper and ammonia remain constant and the bulk of solution is increased, then less cyanide is required. Therefore an increase in bulk may neutralise the excess of cyanide required for an increase of ammonia.

There is a certain strength of ammonia with which proportional results can be obtained. With a slightly alkaline solution this strength is 15 c.c. of strong ammonia to each 300 c.c. of solution.

§ 354. *Standard Solution.*

(a) Dissolve 2000 grains of pure potassium cyanide in 4 pints of water, or 60 grammes in 1 litre of water. If common cyanide be used, half as much again as this may be requisite. It should be of such strength that 1000 liquid grains equal 10 grains of copper, or 50 c.c. equal half a gramme of copper, a stronger solution than this not being advisable. This solution decomposes somewhat in a few days, causing it to become discoloured, so that when a large quantity is made, it should be re-standardised every five or six days. Dr. Percy kept a solution for two years, and obtained from it the following standards:—

October, 1858,	1000 grains =	10.06	grains of copper.
July, 1859,	1000	9.84	” ”
March, 1860,	1000	9.45	” ”
June, 1860,	1000	8.92	” ”

From which it will be seen that it requires considerable time to make any considerable alteration in the strength of pure solutions.

(b) To standardise a cyanide solution; weigh 3 pieces of pure electrotype copper, or best conductivity copper wire (which has been perfectly cleansed in nitric acid), about 5 grains each, and obtain their exact weights on a delicate balance. Put each piece in a 30 ounce flask, and dissolve in a measured quantity of dilute nitric acid; boil to expel nitrous fumes and dilute till the flask is about one third full; then add sufficient ammonia from a measuring glass to render the solution a deep blue colour. Observe the quantity added, so that the same amount may be used in each case. Allow to cool.

(c) Fill the burette, and carefully run off until the liquid stands at zero, which is the uppermost division on the scale. Now place the flask containing the copper solution, which must be quite cold,* under the point of the burette, and run into it a quantity of standard solution; then well shake so as to thoroughly mix the contents and continue until the colour becomes very pale; then add the liquid, drop by drop, with frequent shaking until only a faint trace of colour is perceived after standing a few minutes; then take the reading of the burette scale. Proceed in the same way with the other two samples.

(d) Suppose 5, 6, and 7 grains have been employed with the result that 32 c.c., 38.5 c.c., and 45 c.c., respectively are required, then—

* Some assayers employ a uniform temperature of 15° C.

As 32	: 50	:: 5	: 7.81.
38.5	: 50	:: 6	: 7.79.
45	: 50	:: 7	: 7.77.

The mean of these numbers is taken as the standard, which is found to be 7.79. That is, 50 c.c. of the cyanide solution will just decolourise a solution containing 7.79 grains of copper.

§ 355. *Mode of Conducting an Assay.*

It is assumed that the ore is properly sampled, crushed and passed through a sieve with 80 meshes to the linear inch. *The ore is a carbonate.* Then weigh 15 and 17 grains respectively; place in 2 conical beakers; add a small quantity of hydrochloric acid, and digest at a gentle heat for half an hour; then add a little nitric acid, and heat for another ten minutes until nitrous fumes cease to be given off. Dilute with water; heat; and if the ore is dissolved, transfer to a 30 ounce flask; dilute until one third full as before; cool and add a measured quantity of ammonia till blue; then run in cyanide cautiously to decolourise. Ammonia first precipitates the iron, which may be disregarded, and the colour is observed between the top of the precipitate and the surface of the liquid. When quite cold, cautiously add the cyanide solution, shaking each time, and allowing the precipitate to settle. Great care is required in the finishing stages of the operation which are necessarily slow. About half an hour is required for each decolourisation.

Suppose 15 grains of ore require 40 c.c. of cyanide—

$$50 : 40 :: 7.79 : x = 6.232.$$

$$15 : 100 :: 6.232 : x = 41.55.$$

The ore then contains 41.55 per cent. of copper.

· § 356. *Copper Pyrites.*

(a) Weigh 20 and 25 grains of the finely sifted ore, place each portion in a conical beaker, moisten with

strong sulphuric acid; then add strong nitric acid and digest for an hour, adding a little fresh nitric acid from time to time as the other evaporates, and when all soluble matter is dissolved proceed as before. In oxidising sulphur ores with nitric acid, globules of free sulphur may form, enclosing some of the ore. These may be easily picked out of the diluted solution, ignited, and the residue dissolved in nitric acid. This must be added to the main portion.

(b) Oxide of iron imparts a greenish colour to the ammoniacal solution and it requires a little experience to detect the proper tint. If any uncertainty arises it is better to filter off the precipitate towards the completion. When the assay is finished, the oxide of iron will be free from copper, but if the iron is removed first, it retains a considerable portion of copper, which cannot be entirely removed by washing with ammonia. After the copper has been determined, the iron precipitate may be filtered off; washed; dissolved in hydrochloric acid, and the iron estimated by a standard solution of potassium bichromate as explained in the volumetric iron assay.

(c) Another way of treating pyritic ores is to roast the weighed assay portions in order to remove sulphur and convert them into oxides. Powder the roasted ore in an agate mortar; treat with nitric acid and proceed as with carbonates, as described in § 355. This plan, when proper care is exercised, yields better results than by solution direct.

(d) Grey ores (Cu_2S) are treated in the same way as pyrites, with or without previous roasting.

§ 357. *Interfering Metals.*

As stated at the commencement, some metals interfere with the accuracy of the copper assay by potassium cyanide.

Manganese may be removed by precipitating its oxide with ammonium carbonate and bromine, heating and allowing to stand some time.

The presence of nickel and cobalt is generally detected by the yellowish tinge of the solution after the blue colour has been removed. In such a case precipitate the copper first by sulphuretted hydrogen in an acid solution and re-dissolve the precipitate after filtering and washing.

Copper containing zinc must be treated in the same way. Silver may be precipitated with hydrochloric acid and filtered off before adding ammonia to the copper solution. Dr. Percy investigated this subject. His results are embodied in the table on following page, 5 grains at least of the foreign metal being present.

§ 358. Colouration Test for Copper Slags.

This method is adopted for approximately determining the amount of copper in slags and products containing only a small portion of copper. A series of white glass bottles of exactly the same capacity, preferably square in section, are filled with dilute solutions of copper, coloured blue by ammonia. Each contains a known quantity of copper, say $\frac{1}{10}$ th, $\frac{2}{10}$ th, $\frac{3}{10}$ th of a grain and so on, the intensity of the blue colour being proportional to the amount of copper present. These are kept as standards, for comparison. Fresh standards are required from time to time, as the colour alters slightly on standing.

The slag to be examined is pounded fine and sifted; then a portion, say 25 grains, weighed and dissolved in aqua regia by boiling gently for half an hour until decomposed. Then evaporate to dryness; add hydrochloric acid and a little nitric acid to oxidise the iron, and gently warm to dissolve the metallic matter; add water and warm again for about fifteen minutes; then filter off the insoluble silica and wash. Transfer the filtrate to one of the empty test bottles; add ammonia

and fill up with water, so that the volume may be the same as that of the standards. This solution is then

Weight of Electro-type Copper taken.	Estimation made in presence of	REMARKS.	Grains of Cyanide required.	Calculated Amount of Copper 1000 grains of solution is equal to
5.345	-	-	910	5.873
5.675	-	-	960	5.910
6.305	{ Sesquioxide of iron,	Added as sesquichloride before addition of ammonia, -	1070	5.89
8.150	{ Lead, anti-mony, tin & bismuth,	Added as chlorides before ammonia, -		
6.645	Nickel,	Added as sulphate before addition of ammonia; there was no precipitate formed on adding cyanide, and the solution was not decolourised, but remained yellow after adding 1630 grains.	1350	5.96
6.41	Cobalt,	Added as chloride, and the solution was not decolourised by 2000 grains of the cyanide.		
6.90	Antimony, -	Added as chloride, -	1160	5.948
5.30	Bismuth, -	Added as chloride, -	910	5.810
5.95	Lead, -	Added as chloride, -	1020	5.838
5.335	Tin, -	Added as chloride, -	910	5.863
4.70	Arsenic, -	Added as arsenic acid, -	790	5.974
5.450	Silver, -	Added as chloride. The cyanide acts on it during decolourisation.		
3.955	Silver, -	Added as nitrate. Action as with chloride.		
3.895	Zinc, -	Added as chloride; solution became turbid at close, -	1300	

compared with those in the test bottles, and that with which it most closely agrees, noted. Suppose it agrees with that containing $\frac{9}{10}$ th of a grain of copper, then the percentage is easily computed—

$$25 : 100 :: \frac{9}{10} : x = 3.6 \text{ per cent.}$$

The presence of oxides of nickel, cobalt, etc., which dissolve in ammonia, producing coloured solutions, render this method inaccurate.

SODIUM THIOSULPHATE METHOD.

§ 359. (a) This method is well adapted to the estimation of copper in alloys of that metal when lead and iron are not present in large quantity. The process is based on the re-action between iodine and thiosulphuric acid, the completion being determined by the bleaching effect produced upon a solution of starch added during the experiment.

(b) The re-agents required are—1. A solution of sodium thiosulphate, made by dissolving 700 grains of the pure crystallised salt in 2 pints of water. 2. Crystals of potassium iodide free from iodate. 3. Solution of starch (§ 336, a). 4. Pure acetic acid. 5. Crystals of pure sodium carbonate.

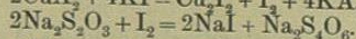
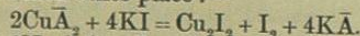
§ 360. *To Standardise the Solution.* (a) Weigh three pieces of electrotype copper, about 5 or 6 grs. each, and dissolve in nitric acid diluted with double its volume of water, using the smallest possible quantity to effect solution. Blow out the red fumes; dilute with water and transfer to a 12 ounce flask; add water till the flask is one third full; then add sodium carbonate in crystals, well shake and continue the addition until the liquid is neutral, which can be ascertained by the copper beginning

to be precipitated. Now add acetic acid in slight excess, and when quite cold, add crystals of potassium iodide equal to about six times the weight of the copper present. When the iodide has dissolved, run in the standard solution until the solution acquires a yellow colour, taking care to frequently shake the contents. A little starch solution (about 3 c.c.) must now be added and the standard solution added a drop at a time until the liquid after shaking is completely bleached. The number of divisions on the burette must now be read off and the strength computed.

(b) When iron is present, the red colour of the acetate renders it difficult to observe the re-action of the thiosulphate.

(c) In case of ores containing iron it is necessary to precipitate the copper by sodium thiosulphate; to filter and dissolve the precipitated copper sulphide in nitric acid, when the assay may be proceeded with as before.

(d) When potassium iodide is added to the acetic acid solution, cuprous iodide is formed and free iodine liberated, which dissolves in the excess of potassium iodide present, the potash uniting with the acetic acid. By the addition of sodium thiosulphate the free iodine is converted into sodium iodide, with the formation of tetrathionate of soda. The starch solution is used to render the termination manifest, the blue iodide of starch being gradually bleached. The following equations show the change which takes place:—



Suppose that 50 c.c. of standard solution to be equal to 9.85 grains of copper and that 10 grains of a sample of Muntz's metal required 30.5 grains of the standard,

$$\text{Then } 50 : 30.5 :: 9.85 : 6.008.$$

The metal contains 60.08 per cent. of copper.

(e) In the case of alloys containing a little lead, a few drops of sulphuric acid should be added after dissolving in nitric acid to precipitate the lead as sulphate.

VOLUMETRIC ESTIMATION OF ZINC.

§ 361. *By a Standard Solution of Sodium Sulphide.*

(a) When a solution of sodium sulphide is added to a solution of zinc containing oxide of iron which has been made alkaline with ammonia, the zinc is precipitated as sulphide first; then the iron, which is at once recognised by the dark colour of iron sulphide, sulphide of zinc being white. By ascertaining the amount of sodium sulphide necessary to exactly precipitate a known weight of zinc, we have a means of determining the amount of zinc in any given compound.

Iron, manganese, copper and silver, when present in a zinc compound in notable quantity, interfere with the re-action and should be previously removed. Cadmium does not interfere.

(b) *Standard Solution.* Counterpoise a dry beaker and weigh in it 700 grains of crystallised sodium sulphide ($\text{Na}_2\text{S}\cdot 9\text{OH}_2$); dissolve in water and make up the solution to 2 pints. The solution should be clear and colourless; any residue must be filtered off. This solution slowly decomposes and requires standardising every three days. It should be kept in bottles of glass free from lead.

Instead of the above method, 500 grains of caustic soda may be dissolved in $\frac{1}{2}$ pint of water, then saturated with sulphuretted hydrogen; then $\frac{1}{2}$ pint of water in which another 500 grains of caustic soda has been dissolved added to the first to remove the smell of the free gas. The solution is then ready for standardising.

(c) *Iron Solution.* Dissolve 50 grains of ferric oxide in hydrochloric acid, or 35 grains of iron wire in nitrohydrochloric acid, and dilute the solution to 1 pint.

§ 362. *To Standardise.* Weigh accurately three or four pieces of pure zinc, about 5 grains each; dissolve in hydrochloric acid; add a little nitric acid; dilute with water; place each quantity in a 30 oz. flask; add water until half full, then 3 c.c. of the iron solution; then add ammonia until the liquid is alkaline. When cold, run in the standard solution from a burette (keeping the liquid in the flask well agitated), until the oxide of iron just begins to turn black. The number of divisions is then read off and the mean of three or four results taken as the standard. Suppose 5.84 grains of zinc required 29 c.c., then 50 c.c. of standard would equal 10.06.

§ 363. *Assay of Zinc Ores.*

(a) The ore to be examined must be crushed fine and passed through No. 80 sieve as usual. Take 20 and 25 grains respectively; place in conical beakers; add hydrochloric acid and a little nitric, using the minimum quantity of acid to effect solution; then heat for about thirty minutes until the ore is completely decomposed. Dilute with water and filter into a 30 ounce flask to remove insoluble matter, which must be washed with warm ammoniacal water. Assuming interfering metals to be absent from the filtrate, dilute till the flask is half full; add 3 c.c. of iron solution, cool, and proceed as in standardising. Take reading of burette and calculate the percentage of zinc in the following way:—

50	c.c. of standard equals	10.06	grains of zinc.	
25	grains of calamine in an assay	required	62.5	c.c.
20	"	"	"	"
	As	50 : 62.5 :: 10.06 :	12.57.	
		50 : 50 :: 10.06 :	10.06.	