of iron and steel when great accuracy is desired: thus Bessemer steel of ·5 per cent. combined carbon should be compared with a similar standard of Bessemer steel, and so for other varieties; so that a number of standards are required for different varieties of metal. Instead of a single tube containing a standard solution for comparison, many steel works and laboratories, where a great number of carbon tests are being constantly made, keep a number of tubes containing coloured solutions, each corresponding to a different percentage of carbon. These are arranged in a wooden frame, with spaces between, to insert the tube containing the steel solution to be tested, the whole forming an instrument called a "colorimeter" (Fig. 75).

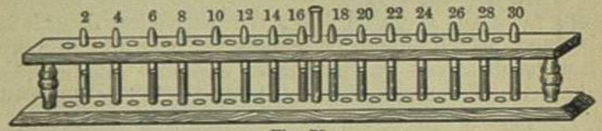

Fig. 75.

(*d*) Mr. J. B. Britton employs a rack containing 15 tubes, each charged with a solution made by digesting roasted coffee in alcohol and diluting with water, so as to obtain the desired tint. The tubes are $\frac{5}{8}$ inch in diameter and about $3\frac{1}{2}$ inches long. The tubes, after being filled, are hermetically sealed. The solution in the tube No. 2 has its colour to correspond exactly to one produced by 1 gramme of iron containing ·02 per cent. of combined carbon dissolved in 15 c.c. of nitric acid. The solution in the tube No. 4 has its colour to correspond with one produced by 1 gramme of iron containing ·04 per cent. of combined carbon, and so with each of the other tubes, each tube increasing in value by ·02 per cent. The last tube is equivalent therefore to ·3 per cent. The process is conducted thus:—1 gramme of the iron or steel, to be tested in the form of fine filings or borings, is weighed out into a large test-tube, and digested with 10 c.c. dilute nitric acid in a beaker containing water maintained at 100° C. till all action ceases; the solution is then cooled by placing the tube in cold water and filtered without the residue being disturbed, through a small dry filter into a test tube of the same size, and made of the same glass as those containing the standard solutions. The insoluble matter is then treated with 5 c.c. of the nitric acid, gently heated and the solution added to the main portion. The entire solution is then agitated by shaking, so as to thoroughly mix and its colour compared. The holes in the rack allow the tube to be placed side by side with the standards; the number fixed to the tube with which it corresponds in colour indicates the percentage amount of carbon in the sample. If the iron or steel contains more than ·3 per cent. carbon, $\frac{1}{2}$ gramme is taken for assay, or if 1 gramme, the solution is diluted with an equal volume of water, well mixed, and half of it poured away. If the metal contains a very small percentage of carbon, as in wrought iron, then 2 grammes are taken for assay.

At the back of the rack, for the purpose of partially screening the light and allowing the different shades of colour to be distinctly discerned, there is tightly stretched some fine white parchment paper. The determinations may be made by this method within ·01 per cent.

ESTIMATION OF THE TOTAL CARBON IN IRON AND STEEL.

As already mentioned, when speaking of combined carbon, this element exists in iron and steel in two forms—free and combined—so that any methods which indicate the amount of carbon in each state will of course give the total quantity of that body present in a given sample. Cast iron is produced in three varieties, the condition of the carbon present modifying its physical properties. When the carbon is almost wholly in the combined form, white iron results; when in the free or graphitic form, grey iron results; and when about equal quantities of free and combined carbon are present, the iron is known as mottled. The method of estimating combined carbon by Eggertz' colour test has already been explained, and the following methods may be used for determining the quantity of free carbon :—

§ 289. *Estimation of Graphite and Silicon.*

In the case of grey pig iron considerable difficulty is experienced in obtaining a typical sample, as it is very possible to get an undue or insufficient amount of graphite in two portions weighed from the same drillings. Such iron should be reduced to as fine a state of division as possible by making the drill take a very fine cut, so that the particles may be exceedingly minute. It has been proposed by one chemist to place a well mixed quantity of such drillings in a porcelain crucible, well cover with pure alcohol, and allow the spirit slowly to evaporate. This causes all the particles loosely to adhere, from which a portion may be broken off for the assay and weighed.

Take 20 grains of grey or 50 grains of white pig iron; place in an evaporating basin; add strong hydrochloric acid; cover with glass plate, and heat until all action ceases. Add water and a little nitric acid, then evaporate to dryness. Heat the dry residue with hydrochloric acid, add water, and gently boil until all soluble matter is dissolved. Filter solution through a paper which has been dried at 110° C. and weighed; thoroughly wash with dilute hydrochloric acid, then with hot water; dry the residue and the filter at 110° C., and weigh when cool. Repeat the drying and weighing at intervals of half an hour until the results are constant. A weighing bottle will be found very convenient for this assay, as the paper and graphite rapidly absorb moisture. Deduct the weight of paper: the remainder is the weight of the graphite, together with any insoluble silica.

Next weigh a clean and dry porcelain crucible; burn the filter paper; ignite the precipitate until every trace of carbon is burnt off; cool in desiccator and re-weigh. The result, after deducting the weight of the crucible and the known weight of the ash of the filter paper, is the amount of silica originally weighed with the carbon. The difference therefore of the two weighings gives the amount of graphite present in the iron. It will be noticed that by this method the silica is also determined at the same time as the graphite.

(*a*) Graphite may also be estimated by dissolving out the contained silica with potash. Take 20 grains, or more, of iron as before; dissolve in hydrochloric acid; add a little nitric acid, then evaporate to dryness; take up with hydrochloric acid; dilute; filter off the silica and graphite and thoroughly wash. Wash the contents of the filter into a porcelain, or better still, a silver dish; evaporate wash water to small bulk and add a piece of pure caustic soda. Digest for an hour; dilute and filter through a weighed paper. The graphite alone remains; thoroughly wash, then swill the graphite into a beaker, and heat for some time with aqua regia to dissolve out any mechanically enclosed matter; dilute; filter through a weighed paper; well wash; dry at 110° C., and weigh.

§ 290. *Estimation of Total Carbon.*

Mr. Thomas Turner, of the Mason Science College, Birmingham, has devised a neat and inexpensive method for the estimation of the total carbon in iron and steel, which is as follows :—

(*a*) For the solution of the iron, copper chloride or sulphate is still often used, and it is stated that the precipitated copper is rather an advantage than otherwise, as it assists in the combustion of the graphite; but this is gradually going out of use since it is found that combustion of the carbon in the residue does not take place until the copper is thoroughly oxidised and this very often takes longer than the whole combustion when other methods are employed.

An excellent solvent is found in ammonium cupric chloride, and this is now extensively used. It may be prepared by dissolving 53·4 parts of ammonium chloride, and 85·4 of crystallised cupric chloride in hot water and crystallising. If the solution is not clear a little hydrochloric acid may be added; the crystals must then be washed with water and dried by pressure. The salt is permanent in air. One uses 15 grammes of the salt, dissolved in 50 c.c. of water per gramme of iron taken. After about fifteen minutes, a gentle heat is applied and the mixture occasionally stirred until the precipitated copper is entirely re-dissolved. After filtering, the residue is washed with warm dilute hydrochloric acid, and should burn white, or very nearly so.

A solution, which is cheaper, though not quite so effective, may be prepared by dissolving 360 grammes of crystallised copper sulphate in about 750 c.c. of hot water and gradually adding 310 grammes of common salt. If the temperature is raised to near the boiling point a precipitate of anhydrous sodium sulphate will form, but this is immaterial. The solution is allowed to cool, when sodium sulphate should crystallise out; the liquid is passed through a filter, and the filtrate made up to a litre. Then 50 c.c. of this solution is capable of dissolving 1 gramme of iron, leaving a residue free from copper. The solution is effected in the same way as before. When it is desired that the solution should be more rapid, a larger amount of the copper solution may be employed. For the estimation of graphite, the mode of procedure is exactly the same as for total carbon, with the single exception that the solvent is hydrochloric acid instead of copper salt. Generally 2 grammes of iron are taken, but a somewhat larger quantity is used when the percentage of carbon is low. The iron being completely dissolved, the solution is allowed to subside for a few minutes and filtered.

(*b*) For filtration, a tube is employed, arranged as in Fig. 76.

Fig. 76.

The tube is of ordinary glass combustion tubing, drawn out at one end, and constricted slightly at the junction of the broad and narrow part. The total length is 11 inches, the broad part being 8 inches long. At A is placed a small pea of baked clay, or some other suitable material, to act as a support; on this is placed about half an inch of sand, which has been heated strongly in a crucible with 5 per cent. of nitre to remove any organic matter. Upon this is placed a small plug of asbestos to act as a filter, and upon this again is about a quarter of an inch of white sand. By means of a small funnel the solution is introduced, while the narrow end of the tube passes through the cork of a flask connected with a filter pump. To ensure rapid filtration one should begin with a small pressure, and gradually increase this as necessary, and of course the precipitate should be put in last. The residue is washed twice with hot dilute hydrochloric acid and then with distilled water. The tube is then gently warmed by means of a Bunsen burner, and a stream of air aspirated through the residue until it is quite dry. The object of the lower layer of sand is chiefly to remove the residue from the constricted portion of the tube, because that part would be liable to collapse in the next part of the process in which the tube has to be very strongly heated. The upper layer of sand stops the larger particles of the residue and prevents the asbestos becoming clogged and so greatly assists in the filtration; it also serves to distribute the residue, and thus causes it to burn more readily than it would do if it were compact. It is important, however, to avoid the use of too large a quantity of sand, as in that case the bulk of the residue which has to be dried is considerable, and much time is lost. When properly worked this method should give very little, if any, greater bulk of total residue, including the sand, filter, etc., than that obtained by solution in copper sulphate. If need be, in iron containing little silicon, solution and filtration may be completed in an hour, and the residue obtained in a form fit for direct combustion; and, as there is no transference, with a little experience a determination of total carbon may be performed in two hours. The tube itself should withstand a number of combustions, though it is preferable to remove the silica after each combustion, so as to avoid double error in case of any mistake. The residue being prepared and dried, it is ready to be burnt. For this purpose a special form of simple combustion furnace is employed. It consists of a stand made of sheet iron, about 4½ inches broad, 8½ inches high, 4 inches long at the top, and 8½ inches long at the bottom, being made taper for greater steadiness and convenience. This stand supports a sheet iron trough, 5 inches long, for the purpose of carrying the combustion tube. Fire-bricks are used to obtain the necessary temperature and two fair-sized Bunsen burners are employed as a source of heat. This furnace stands upon an ordinary working bench, the temperature attained being sufficient to thoroughly soften good combustion tubing and to cause graphitic residues from cast iron to burn in less than an hour in a current of air.

(*c*) The operation of combustion is very similar to that usually adopted, except that all is in miniature and on a working bench. A drying tube and potash bulbs are attached to the narrow end of the glass tube, while a cork and tube is attached to the open end. By means of an aspirator a slow stream of air, free from carbon dioxide, is drawn through the apparatus and heat gradually applied. The residue is noticed from time to time, and when the silica has turned white, or light brown with iron rich in silicon, the combustion is completed. This is accomplished in the case of steel in half an hour from the time when the full heat is applied and I have never yet had an iron requiring more than an hour. In other words, the whole combustion often takes less time than the mere oxidation of the copper alone in a stream of oxygen, when the copper sulphate method is employed. Fig. 77 shows the whole apparatus, the aspirator alone being omitted.

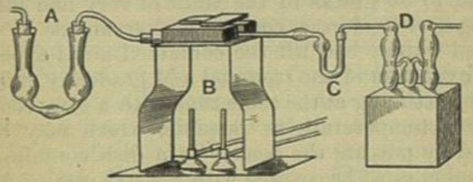

Fig. 77.

A. Potash tube. B. Combustion furnace. C. Drying tube. D. Potash bulbs.

ESTIMATION OF SILICON IN IRON AND STEEL.

§ 291. In treating samples of iron and steel in order to determine the amount of silicon present, it should be kept in mind that this element may exist in chemical combination with the iron or steel and also in the oxidised condition as silica in the enclosed slag, which, being a mechanical impurity, has no relation whatever to the real composition of the metal. It is therefore important to distinguish between these two amounts, so that some solvent is required which will dissolve the iron and leave the enclosed slag (*i.e.* silicate) unaffected. Such a solvent was discovered by Dr. Eggertz in bromine, which, when mixed with water, dissolves the iron without the slightest action on the accompanying slag. But bromine is a most irritating and objectionable substance to have to deal with in large quantities, so that trials were made to substitute iodine in its place and with equal success, although the action of the iodine is slower than that of bromine in effecting solution. The silicon set free from the iron is oxidised to silica, which is soluble in a boiling solution of carbonate of soda; while that in combination in the slag is unacted upon.

§ 292. To estimate silicon in iron by the iodine method, take 25 to 30 grains in the state of very fine filings or drillings. Place in a conical beaker about 15 c.c. of distilled water; boil till the contained air is expelled to avoid oxidation of the iron and add gradually 200 grains of iodine, stirring at the same time with a glass rod, using as low a temperature as possible, which may be best effected by putting the beaker in a dish containing ice. The beaker must be covered with a watch glass. Add the iron and allow the solution to remain in the cold for several hours with occasional stirring. The low temperature enables the iron to be dissolved without evolution of gas and also to a great extent avoids the oxidation of the iron. When the iron is completely dissolved, wash any deposit from the sides by shaking the solution; then dilute to three times its bulk with very cold distilled water in order to prevent the separation of basic salts of iron; well mix and allow residue to settle. The lighter scales of graphite remain in suspension. Pour the liquid on to a filter, 2 inches in diameter, until there remains only a heavy dark powder of slag at the bottom of the beaker; then add a few drops of hydrochloric acid and stir with a glass rod. If this produces a disengagement of hydrogen it is a proof that all the iron has not been dissolved, and a little iodine and sodium carbonate must be added to complete the solution. The acidified liquid must be quickly poured on to the filter to prevent the decomposition of the slag. Well wash the whole residue on the filter with cold water until the washings fail to give a precipitate with ferrocyanide of potassium, showing that all the iron has been removed. Evaporate filtrate to dryness with the addition of hydrochloric acid; boil the dry residue with hydrochloric acid to ascertain whether any silica has gone into solution with the iron, in which case, it must be filtered off, washed and added to the main residue.

The residue on the filter paper consists of graphite, silica and slag. Wash this residue into a platinum dish; evaporate the wash water cautiously to a very small bulk, then add a concentrated solution of sodium carbonate and heat for an hour on a water bath, adding fresh solution if necessary and stirring from time to time with a platinum spatula in order to divide any lumps in the insoluble residue. Then pour off the clear supernatant liquid from the insoluble mass in the dish on to a small weighed filter; add more sodium carbonate to the residue and boil for another hour; then pour the whole contents on to the filter and well wash with hot water.

The filtrate contains the silicon which was originally in combination with the iron, while the insoluble residue contains the slag, graphite and any oxide of iron. Acidify the filtrate with hydrochloric acid and evaporate to dryness. Digest with hydrochloric acid and again evaporate to render the whole of the silica insoluble; moisten with hydrochloric acid; add water; boil and filter; thoroughly wash, dry, ignite, and weigh the silica, if white.

The weighed filter containing the slag and graphite is dried at 110° C. and weighed. It is then ignited in a weighed crucible until all the carbon is burnt off, allowed to cool and again weighed. The ignited residue is then boiled with water saturated with caustic soda, which dissolves silica. The solution is then filtered off and the residue washed and weighed.

§ 293. *Chlorine Process.*

This process was carried out by Mr. Watts with satisfactory results. A bottle is fitted with an india-rubber bung, having two holes and filled with oxide of manganese in lumps. Through one hole passes a tube to near the bottom of the bottle, its upper end being provided with a glass stop cock and bulb filled with hydrochloric acid; through the other hole passes a glass tube reaching just inside the bottle, bent at right angles and also provided with stop cock; this is the delivery tube for the chlorine gas and is connected with three wash bottles, the first containing water and the others strong sulphuric acid, so as to obtain the chlorine free from moisture. The oxygen of the air must also be removed; this is done by passing the gas through a tube containing lamp black, which has been previously strongly heated to free it from moisture and tarry matter; the column of lamp black is kept in position by plugs of gas carbon, and should be 6 or 8 inches long and occupy only the centre of the tube. This is followed by a combustion tube, the other end of which is bent at an angle of 110°, so as to dip into water placed in a flask. In this tube the iron to be assayed is placed. All the stoppers are of india-rubber and coated with paraffin to prevent leakage.

The iron in form of drillings or turnings is weighed into a porcelain boat and placed in the combustion tube. The air is expelled and the tube filled with dry chlorine, then it is heated to low redness, while a constant stream of dry gas is maintained. The chlorine is generated by placing the bottle containing the manganese oxide in a vessel of boiling water and running in a quantity of hydrochloric acid. The effect of chlorine on red hot iron is to volatilise it as chloride, which condenses in the cooler part of the tube, while at the same time silicon tetrachloride is formed and being volatile, passes into the water and is decomposed. The water on evaporation yields silica, which represents the silicon originally in combination with the iron; the slag mixed with carbon remains unaltered in the boat.

This method was found by Turner to be attended with two great disadvantages; the total amount of silicon as compared with other methods is too low, and the residue left in the boat, even after boiling with dilute hydrochloric acid before burning off the carbon, contains variable and sometimes considerable amounts of substances other than slag. The source of error may be removed by adopting the following modification.

§ 294. The iron or steel is placed in a porcelain boat and burned in a stream of dry chlorine free from air. The excess of gas passing through the combustion tube is washed by passing through water contained in a Varrentrapp's bulb. When the combustion is completed as indicated by the entire absence of red vapours near the boat, the current is maintained for five or ten minutes and the solution afterwards evaporated to dryness. The residue is extracted with hydrochloric acid to remove any iron, etc., sometimes carried over, then filtered, washed and ignited. The residue left in the boat contains carbon, slag, a part of the manganese and a little iron as chloride. It may be transferred to a test tube; boiled with a little dilute hydrochloric acid; filtered; dried and ignited.

This residue consists of slag and other substances, so that it is necessary to estimate the silica by fusion with fusion mixture, as in § 297. The combined results furnish the total silicon present in the sample.

This process is well suited for the estimation of silicon in silicon-ferro-manganese and highly siliceous pig iron, these varieties of metal burning readily in chlorine. The method is rapid and fairly accurate with all classes of iron, and it distinguishes between the unoxidised silicon and the slag.

§ 295. The usual method of estimating silicon in iron and steel is to dissolve a convenient quantity in hydrochloric acid, and when all action ceases, to add a little nitric acid and evaporate to dryness, by which means the silicic acid is dehydrated and becomes insoluble in hydrochloric or nitric acids. Fifty grains is a convenient quantity for steel and 25 grains for cast iron. In the latter case, graphite in greater or less quantity is present and even in steel a little carbonaceous matter is sometimes left behind after solution in acid. The carbon, however, left in the siliceous residue is entirely removed by ignition, when the silica can be weighed and the percentage of silicon computed. In cases where greater accuracy is desired, the graphite and silica may be washed into a silver dish; the excess of water evaporated; a lump of pure caustic soda added; the mixture digested on a water bath for an hour and the silicon determined as described in § 292. These methods give good results with steel, or with iron containing less than three per cent of silicon, but are untrustworthy when the percentage of silicon is considerable, as in speigel-eisen and silicon-iron.

§ 296. Another plan which is sometimes adopted on account of its rapidity, is to dissolve the iron or steel in concentrated hydrochloric acid and to filter without evaporation. This plan is quite unreliable and should never be used when any approach to accuracy is desired, as part of the silicon always remains in solution although the amount is less with strong acid than with dilute.

§ 297. A third method consists of dissolving in hydrochloric acid as before; evaporating to dryness; dissolving the iron compound in hydrochloric acid; then filtering off and washing the insoluble residue, which contains the silica and graphite. Wash the residue into a platinum crucible; evaporate the wash water and add four times the quantity of pure carbonates of soda and potash; well mix with a platinum wire. Heat gently at first so as to cause the mass to clot together, then gradually raise the temperature to a high degree and maintain at this point until no more bubbles of gas are given off and the whole is in a state of tranquil fusion.

The materials should not more than half fill the crucible which should be covered with a lid. Put the crucible and contents, when cool, into a beaker, cover with clock glass, boil first with water, then add hydrochloric acid and boil. Remove the well washed crucible and, if the solution is complete, the liquid will be clear, except for a few flakes of silica and the graphite. (If a heavy powder subsides, the decomposition has been incomplete, and the residue must be again fused with alkali.) Evaporate the whole to dryness, when the silica and graphite, being insoluble in hydrochloric acid, may be well washed and treated as before by ignition to remove graphite. Weigh the residual silica. (See § 292.)

§ 298. An excellent method proposed by Drown is preferable to evaporation with hydrochloric acid, but is not applicable when it is desired to estimate sulphur as well as silica in the same sample. Weigh 25 to 50 grains of iron, which need not be very finely divided, place in an evaporating dish, and very cautiously add 10 to 15 c.c. of nitric acid drop by drop, keeping the dish covered with a clock glass. When the action has ceased, add 3 to 4 c.c. of strong sulphuric acid and digest until the metal has dissolved. Evaporate nearly to dryness; add water; boil and filter hot. Wash the residue with strong hydrochloric acid; then with water; dry; ignite and weigh. This method, like the preceding simple processes cannot be employed for iron containing a high percentage of silicon and manganese on account of the impurity of the residue, as well as the length of time taken in dissolving.

§ 299. The following methods are reliable, and recommended for adoption in iron and steel works:—

Take 150 grains of steel, or
100 grains of white pig iron, or
50 grains of grey or mottled pig iron.

First reduce a considerable portion to a small state of division, select a typical sample, and weigh out the required quantity; place in a No. 5 Berlin porcelain dish and cover with a clock glass having a hole at the edge through which a pipette may be introduced; then cautiously add 15 to 25 c.c. of nitric acid, specific gravity 1·2, by means of the pipette, and when the first violence of the action has subsided, heat gently until the metal has dissolved. Wash the cover with acid and water; evaporate the solution carefully to dryness, avoiding loss by rapidly stirring with a glass rod until all the acid has evaporated. Now gradually increase the heat over a ring burner till all nitrous fumes are expelled; cool; add 10, 25, or 35 c.c. of hydrochloric acid, according to the quantity of metal present and allow to stand for an hour. Warm gently until all iron compounds seem to be dissolved, then boil for five minutes; rinse the deposit on the cover into basin and evaporate to a syrup; dilute with boiling dilute hydrochloric acid (1 to 20); boil for a few minutes; allow to settle for ten minutes and filter through a thick English or Rhenish filter previously exhausted with acid and water. (The usual way is to drop hydrochloric acid round the filter until thoroughly wetted, then to remove acid with boiling water.) Wash precipitate on to filter with hot dilute hydrochloric acid (1 to 20), rinse out basin with strong hydrochloric acid, and finally rub any residue adhering to sides of basin with a "finger tip" (which acts better than rubber on glass rod) or a feather; rinse into filter; drop concentrated acid round edge of filter after the water has drained off; then wash with boiling distilled water until all traces of iron and acid are removed. (Test for iron in the washings with sulphocyanide of potassium and for acid with litmus paper.) It is better to wash the silica, etc., into the cone of the filter, so as to facilitate subsequent operations.

Now dry the precipitate and filter in a water oven or a hot air bath; then open the dried filter paper; transfer the silica to a clock glass placed on glazed paper and cover with a funnel; then burn the paper in a weighed platinum crucible and cover; add the silica; cover with lid and heat very gently at first, as silica is carried away by rapid burning; then ignite strongly, preferably in a muffle or with a blowpipe, until the mass is perfectly white, stirring several times with a platinum wire when much carbon is present to assist in its combustion. Allow to cool, and weigh the SiO_2.

§ 300. As stated on a previous page, the silica obtained from common irons is often impure, so that a further examination of the residue becomes necessary when an accurate result is required. The most reliable process known for this purpose is the "hydrofluoric acid" method. A store of re-distilled hydrofluoric acid should be kept in gutta-percha bottles where a number of silicon assays are frequently being made; but as this acid generally leaves a residue on evaporation, the amount must be determined for each portion, which is done as follows:—

As a measure, the lid of a platinum crucible may be used or a small platinum capsule, always using the same measure in subsequent assays. Take one measure of hydrofluoric acid, pour into a weighed platinum crucible, add 2 c.c. of sulphuric acid (1 to 1) and carefully evaporate to dryness to avoid spitting, gently ignite, weigh, and note the amount of residue in one measure of the acid.

Now add one measure of the hydrofluoric acid to the before-mentioned ignited silica residue and 2 c.c. of sulphuric acid (1 to 1), evaporate most carefully to dryness, ignite as before and weigh. The loss in weight is due to silica removed as gas, and after making allowance for the residue introduced by the hydrofluoric acid, the quantity of pure silica is ascertained. The following result will show the mode of calculation:—

		Grains.
Weight of crucible, cover, and siliceous residue	=	173·56
Weight of crucible	=	172·10
Weight of siliceous residue	=	1·46
Less residue in one measure of acid	=	·04
Weight of siliceous residue from iron	=	1·42
Weight of residue after treating with hydrofluoric acid	=	·21
Weight of pure SiO_2		1·21

As 100 grains of iron were taken and $\frac{7}{15}$ or ·4667 of SiO_2 is silicon, then 1·21 × ·4667 gives the percentage. The evaporation must be conducted in a fume chamber with a good draught.

The bodies most likely to be present in silica obtained by evaporation with hydrochloric or sulphuric acid are oxide of iron, phosphorus compounds, titanic acid, oxide of vanadium (rather rare), and sand.

Care must be taken in working with hydrofluoric acid, as it is highly poisonous, and the operation should be performed in a fume chamber.

§ 301. Mr. Turner performed a series of experiments on a sample of Northampton pig iron with a view to test the value of the various methods of estimating silicon, and found that it was practically almost impossible to obtain a white residue by treatment with aqua regia, evaporating, and extracting with hydrochloric acid; for although the residue was boiled four times with strong hydrochloric and four times with water, filtered, well washed and ignited, a distinct colour was observed. The sample contained 1·84 per cent. of phosphorus. In the case of other acids it is very difficult to obtain a pure residue, but the colour is not so marked. The same iron was dissolved in sulphuric acid, and evaporated to dryness when a white residue was obtained, but was too heavy, showing the presence of impurities. On fusion with acid potassium sulphate, both iron and phosphorus were extracted, leaving a snow-white silica, whose weight was lower than with the aqua regia or sulphuric acid methods. The latter method must always be employed with caution, as there is nothing in the colour of the residue or solution to indicate when iron has been removed, so that the washings should always be tested until quite free from iron.

The following conclusions may be inferred from the foregoing:—

1. That with cast irons of specially good quality the silicon can be correctly estimated by evaporation with dilute sulphuric acid.
2. With phosphoric irons the residue obtained, though white, is often impure and should be further treated in order to obtain accurate results.
3. With phosphoric irons containing titanium, the silica is contaminated not only with iron, but also with titanic

acid and phosphoric acid. The residue may be very nearly white and still contain 20 per cent. of substances other than silica.

4. On treatment with aqua regia, the colour of the residue is usually an indication of its purity.

Any vanadium there may be in the iron shows itself in the silica residue. It may be detected by adding hydrochloric acid and gently warming, when a deep brownish green colour is produced with evolution of chlorine.

Nearly all the sand in the residue will be left after acting on the mass with hydrofluoric acid, for, owing to the rapidity of its action on amorphous silica, the acid is weakened to such an extent that sand is not appreciably attacked.

In irons containing more than half a per cent. of phosphorus or any titanium, the fluorine method is invaluable where anything like accuracy is desired.

ESTIMATION OF COPPER IN IRON.

§ 302. This is a substance often present in iron and diminishes the malleability and ductility when over ·1 per cent.; the usual amount is about ·03 per cent. According to C. Rump, the purest iron of commerce is not free from copper. This is especially the case with iron smelted with coke, since coal almost always contains copper pyrites. Swedish iron generally contains only a trace of this element.

Dissolve 200 grains of iron borings or turnings in hydrochloric acid (1 to 1); filter; wash residue; dry and ignite in a porcelain crucible. Allow to cool; moisten with nitric acid; evaporate again to dryness and ignite. Now extract with hydrochloric acid, filter and add filtrate to the main solution of iron. Pass a rapid stream of sulphuretted hydrogen through the solution for ten minutes; allow to settle in a warm place until nearly all odour of sulphuretted hydrogen has disappeared and the precipitate has settled to the bottom. Filter; wash thoroughly with hot water; dry; burn paper and heat precipitate in a weighed porcelain crucible in a muffle until the sulphide is completely roasted to oxide; ignite more strongly, and weigh the CuO.

79 parts of CuO contain 63 parts of copper.

ESTIMATION OF SULPHUR IN IRON AND STEEL.

§ 303. Sulphur is generally oxidised to sulphuric acid by means of nitric acid, chlorine, bromine, or other oxidising agents and the amount of sulphuric acid determined by means of a solution of barium chloride. It is of course essential that the body employed for bringing the iron into solution as well as the agent used to effect the oxidation should be free from sulphur. The amount of metal taken for assay will also vary with the relative amount of sulphur in the iron. In the case of common iron 50 grains will suffice, in other cases 200 grains will be required.

Weigh out the sample; place in a large beaker; add 20 to 50 c.c. of pure hydrochloric acid and 10 to 25 c.c. of pure nitric acid; cover with clock glass and heat gently on a sand bath or hot plate. Drop in 2 or 3 crystals of potassium chlorate and slowly evaporate to dryness; then heat carefully to expel the nitric acid. Remove; allow to cool; add sufficient hydrochloric acid to dissolve all the iron and evaporate to the consistence of syrup. Now add a few drops of hydrochloric acid to dissolve the crust formed on the surface; dilute with water; boil and filter through cotton wool, which separates the silica and graphite. The filtrate contains the sulphuric acid and should be free from excess of hydrochloric acid, as acid solutions of ferric chloride dissolve small quantities of barium sulphate. Now add 2 to 5 c.c. of barium chloride solution (containing 1 part of $BaCl_2$ to 10 parts water) and allow to stand for a few hours in a warm place. After the precipitate has settled, add a drop or two of the re-agent to ascertain if all the salt is thrown down, then filter through an ashless filter paper without disturbing the precipitate; then wash precipitate on to filter; well wash with distilled water; dry; burn paper in a weighed platinum crucible; then add precipitate; ignite at a moderate heat; allow to cool and weigh the $BaSO_4$. The result multiplied by ·13734 (the coefficient for sulphur) gives the amount of sulphur present in the sample of iron taken.

§ 304. The above method of estimating sulphur is not applicable in all cases, especially in iron and steel containing small quantities of sulphur, as some of the sulphur is probably evolved in the form of sulphuretted hydrogen; so that the following excellent method is to be preferred, except in the case of white iron, which is not easily acted on by hydrochloric acid.

Take 200 grains of iron or steel, or 100 grains of ordinary grey pig iron; but, as some grey forge pigs contain little sulphur, 200 grains should be employed in such cases. The operation must be conducted so as to exclude the air as much as possible. The apparatus shown in the accompanying figure may be employed for the purpose. The iron is placed in the flask E; hydrochloric acid introduced from bulb tube B, and the gas passed through the empty bottle F, in which any solid matter mechanically carried over may be deposited; then into the U-tube G, which contains a solution of bromine and potassium bromide, and from thence through a vessel H containing distilled water. The action is based on the fact that when iron containing sulphur is heated with hydrochloric acid, the sulphur is evolved as sulphuretted hydrogen. By passing this

gas through a solution of bromine it is completely absorbed and oxidised to sulphuric acid which is subsequently precipitated with barium chloride.

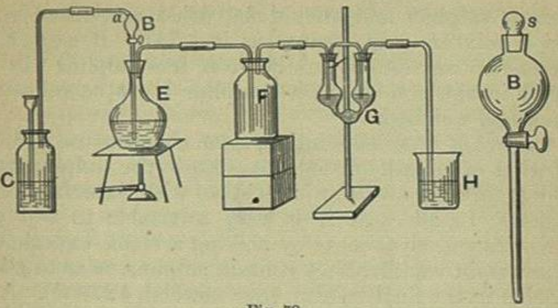

Fig. 78.

To conduct an assay, place the finely divided iron in the flask E, fill the bulb tube B with hydrochloric acid, and to the U-tube G add 2 c.c. bromine, 15 grains of potassium bromide and 20 c.c. water, which should about two thirds fill the two upper bulbs; in this U-tube, the glass tubes are so arranged as to cause the gas to pass twice through the bromine solution. When the whole apparatus is fitted together, run into the flask a little hydrochloric acid and gently heat, continuing to add fresh acid as required until the iron is completely dissolved. Then boil for two or three minutes; replace stopper S by the cork *a*, which is connected with the bottle C, in which are placed bits of marble, for generating a current of carbonic acid by the action of dilute hydrochloric acid. The carbonic acid passing through the flask sweeps the last remnants of sulphuretted hydrogen through the bromine solution. Transfer the bromine solution to a beaker; carefully evaporate to dryness; take up with water and a little hydrochloric acid; then precipitate the sulphuric acid by means of a solution of barium chloride, as in the former method. It is also advisable to test the iron solution for sulphuric acid by evaporating to a small bulk and adding 1 c.c. of barium chloride. Any insoluble residue in the flask may also contain sulphur and should be dried and fused with fusion mixture and treated as in § 297. If copper be present to any extent in the iron, free sulphur will be found in the residue, which sulphur must be collected, dried and weighed.

Instead of bromine solution, some chemists use a dilute solution of potash or soda to absorb the sulphuretted hydrogen, and afterwards oxidise with bromine in a beaker. In all cases it is very advisable to test the re-agents and absorbents by making a blank experiment to ascertain whether they contain sulphur, so as to allow for this in the final result. (See method, § 278 (*b*). Also volumetric method, § 372.)

§ 305. *Eggertz' method for small quantities of Sulphur.*

Two grains of finely divided pig iron are placed in a stoppered bottle with 16 grains of water and 8 grains of sulphuric acid. A clean plate of silver, $\frac{3}{4} \times \frac{3}{8}$ inch, is suspended by a wire in the upper part of the bottle for fifteen minutes when the discoloration will be proportional to the amount of sulphuretted hydrogen evolved. The plate is then compared with a series of standard colours, each of which corresponds to a definite quantity of sulphur as determined by experiment on samples whose composition is known. Thus plates are obtained of coppery yellow, bronze, brown, blue, and so on, corresponding to ·02, ·04, ·06, etc., per cent. of sulphur. Full particulars of this process will be found in Crookes' Select Methods in Chemical Analysis, pages 160-164.

ESTIMATION OF MANGANESE IN IRON AND STEEL.

§ 306. The usual method of assay for manganese is as follows :—

Take 50 grains of steel or 15 to 20 grains of pig iron, containing upwards of ·5 per cent. of manganese ; place in an evaporating basin ; add strong hydrochloric acid in sufficient quantity to well cover the finely divided metal ; cover with a clock glass and heat gently. When the action ceases, add nitric acid in equal quantity ; dilute with water and again heat until the iron is dissolved, adding fresh nitric acid if necessary. Evaporate cautiously to dryness and heat the residue strongly to destroy all organic matter. Re-dissolve in hydrochloric acid and a little nitric ; add water and boil until all is dissolved, except silica and graphite. Filter, if the residue is large, through cotton wool or filter paper ; if small, this filtration may be neglected, as it will be removed in the next stage with the iron. Transfer solution to a quart beaker ; make up to a pint with boiling water and add cautiously a dilute solution of ammonium hydrate, until a permanent precipitate is obtained, without any odour of free ammonia, showing that the liquid is nearly neutral. Now add 15 to 20 c.c. of a concentrated solution of sodium acetate, or better, ammonium acetate ; raise the liquid to the boiling point and keep at that temperature for two or three minutes ; allow the precipitate of basic acetate of iron to settle, which should be of a brick red colour ; if it be dark red, an insufficient amount of ammonium acetate has been added and more of that salt must be introduced. Wash two or three times with dilute acetate of ammonium by combined decantation and filtration into a 30-ounce flask, when the filtrate should be quite clear and colourless ; well wash the precipitate, after transferring it to filter, with hot water. If pig iron is being assayed, the precipitate will contain manganese. This must be re-dissolved and the iron re-precipitated as before with acetate of ammonia. If steel is being assayed, one precipitation will be sufficient. The two filtrates are then concentrated by evaporation, transferred to a flask, cooled, and 10 c.c. of bromine added, a little at a time, with frequent shaking, when the solution should be of a deep red colour. Then cautiously add strong ammonia in excess, well shaking after each addition, and gradually raise the liquid to boiling. In half an hour the black oxide will completely separate out. Allow precipitate to settle; filter and wash with hot water: any particles of precipitate which adhere to sides of flask may be removed by rubbing with scraps of ashless filter paper and glass rod. Dry; burn paper in a weighed platinum or porcelain crucible; ignite precipitate strongly, finishing with five minutes over blowpipe flame, when the black MnO_2, changes to the coffee coloured Mn_3O_4; cool in desiccator, and weigh the Mn_3O_4.

This precipitate may contain silica, especially if a new glass flask has been used. Also when copper is present in the iron, that metal will be present in the manganese precipitate. The copper in such case may be precipitated before the iron and manganese with sulphuretted hydrogen, as described in § 302. The filtrate from the manganese precipitate retains a little manganese. Evaporate to dryness; re-dissolve in water and test for manganese with bromine and ammonia as before; add the result to the main portion; ignite and re-weigh. The weight of the Mn_3O_4 obtained, multiplied by ·7205, gives the weight of metallic manganese in the portion assayed.

Volumetric methods for estimating manganese are given in § 371.

§ 307. The estimation of small quantities of manganese in the presence of much iron by converting the latter into ferric acetate is troublesome on account of the large volume of liquid to be boiled and filtered; an operation which must be repeated where accuracy is desired, as some of the manganese is carried down with this precipitate. Moreover, a student frequently fails to effect complete precipitation of the iron, or obtains it in such a condition that filtration is very difficult.

Mr. Chas. L. Bloxam has devised the following process to simplify the estimation :—"The metal is dissolved in hydrochloric acid in a beaker; the solution evaporated to dryness; the residue taken up with hydrochloric acid and water as usual, and the graphite and silica filtered off. The filtrate is then heated, and a few crystals of potassium chlorate added to oxidise the iron, etc.; then cooled and carefully neutralised with ammonia; an excess of acetic acid added to convert the whole of the iron into acetate; then an excess of sodium phosphate is introduced, by which the iron is precipitated as ferric phosphate. Filter and re-dissolve in hydrochloric acid without washing and re-precipitate as above. The two filtrates are mixed; an excess of ammonia added and the solution boiled, when the manganese is precipitated as the crystalline very insoluble ammonium phosphate, which is filtered off and washed. As soon as the washings leave no residue on evaporation, the wet precipitate with the filter is placed in a weighed platinum crucible, covered with lid and ignited. It then has the formula $Mn_2P_2O_7$. It is well to keep the ammoniacal solution near the boiling point for an hour and allow to stand some hours before filtering. The ignited precipitate should be re-dissolved in hydrochloric acid and the solution mixed with ammonium acetate to detect any ferric phosphate, which may be ignited, weighed, and deducted from the manganese precipitate."

§ 308. *Estimation of Manganese by Electrolysis.*

"The manganese solution, after removing all iron salts, is placed in a platinum crucible, which serves as the negative electrode, the positive being formed by a spiral of platinum wire. The manganese is deposited on the crucible in the form of dioxide. The accuracy of the result is not impaired by the presence of copper, cobalt, nickel, zinc, magnesium, aluminium, alkalies, or alkaline earths. By this method ·0005 grm. of MnO_2 can be easily estimated, and ·000025 grm. detected by the rose coloration which it exhibits." (*A. Riche.*)

ESTIMATION OF PHOSPHORUS IN IRON AND STEEL.

§309. Two methods are in common use for the estimation of phosphorus in iron and steel, each of which possesses advantages in particular cases. One is known as the magnesia method and the other as the molybdate method. The general opinion seems to be, that a combination of the two methods yields the most correct results. The magnesia process gives results a little below the truth, the precipitate being sensibly soluble in its mother-liquor; while the phospho-molybdate precipitate is liable to retain a little molybdic acid. The latter method, however, yields a comparatively large and heavy precipitate, containing only a small percentage of phosphorus and is 17 times heavier than the corresponding magnesia precipitate and therefore more suitable for the determination of small quantities of phosphorus; it also has the great advantage of being quicker.

§ 310. *Phospho-Magnesia Method.*

Take 25 grains of phosphoric pig iron or 50 grains of steel. If the phosphorus is very small, 200 grains will be necessary. Dissolve in 20 to 30 c.c. of hydrochloric and 10 to 15 c.c. of nitric acid in a 20 oz. beaker; first adding the acid, then the metal a little at a time, as the action is somewhat violent at first; cover with a clock glass and heat gently until the iron is dissolved. Evaporate to dryness; heat strongly to destroy organic matter and take up with hydrochloric acid and water; filter off any silica and graphite; dilute considerably with cold water and add sufficient sodium sulphite to reduce the whole of the iron to the ferrous condition. Boil to remove all excess of sulphurous acid; add a little ferric chloride and cautiously neutralise with ammonium carbonate. The ferric chloride causes a precipitate of basic salt to separate on boiling, which contains all the phosphorus, if sufficient ferric chloride has been added. The iron salt, which has been reduced to the ferrous condition by the sodium sulphite, remains in solution. The precipitated iron phosphate is white if no ferric salt is in excess; but it is best to have a little excess of the ferric chloride, so as to insure the complete precipitation of the phosphoric acid. The precipitate will be of a red colour. Filter; wash once and re-dissolve the precipitate in hydrochloric acid; filter the liquid and to the filtrate add half an ounce of citric acid. Now add strong ammonia until the liquid smells strongly of the gas; then add 2 c.c. of the magnesia mixture (described in § 104, *d*) and allow to stand several hours, occasionally stirring with a glass rod; filter; wash with ammonia containing four times its volume of water; dry; ignite in a weighed platinum crucible; allow to cool and weigh the $P_2O_7Mg_2$. The weight multiplied by ·2793 gives the phosphorus.

The precipitate may contain arsenic, if it is present in the iron. Re-dissolve in hydrochloric acid; dilute; warm to 60° C. and pass a current of sulphuretted hydrogen, when the presence of arsenic is indicated by a yellow precipitate; allow to stand several hours. Filter on to weighed paper; dry, and add bisulphide of carbon to dissolve any free sulphur; dry at 100° C. and weigh. The precipitate multiplied by ·610 gives the arsenic.