and ammonium oxalate as before. Filter, and evaporate filtrate to small bulk; neutralise with hydrochloric acid; add baryta water as long as a precipitate forms; boil; filter and well wash. The filtrate contains the potash and soda. Evaporate to dryness in a porcelain dish; add pure nitric acid, and again evaporate to dryness to destroy ammonium chloride. Re-dissolve in water; add hydrochloric acid and evaporate to dryness. Repeat this to remove all the nitric acid. Re-dissolve in water; evaporate the solution to dryness in a weighed platinum dish; heat gently and weigh the mixed chlorides. Re-dissolve in water and a little hydrochloric acid; add platinum chloride and proceed for potassium as in § 208. The amount of potassium chloride deducted from the weight of the mixed chlorides gives the sodium chloride.

ANALYSIS OF ASHES OF WOOD, COAL, ETC.

§ 277. The following constituents may be expected to be present:—Potash, soda, lime, magnesia, oxides of iron, manganese, and aluminium; sulphuric, phosphoric, hydrochloric, silicic, and carbonic acids. Sometimes baryta, strontia, copper, and cyanates.

(*a*) Estimate the carbonic acid either by the method given in § 233, or that in § 275. If the combustible matter of the fuel has been removed at a high temperature, the amount of carbonic acid will be very low owing to the decomposition of the carbonates, except in the case of the carbonates of the alkalies and baryta.

(*b*) Take 100 grains of the ash, place in a flask and digest with dilute hydrochloric acid in excess until the carbonic acid is expelled; then gently boil for an hour; transfer to an evaporating basin and evaporate to dryness. Take up with hydrochloric acid; heat; dilute; boil and filter off the insoluble silica and silicates. Treat this residue as described in § 276.

Concentrate the filtrate and washings by evaporation if necessary and make up the solution to a litre. Measure off 250 c.c.; boil; add barium chloride for the estimation of sulphuric acid, as in § 214.

(*c*) Take another 250 c.c., and estimate the alkalies as described in § 276 (*f*).

(*d*) The remaining 500 c.c. may be employed for the estimation of lime, magnesia, phosphoric acid, etc. Neutralise with ammonia; heat gently and add 1 ounce of a saturated solution of ammonium acetate, when the solution should have a distinctly red colour; transfer to a porcelain dish and boil until the red colour is destroyed, showing that the iron acetate has been decomposed; filter and well wash with hot water.

The precipitate contains iron, aluminium, phosphorus, and manganese. Dissolve in dilute hydrochloric acid; neutralise with ammonia and add ammonium sulphide. Digest for two hours; filter and wash with water containing ammonium sulphide.

The filtrate contains the phosphoric acid, which is estimated by magnesia mixture. (See § 215.)

The precipitate may contain iron, aluminium, and manganese. Dissolve in hydrochloric acid; boil to expel sulphuretted hydrogen; add a little nitric acid and again boil. Mix this solution with the filtrate from the basic iron acetate, precipitate the iron and aluminium as above, and concentrate by evaporation.

Add bromine to the filtrate; cork up the flask; allow to stand for an hour; add ammonia; boil; filter off the precipitate of manganese oxide; wash; dry; ignite and weigh.

Estimate lime and magnesia in filtrate as described in § 276.

(*e*) For the determination of hydrochloric acid, dissolve a portion of the ash in nitric acid; add silver nitrate and estimate the chlorine from the amount of AgCl obtained.

ASSAY OF SULPHUR.

§ 278. The substance must be dried at 100° C., ground very fine, and passed through a sieve with 80 meshes to the linear inch.

(*a*) Take 20 grains, or more if the amount of sulphur is small, mix with 500 grains of a deflagrating mixture, consisting of two parts common salt and one part nitre, previously powdered and dried.

Place the mixture in a platinum crucible in sufficient quantity to about half fill it, partly cover with lid; then gradually heat the crucible by means of a spirit lamp until the mass is completely deflagrated; add the remaining portions in small quantities until the whole is fused.

Allow to cool; place the crucible and its contents in a beaker; add water; boil; then add hydrochloric acid; remove crucible; well wash, and boil the solution until all action ceases. Filter off the insoluble silica, etc.; well wash; add a hot solution of barium chloride in sufficient amount to precipitate the sulphuric acid; well stir with glass rod; allow to settle; filter; wash; dry; burn paper in a weighed platinum crucible; ignite at a moderate temperature and weigh the $BaSO_4$. This multiplied by ·13734 gives the sulphur.

(*b*) Instead of the above fusion mixture the following may be used for 20 grains of the assay sample: 300 grains of salt, 100 grains of potassium chlorate and 100 grains of anhydrous carbonate of soda.

It is of the first consequence that the fluxes should be pure and free from sulphur, unless a check assay is made. A naked coal gas flame should never be used, or sulphur may be obtained from the gas.

§ 279. The author adopts the following plan, in which ordinary salts may be used:—

Weigh out two portions of fluxes, and add the assay sample to one of them; transfer each to a crucible; place both side by side in a gas muffle at a low temperature and regulate the temperature as required. The two portions are then dissolved, and the sulphur estimated in each. The amount of sulphur found in the blank experiment deducted from that found in the assay gives the true amount of sulphur. This method is suitable for estimating sulphur in coal, coke, pyrites, and other insoluble bodies.

§ 280. Sulphur in coke may be estimated by roasting 20 grains of the finely powdered coke with three times its weight of pure calcined magnesia. Introduce the mixture into a small porcelain dish; add a quantity of ammonium nitrate; place in a gas muffle; gradually raise the temperature to a red heat and maintain at this point until all the carbon is burnt off and the whole mass is white. Allow the dish to cool; transfer substance to a beaker; add hydrochloric acid and boil till the soluble portion of the mass is dissolved. Filter and well wash; then nearly neutralise the acid filtrate with ammonia; add sufficient barium chloride to precipitate the sulphuric acid; allow to stand for an hour, and treat $BaSO_4$ as in former methods. The sulphur by this plan is oxidised by the air, and absorbed by the magnesia forming $MgSO_4$, which is soluble in hydrochloric acid.

§ 281. Sulphur in ores, slags, etc., may be determined by dissolving the sample in aqua regia; evaporating to dryness; taking up with hydrochloric acid and water; then filtering off the insoluble siliceous matter; evaporating to remove excess of acid; diluting largely with water and precipitating with barium chloride as usual. If barium should be present in the ore as well as sulphur, then the sample must be fused with alkalies as in §§ 278-9 and the sulphuric acid determined in the filtrate.

For mode of estimating sulphur in iron and steel see §§ 303-5.

§ 282. *Mr. A. H. Pearson's Method for Pyrites.* Take 20 grains of the finely powdered mineral; mix with 2 grains of potassium chlorate; place in an evaporating basin; add pure nitric acid; cover with an inverted funnel, and keep the liquid gently simmering for at least half an hour, adding a crystal of potassium chlorate occasionally. When the oxidation is complete, well swill the funnel; wash down the sides of basin and evaporate the solution to a syrup; add strong hydrochloric acid and evaporate to dryness. Moisten the mass when cold with strong hydrochloric acid; allow to stand some time; add a little water; boil and filter off the insoluble silica.

Add 20 grains of solid tartaric acid to filtrate to prevent precipitation of iron salts and heat near to boiling. Then precipitate the sulphuric acid from the clear solution with barium chloride as usual. Filter; well wash by decantation with hot water; then with a hot solution of ammonium acetate to dissolve any barium salt that may adhere to the sulphate; transfer precipitate to filter; well wash with hot water; dry; ignite and weigh the barium sulphate, $BaSO_4$.

In all cases where nitric acid is employed to oxidise a body, it must be removed before adding the barium chloride, as barium sulphate is somewhat soluble in free nitric acid.

§ 283. Mr. P. Waage recommends the use of bromine in preference to nitric acid, chlorine, and potassium chlorate. He has for some time successfully employed bromine for pyrites, mispickel, nickel regulus and precipitated sulphides, both for the estimation of sulphuric acid and for the metals.

The powdered substance is shaken with bromine and water in a flask, the mouth of which is closed with a small funnel, adding fresh bromine if required until the substance is dissolved. A gentle heat is advisable towards the finish. 15 parts by weight of bromine are required for 1 part of sulphur. The solution is concentrated by evaporation, treated with hydrochloric acid, filtered, and the filtrate employed for the precipitation of $BaSO_4$ in the usual way.

Precipitated sulphides on a filter paper may be dissolved by bromine water. Perforate the paper, and wash the mass into a conical beaker by means of the same solvent.

ANALYSIS OF IRON AND STEEL.

Estimation of Iron.

§ 284. Weigh out 10 grains of the sample, which has been reduced to a fine state of division by drilling out about 100 grains from a piece of perfectly clean iron or steel; place in a porcelain basin; add 10 c.c. of pure hydrochloric acid and 5 c.c. of pure nitric acid. Boil at a very gentle heat until the metal is dissolved, and only a residue of free carbon and silica remains. Now evaporate carefully to dryness, keeping the top covered with a clock glass to prevent loss by spurting, and continue the heating until the residue is black; allow to cool; then moisten the contents with hydrochloric acid; swill down the sides and the clock glass cover (preferably with acid), using a glass rod, the end of which is tipped with a piece of india-rubber tubing to remove any residue sticking to the vessel; again cautiously evaporate to dryness; cool and again add hydrochloric acid and digest until the soluble contents are brought into solution. Evaporate to a small bulk if necessary; dilute with water; boil for a short time and transfer the whole contents to a funnel the neck of which has been stopped with cotton wool to filter off the insoluble silica and carbon; well wash with hot water and dilute further if necessary to make the solution up to a quarter of a pint.

Mix the dilute solution with a large quantity of ammonium chloride (20 parts of AmCl to 1 of MnO, etc.), then add a saturated solution of ammonium carbonate gradually with frequent shaking as long as the precipitated iron re-dissolves, which takes place with difficulty towards the end. (It is best to finish with a dilute solution.) As soon as the liquid has lost its transparency without showing any signs of a precipitate the action is complete. When this point is reached, heat slowly to boiling and continue the boiling for a short time after the carbonic acid has been entirely expelled. The ferric oxide separates as a basic salt, which rapidly settles. Pour the clear liquid through a filter and wash several times by decantation and filtration with hot water.

The iron precipitate will probably contain alumina. Dissolve it in hydrochloric acid and neutralise the acid with a strong solution of sodium hydrate. Then pour the solution gradually into an excess of nearly boiling solution of sodium hydrate in a platinum or silver dish, stirring all the time. Then filter and well wash the precipitate. As the precipitate retains some alkali it should be re-dissolved in hydrochloric acid, boiled with some nitric acid, re-precipitated with ammonia, as in § 185, and the ignited Fe_2O_3 weighed. From this oxide the iron may be computed.

Another method of separating oxide of iron from alumina is given in § 196.

Iron may be much more rapidly, and as accurately, estimated by the volumetric methods afterwards described, when the standard solutions are once made and standardised.

§ 285. *Estimation of Ferrous Oxide in the presence of Ferric Oxide.*

The separation and estimation of these oxides separately in silicates is sometimes necessary. A process has been already described, see § 201.

The following method is due to Avery, who found that silica and many silicates could be completely dissolved by a mixture of some normal fluoride with a strong acid, either concentrated or dilute.

A sample of the silicate is first very finely powdered and sifted; then 25 grains are placed in a platinum crucible; 30 to 40 grains of powdered fluor-spar, free from iron, added and the contents well mixed. Pour in pure hydrochloric acid till the mixture is well covered and heat gently until the iron is dissolved.

During the process it is essential that the air should be excluded, or some of the protoxide of iron will be converted to sesquioxide. This is effected by placing the crucible in a small beaker, the edge of which is ground so as to fit tightly to a ground glass plate which covers it (Fig. 73). This glass plate is perforated with two holes through which pass two glass tubes. One tube is connected with a tap for delivering a constant stream of coal gas (which must be purified from sulphuretted hydrogen by passing through potash bulbs) and the other communi-

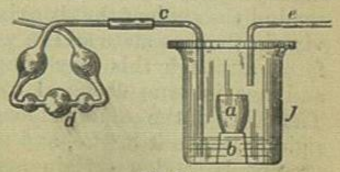

Fig. 73.

cates with the atmosphere; at the mouth of this tube the escaping gas may be burnt. *a* is the platinum crucible, *b* a lead support, *c* the gas delivery tube, *d* the potash bulbs, *e* the escape pipe. The beaker *f* containing a little water at the bottom through which the gas bubbles, is heated on a water bath. In from an hour to an hour and a half the decomposition is complete; the solution is then diluted, and the ferrous oxide determined by a standard solution of potassium bichromate, as described in § 365.

§ 286. Mr. Allen effects the solution of difficultly soluble ores by heating 10 to 15 grains in a sealed piece of combustion tubing half filled with fuming hydrochloric acid, which in this case dissolves the ore under pressure. It is first heated on a water bath for three hours, then for another hour at 150° C. The tube is then allowed to cool and the end broken under water. The ferrous oxide is then estimated by bichromate as in § 365. This method should only be used by persons who have had some experience in this kind of work, or a serious accident may happen.

ESTIMATION OF COMBINED CARBON.

§ 287. As carbon plays such a prominent part in modifying the character of iron it may be as well to remind the student that it exists in pig iron in two forms, viz., in the free state and in what is called the combined form, although this may simply be carbon in solution and not in true chemical combination with the iron. The effect of the combined form is to harden, increase its rigidity, make it brittle, and to reduce its tenacity when present beyond a certain amount. The effect of the graphitic condition is to make the metal softer and weaker than when in the combined form. The two conditions may be produced by the rate of cooling, and by variations in the amount of other elements also present in the iron. Thus manganese, sulphur, and probably phophorus induce the carbon to pass into the combined form, while silicon has the contrary effect, causing it to crystallise out in the form of graphite. Hence it is probable that two samples taken from the same charge, unless cooled and mechanically treated under exactly the same conditions, will show different proportions of combined carbon, and even different parts of the same ingot may exhibit a difference, although the total quantity of carbon may be the same in all parts. In the case of iron containing less than ·15 per cent. of carbon, the metal is not sensibly hardened by sudden cooling, so that the results obtained from estimating the combined carbon in mild steels by the colour test, are much more reliable than those from the harder varieties, *i.e.*, those containing higher amounts of carbon. From the above remarks it will be seen that it is of the greatest importance to know, in the case of a sample of strong steel or cast iron, whether the assay has been made on a piece cast in a chill and cooled quickly, or cast in dry sand and cooled slowly.

§ 288. *Eggertz' Colour Test.*

(*a*) When iron, containing carbon in the combined form, is dissolved in nitric acid containing an equal volume of water a brown solution is obtained, the intensity of the colour being directly proportional to the amount of combined carbon present. When pure iron is dissolved in nitric acid and water, as above, and allowed to cool, a practically colourless solution is obtained. The nitric acid employed must be pure and especially free from chlorine, which communicates to the iron solution a yellowish colour. (Crookes states that ·0001 gramme of chlorine in a solution of ·1 gramme of iron in 2·5 c.c. of nitric acid produces a decidedly yellow colour. Dilute this solution with 1·5 c.c. of nitric acid and 4 c.c. water, the colour is still observed, but less in proportion as the solution is diluted.) The quantity of nitric acid employed for dissolving the steel must be in proportion to the amount of carbon assumed to be present. Thus, with combined carbon under ·3 per cent. use 2 c.c. of acid; with ·5 per cent. and under, use 3 c.c.; under ·8 per cent., use 4 c.c.; for white cast iron use 5 c.c. The amount of metal taken for assay may be two grains for mild steel, 1 grain for strong steels, and not more than $\frac{1}{2}$ grain for white cast iron.

(*b*) *Mode of conducting the Operation.*

In the first place a standard steel is necessary containing an amount of combined carbon, which has been very accurately determined by the combustion method, and a bottle containing nitric acid diluted with an equal bulk of water. Suppose this standard to contain ·35 per cent. of combined carbon.

Weigh out very accurately 2 grains of the standard steel, which must be in the form of very fine drillings, or filings and transfer, to a specially made narrow test tube, which must be dry, or some particles will stick to the sides, and it is essential they should all fall to the bottom. A good way of introducing the steel which avoids the necessity of a perfectly dry tube, is to cut a narrow strip of writing paper, fold it once down the middle so as to form a triangular trough. Place the steel in the paper, hold the tube in a horizontal position and pass the paper carefully to the bottom, then by tapping the paper the steel falls out without touching the sides (Fig. 74). Now add 2 c.c. of the acid and place ready for dissolving. Then weigh an equal quantity of the steel to be assayed, introduce it into another tube similar to the former one and add the same quantity of acid, or $\frac{1}{2}$ c.c. more if the steel is stronger than the standard, according to instructions in § 288 (*a*). Place the two tubes in a beaker containing hot water and keep the water just boiling until the steel in each case is dissolved; about twenty to thirty minutes being generally required. If a reddish yellow deposit is obtained, which somewhat clouds the solution, it may often be dissolved by shaking or carefully heating the tube in the flame of a Bunsen's burner. When the steel is thoroughly dissolved, and the solution quite clear, transfer the solution of the standard steel to a graduated tube; swill out the tube, in which the steel has been dissolved, with water, using only a few drops at a time. Dilute, until the solution stands exactly at 3·5 c.c in the graduated tube, the depth of colour in which may be taken to represent ·35 of carbon. Transfer this solution back again to the tube in which it has been dissolved and place in a test-tube rack for comparison. Now treat the assay steel in the same way, by transferring it to graduated tube, diluting with water and agitating until the same degree of colour is attained as in the standard. Suppose the reading to give 4·5 c.c.; then, as the same quantity of metal in each case has been taken, and the intensity of the colour is proportional to the amount of carbon present, and the proportion of the volumes indicates the relative proportion of colour, the steel contains ·45 of carbon. But the standard is known to contain ·35 per cent. of carbon, therefore the assay steel must contain ·45 per cent. of carbon.


Fig. 74.

The following tubes are 10 inches long with a bore of $\frac{3}{8}$ inch, which must be perfectly uniform throughout. The graduated tube must be exactly the same size and divided into $\frac{1}{10}$ c.c. The water for dilution is most conveniently added by means of a glass tube drawn out at one end so as to introduce it one drop at a time.

(*c*) It is not sufficient to have one standard for all kinds of iron and steel when great accuracy is desired: thus Bessemer steel of ·5 per cent. combined carbon should be compared with a similar standard of Bessemer steel, and so for other varieties; so that a number of standards are 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).

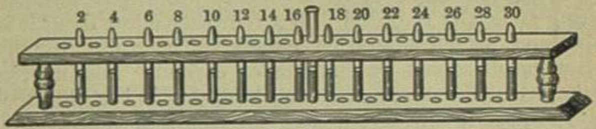

Fig. 75.

(*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