

(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:—

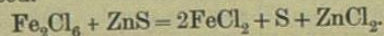
50 c.c. of standard equals 10.06 grains of zinc.	
25 grains of calamine in an assay required 62.5 c.c.	
20 " " " " " "	50 "
	As 50 : 62.5 :: 10.06 : 12.57.
	50 : 50 :: 10.06 : 10.06.

Multiplying these results by 4 and 5 respectively 50.28 and 50.30 per cent. of zinc is obtained.

(b) It is desirable to have the oxide of iron present in the flocculent condition, so that it is better to add ammonia to the 3 c.c. of ferric chloride before mixing it with the ammoniacal solution of zinc. As before remarked the solution must be constantly agitated while running in the standard, otherwise the oxide of iron may be blackened before the complete precipitation of zinc sulphide. When the change from reddish brown to black takes place the standard solution must only be added one drop at a time.

§ 364. *Estimation of Zinc by a Standard Solution of Potassium Bichromate.*

This process depends on the fact that when zinc sulphide is mixed with ferric chloride and hydrochloric acid, ferrous chloride, zinc chloride and free sulphur are produced.



The amount of ferrous chloride is then estimated by a standard solution of potassium bichromate, and the proportional quantity of zinc ascertained; for 2 atoms of iron which equal 112, represent 1 atom of zinc which equals 65.

20 or 25 grains of ore are dissolved as before, evaporated, precipitated with ammonia and ammonium carbonate; digested until the zinc precipitate is re-dissolved, then filtered, and washed. The filtrate and washings contain the zinc, which is precipitated with sodium sulphide or ammonium sulphide, then filtered and washed with warm ammonia water. The filter and its contents are transferred to a beaker, a slightly acid dilute solution of ferric chloride added, the beaker covered and the whole digested for ten to fifteen minutes; sulphuric acid is then poured in and a gentle heat con-

tinued until the free sulphur coagulates. The solution is then filtered, well washed with hot water, and the amount of ferrous chloride in the filtrate determined. This process is described under the head of Iron Assays, § 366. Suppose 50 c.c. of bichromate solution indicate 10 grains of iron,

	iron.	iron.	zinc.	zinc.
Then	112	: 10	:: 65	: 5.80.

VOLUMETRIC ESTIMATION OF IRON.

§ 365. Two principal methods are in use; one is due to Marguerite and known as the Permanganate method, the other to Dr. Penny, known as the Bichromate method. These depend on the circumstance that, when iron is in solution as ferrous chloride, it may be oxidised to ferric chloride by means of an oxidising agent, the amount of which is proportional to the quantity of iron present. The above two methods differ in the nature of the oxidising agent employed and the mode of judging the completion.

§ 366. *Potassium Bichromate Method.*

(a) For general work this method is preferable to the permanganate process, for the following reasons.

1. Bichromate solution is less liable to decomposition by long keeping than permanganate, and requires less frequent standardising.
2. The result obtained is more reliable, not being subject to error through evolution of chlorine.
3. In some cases it occupies less time, as filtration is necessary with the permanganate method when carbonaceous or organic matter is present, and the solution need not be cooled.

On the other hand, an external indicator is required, and the completion somewhat prolonged.

(b) When potassium bichromate solution is added to a solution of a proto-salt of iron, the latter is oxidised into a sesqui-salt with the production of a potash salt and a sesquisalt of chromium. The following re-action occurs when the iron dissolved in hydrochloric acid is treated with bichromate— $6\text{FeCl}_2 + 14\text{HCl} + \text{Cr}_2\text{O}_7\text{K}_2 = 3\text{Fe}_2\text{Cl}_6 + 2\text{KCl} + 7\text{OH}_2 + \text{Cr}_2\text{Cl}_6$. To indicate the completion, a very weak, nearly colourless, solution of potassium ferricyanide is used, which produces a greenish blue tint when mixed with proto-salts, but is unaltered by sesqui-salts of iron. An excess of acid must be present.

§ 367. *Standard Solution.*

(a) Crush up a quantity of pure crystals of potassium bichromate; weigh 305 grains and dissolve in warm water; filter if necessary; then make up the solution to 4 pints.

(b) *Indicator.* Dissolve 1 grain of potassium ferricyanide in 4 ounces of water and preserve in a stoppered bottle.

(c) *To Standardise.* Place a small quantity of hydrochloric acid and an equal bulk of water in a conical beaker, stopped with a funnel, boil until all air has been expelled and the flask is full of the vapours of the acid. Then add a weighed piece of practically pure and clean iron wire to the boiling acid, and gently boil till it is dissolved. The solution must be colourless.

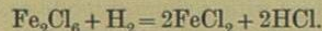
In the meantime fill up the burette, either a 50 c.c. or a 1000 grain, with the bichromate solution, and level for use. Then dilute the colourless solution of iron; transfer to a large evaporating dish (No. 7); dilute to about half a pint and run in the standard solution, constantly stirring meanwhile.

(d) To indicate the progress, a number of spots of the ferricyanide solution are placed on a white tile about

4 inches square, one spot being touched by a drop of liquid carried from the basin by a glass rod, after each addition of the standard solution. As long as any ferrous chloride is unoxidised, the union of the two drops will produce a blue colour which becomes very faint towards the conclusion; the termination of the titration being complete when no colour, or only the faintest tint is observed. The mean of three experiments gave 10.232 grains of iron as equivalent to 1000 liquid grains of the standard bichromate solution.

§ 368. *Estimation of Iron in Ores.*

(a) *Hæmatite.* Crush a quantity and pass through a No. 80 sieve. Weigh 10 and 12 grains respectively. Place each in a conical beaker; add strong hydrochloric acid and gently boil until dissolved, or until only insoluble silica remains; then add water until the beaker is one third full. The iron is in solution in the ferric condition, and requires to be completely reduced to the ferrous condition. This may be effected by adding a little zinc free from iron, which generates hydrogen, and this being in the nascent condition gradually reduces the yellow ferric chloride solution to colourless ferrous chloride, thus—



Transfer to an evaporating dish; well swill out the beaker and make up the solution to half a pint as before; then run in the standard solution until the contents cease to produce a faint blue tint with a spot of the ferricyanide on the white tile.

Suppose 624 and 748 thousandths are required, then—

$$\text{As } 1000 : 624 :: 10.232 : x = 6.385.$$

$$,, \quad 1000 : 748 :: 10.232 : x = 7.653.$$

$$10 : 100 :: 6.385 : 63.85.$$

$$12 : 100 :: 7.653 : 63.97.$$

For Spathic, Northampton, and clay iron ore, take 20 and 25 grains.

(b) *Northampton Ore.* Dissolve 20 and 25 grains in strong hydrochloric acid; dilute and transfer to a pint flask; dilute until half full. Then add 30 grains of sodium sulphite (Na_2SO_3) in crystals, and keep in a warm place till nearly decolourised, which takes about fifteen minutes; then boil until all odour of sulphurous acid ceases, and pour into dish for titration with the standard solution as before.

(c) *Blackband.* Take 20 and 25 grains and calcine in muffle for fifteen minutes, then dissolve in hydrochloric acid, decolourise with zinc and proceed as usual.

(d) *Tap Cinder.* Take 10 and 12 grains and dissolve in hydrochloric acid. It is well in this case to add a few bits of glass to prevent gelatinous silica from sticking to the ore. Titrate as usual.

(e) *Titaniferous Iron Ore.* Take 20 and 25 grains of the finely divided ore and boil with strong hydrochloric acid for an hour until decomposed, then add water and reduce with sodium sulphite as in (b). Two experiments gave 37.20 and 37.108 per cent. respectively.

Now, when zinc is used, incorrect results are obtained, so that zinc cannot be used in the reduction of solutions obtained from ores containing titanous acid, because it converts the tetrachloride of titanium (TiCl_4) into sesquichloride (Ti_2Cl_6), so that sulphite of soda must be used as described with the Northampton ore. When zinc is employed, the ferric chloride is reduced first, and if quickly poured off when the solution becomes colourless, the iron might be approximately estimated; but if left too long the solution turns violet and afterwards blue.

20 and 25 grains of ore were treated with zinc instead

of with sodium sulphite as above, and gave 44.75 and 42.68 per cent. of iron respectively. Compare these results with the former when sodium sulphite was used as the reducing agent.

§ 369. In the case of mixed ores like magnetite, and compounds containing both ferrous and ferric oxides, it is often required to know the amount of each oxide present. This may be done as follows:—

1. Dissolve 10 to 20 grains in hydrochloric acid or aqua regia if necessary; dilute; decolourise with zinc, and estimate the total amount of iron present by the standard solution.

2. Weigh another portion and dissolve with sulphuric acid in a flask through which a stream of carbonic acid is constantly passing; dilute; transfer to dish, and titrate with standard solution as before; or use the method in § 201 (c). The result gives the amount of iron present as ferrous oxide. The difference between this and the former result gives the amount of iron present as ferric oxide. (See § 201.)

(a) When sodium sulphite is used as the reducing agent, care must be taken to add it in sufficient quantity, and that the iron solution contains free acid. The completeness of the reduction may be ascertained by adding a drop of the iron solution to a drop of potassium sulphocyanide, which should impart merely a rose pink colour; then the sulphurous acid may be boiled off. If any unreduced ferric salt is present, the sulphocyanide will give a blood red colour.

(b) Some magnetites and hæmatites are difficultly soluble in hydrochloric acid. They may be reduced to the metallic state by heating a weighed portion—say 10 grains—in a porcelain crucible having a hole through the lid through which a stream of coal gas is constantly

passing (Fig. 69). The reduced metal is then readily soluble in hydrochloric acid.

§ 370. *Potassium Permanganate Method.*

(a) The permanganate solution, even when very weak, has a decidedly purple colour, which is immediately discharged as long as any ferrous salt remains unoxidised; but immediately this is accomplished, a single drop of permanganate in excess gives a characteristic rose tint to the solution, so that the exact termination is easily recognised.

(b) *Standard Solution.* Dissolve 197 grains of pure potassic permanganate in 4 pints of water. As this solution is affected by the presence of organic matter, it must be kept in a stoppered glass bottle.

(c) *To Standardise.* Dissolve about 5 grains of pure iron wire, accurately weighed, in hydrochloric acid, using the precautions given in § 367 (c); transfer the diluted colourless solution to a 20 ounce flask, and carefully run in the standard solution, with frequent shaking, until the rose tint appears and remains permanent; then take the reading of the burette, perform three experiments, and take the mean as the correct standard. The ores are dissolved, then reduced by zinc or sodium sulphite, as in former method. (See § 368.)

VOLUMETRIC ESTIMATION OF MANGANESE.

§ 371. (a) The following volumetric method, founded on the precipitation of manganese as dioxide, in presence of ferric chloride, is recommended by Mr. J. Pattison. The re-agents employed are—(1) The clear liquid obtained by the decantation from a 1.5 per cent. solution of bleaching powder; (2) light granular calcium carbonate obtained

by precipitating an excess of calcium chloride with sodium carbonate at 180° F.; (3) a 1 per cent. solution of ferrous sulphate in dilute sulphuric acid (1 to 4); (4) a standard solution of potassium bichromate, equivalent to 1 part of iron in 100 of solution.

(b) 10 grains of ore dried at 212° F. are dissolved in a 20 ounce beaker in about 100 grains of hydrochloric acid (specific gravity, 1.18). Calcium carbonate is then added until the free acid is neutralised and the liquid turns slightly reddish; 6 or 7 drops of hydrochloric acid are then added, and 1000 grains of the bleaching powder solution, or 500 grains of saturated bromine water; then boiling water is run in until the temperature is raised from 140° to 160° F.; 25 grains of calcium carbonate are then added and the whole well stirred. If the supernatant liquid has a pink colour, the permanganate is reduced by a few drops of alcohol. The precipitated oxides of iron and manganese are filtered off and washed; 1000 grains of the acidified ferrous sulphate solution are measured into the 20 ounce beaker already used, and the filter with its washed contents added. A certain quantity of the ferrous sulphate is oxidised by the MnO_2 ; this quantity is estimated by the standard bichromate solution, and from it the quantity of MnO_2 is estimated. The iron present must be at least equal in weight to the manganese during precipitation in order to ensure the absence of lower oxides. This method is applicable to the analysis of ferro-manganese, spiegel-eisen and manganese slags. (Watt's Dictionary, 3rd Suppl., page 1264.)

VOLUMETRIC ESTIMATION OF SULPHUR.

§ 372. Mr. C. R. A. Wright recommends the following method for technical purposes:—

"Dissolve a suitable quantity of the mineral, or substance containing sulphur in an evaporating dish by means of nitric acid or other oxidising agent free from sulphuric acid; evaporate to a small bulk to expel excess of acid; dilute with water; boil and nearly neutralise with ammonia.

"Run in a dilute solution of barium chloride of known strength until no further precipitation occurs. The exact point is found by filtering off a small portion into a test tube and adding a drop of the standard. If a precipitate forms, add this filtrate to the original solution, well mix, and repeat the filtering a second time. In case the finishing point is overreached, a solution of sodium sulphate of a strength equal to that of the barium chloride is cautiously added to bring it back to the point where no further precipitation occurs, as determined by means of filtering and testing. In such a case the volume of sodium sulphate used is subtracted from the total volume of barium chloride required.

"For standard solution, instead of having a deci-normal solution of 20.8 grammes to the litre, which corresponds to .32 of sulphur for 100 c.c., that amount of barium chloride, which is equivalent to .5 gramme of sulphur, may be dissolved in a litre of water, namely 32.5 grammes; then if 1 gramme of ore be dissolved, each c.c. of standard solution will represent .5 per cent. of sulphur.

"The standard solution of sodium sulphate must then contain 22.19 grains of anhydrous sodium sulphate. This method will not yield perfectly accurate results. In presence of lead, the method is not applicable in consequence of the formation of insoluble lead sulphate."

APPENDIX.

TABLE I.

TABLE OF ELEMENTS WITH THEIR SYMBOLS, ATOMIC WEIGHTS, AND SPECIFIC GRAVITIES.

METALS.

Names.	Symbols.	Atomic Weights.	Specific Gravity.
Aluminium, - - -	Al	27	2.56
Antimony, - - -	Sb	120	6.72
Arsenic, - - -	As	75	5.67
Barium, - - -	Ba	137	3.75
Bismuth, - - -	Bi	207.5	9.8
Cadmium, - - -	Cd	112	8.6
Caesium, - - -	Cs	133	1.88
Calcium, - - -	Ca	40	1.58
Cerium, - - -	Ce	141	6.68
Chromium, - - -	Cr	52.4	6.8
Cobalt, - - -	Co	58.6	8.5
Copper, - - -	Cu	63.2	8.8
Didymium, - - -	Di	145	6.5
Erbium, - - -	E	112.6	-
Glucinum, - - -	Gl	9	2
Gold, - - -	Au	196.8	19.32
Indium, - - -	In	113.4	7.4
Iridium, - - -	Ir	192.5	22.4
Iron, - - -	Fe	56	7.86
Lanthanium, - - -	La	138.5	6.2
Lead, - - -	Pb	206.4	11.37
Lithium, - - -	Li	7	.58
Magnesium, - - -	Mg	24	1.74
Manganese, - - -	Mn	55	8
Mercury, - - -	Hg	200	13.59
Molybdenum, - - -	Mo	96	8.6
Nickel, - - -	Ni	58.6	8.8
Niobium, - - -	Nb	94	6.27
Osmium, - - -	Os	195	22.48
Palladium, - - -	Pd	106.2	11.5
Platinum, - - -	Pt	194.3	21.5
Potassium, - - -	K	39	.87