CALCIUM.

Calcium is usually thrown out of solution in the form of oxalate, the precipitate ignited, and the resulting carbonate weighed.

Process.—Dissolve 0.3 grm. or 0.4 of dried colorless crystals of calc-spar in about a third of a litre of water acidulated with hydrochloric acid, heat the solution to near the boiling-point, add excess of solution of oxalate of ammonium, then ammonia, until, after stirring, the liquid smells strongly ammoniacal; set aside in a warm place for twelve hours. Carefully pour off the supernatant liquid, passing it through a filter; add hot water to the precipitate, set aside for half an hour, again decant, and after once more washing transfer the precipitate to the filter, allowing all contained fluid to pass through before a fresh portion is added. Wash the precipitate with hot water, avoiding a rapid stream or the precipitate may be driven through the pores of the paper. Dry, transfer to a weighed crucible, and incinerate, as described for sulphate of barium, and slowly heat the precipitate till the bottom of the crucible is just visibly red when seen in the dark. As soon as the residue is white or only faintly gray remove the lamp, cool, and weigh.

The resulting carbonate of calcium should have the same weight as the calc-spar from which it was obtained. If loss has occurred, carbonic acid gas has probably escaped. In that case moisten the residue with water, and after a few minutes test the liquid with red litmus- or turmeric-paper; if an alkaline reaction is noticed, it is due to the presence of caustic lime. Add a small lump of carbonate of ammonium, evaporate to dryness over a water-bath, and again ignite, this time being careful not to go beyond the prescribed temperature. The treatment may, if necessary be repeated.

Proportional Weights of Equivalent Quantities of Calcium Salts.

Oxide (quicklime)	CaO	56
Hydrate (slaked lime)	$Ca2HO$	74
Carbonate	$CaCO_3$	100
Sulphate (anhydrous)	$CaSO_4$	136
Sulphate (crystalline or precipitated)	$CaSO_4,2H_2O$	172
Chloride	$CaCl_2$	110.8
Phosphate (of bone)	$(Ca_32PO_4)310 \div 3$	103.3
Superphosphate	CaH_42PO_4	234

MAGNESIUM.

Process 1.—The light or heavy carbonate of magnesium of pharmacy may be estimated by heating a weighed quantity to redness in a porcelain crucible. If it has the composition indicated by the formula given in the British Pharmacopœia ($3MgCO_3,Mg2HO,4H_2O$), it will yield 42 per cent. of magnesia (MgO). According to that work, the purity of even sulphate of magnesium ($MgSO_4,7H_2O$) may be determined by boiling a weighed quantity with excess of carbonate of sodium, collecting the precipitate, washing, drying, igniting, and weighing the resulting magnesia (MgO). The crystalline sulphate should afford 16.26 per cent. of oxide. The official solution of carbonate of magnesium in carbonic acid water (*Liquor Magnesiæ Carbonatis*, B. P.) should yield five grains of pure oxide of magnesium per fluidounce.

Process 2.—The general form in which magnesium is precipitated is as phosphate of ammonium and magnesium ($MgNH_4PO_4,6H_2O$); this, by heat, is converted into pyrophosphate of magnesium ($Mg_2P_2O_7$). Accurately weigh a small quantity (0.4 to 0.5 grm.) of pure dry crystals of sulphate of magnesium, dissolve in two or three hundred cubic centimetres of cold water in a beaker, add chloride of ammonium, ammonia, and phosphate of sodium or ammonium, agitate with a glass rod (without touching the sides of the vessel, or crystals will firmly adhere to the rubbed portions), and set aside for twelve hours. Collect on a filter, wash the precipitate with water containing a tenth of its volume of the strongest solution of ammonia, until the filtrate ceases to give a precipitate with an acidulated solution of nitrate of silver. Dry, transfer to a crucible, burn the filter in the usual way, heat slowly to redness, cool, and weigh.

Proportional Weights of Equivalent Quantities of Magnesium Salts.

Pyrophosphate	$Mg_2P_2O_7$	222
Sulphate	$2(MgSO_4,7H_2O)$	492
Oxide	$2(MgO)$	80
Official carbonate	$(3MgCO_3,Mg2HO,4H_2O) \div 2$	191

ZINC.

Zinc is usually estimated as oxide (ZnO), occasionally as sulphide (ZnS). $Zn = 64.9$.

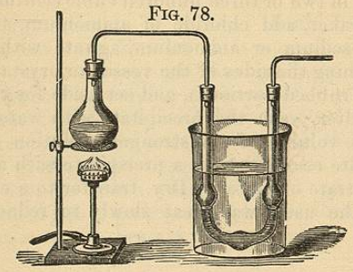
Process.—Dissolve a weighed quantity (0.5 to 0.6 grm.) of sul-

phate of zinc in about half a litre of water in a beaker, heat to near the boiling-point, add carbonate of sodium in slight excess, boil, set aside for a short time; pass the supernatant liquid through a filter, gently boil the precipitate with more water, again decant; repeat these operations two or three times; collect the precipitate on the filter, wash, dry, transfer to a crucible, incinerate, ignite, cool, and weigh. 286.9 (= molec. weight) of sulphate should yield 80.9 (= molec. weight) of oxide.

MANGANESE.

To ascertain its value for evolving chlorine from hydrochloric acid a weighed quantity of finely-powdered black oxide of manganese is heated in a small flask with pure hydrochloric acid, and the resulting chlorine conveyed into a U-tube containing solution of iodide of potassium. The amount of iodine thus freed is estimated by the volumetric solution of hyposulphite of sodium. 126.6 of iodine indicate 35.4 of chlorine. Manganese may also be estimated by the reaction and apparatus described under "Oxalates," page 665. (See Fig. 78).

FIG. 78.



ALUMINIUM.

Aluminium is always precipitated as hydrate ($Al_2 6HO$) and weighed as oxide (Al_2O_3).

Process.—Dissolve about 2 grammes of pure dry ammonium alum in half a litre of water, heat the solution, add chloride of ammonium and a slight excess of ammonia, boil gently till the odor of ammonia has nearly disappeared, set aside for the hydrate to deposit, pass the supernatant liquid through a filter, wash the precipitate three or four times by decantation, transfer to the filter, finish the washing, dry, burn the filter, ignite in a covered crucible, and weigh.

$Al_2 3SO_4 K_2SO_4, 24H_2O$	948
$Al_2 3SO_4, (NH_4)_2SO_4, 24H_2O$	906
Al_2O_3	102
Per cent. of Al_2O_3 yielded by ammonium alum	11.26

QUESTIONS AND EXERCISES.

1040. Give details of the manipulations observed in gravimetrically estimating salts of potassium or ammonium.

1041. What quantity of chloride of sodium is contained in a sample of rock-salt 0.351 gramme of which yields 0.426 of sulphate of sodium? *Ans.* 99.83 per cent.

1042. To what amount of the ammonium alum is 10.888 of a gramme of the double chloride of platinum and ammonium equivalent? *Ans.* 1.817 grammes.

1043. Find the weight of sulphate of barium obtainable from 0.522 of nitrate. *Ans.* 0.466.

1044. Describe the usual method by which salts of calcium are estimated.

1045. By what quantitative processes may the official salts of magnesium be analyzed?

1046. Calculate the proportion of pure sulphate of zinc in a sample of crystals 0.574 of which yield 0.161 of oxide. *Ans.* 99.46 per cent.

1047. Ascertain the weight of alumina (Al_2O_3) which should be obtained from 1.812 grammes of ammonium alum.

IRON.

Iron and its salt are gravimetrically estimated in the form of ferric oxide (Fe_2O_3).

Compounds containing organic acidulous radicals are simply incinerated, and the resulting oxide weighed. Thus, 1 gramme of the official citrate of iron and ammonium (*Ferri et Ammoniæ Citras*, B. P.), incinerated, with exposure to air, leaves not less than .27 of ferric oxide. A small quantity of the salt is weighed in a tared covered porcelain crucible, flame cautiously applied until vapors cease to be evolved, the lid then removed, the crucible slightly inclined and exposed to a red heat until all carbonaceous matter has disappeared. The residual ferric oxide is then weighed. The tartrate of potassium and iron (*Ferrum Tartaratum*, B. P.) is treated in the same manner, except that the ash must be washed and again heated before weighing, in order to remove carbonate of potassium produced during incineration: 5 grammes should yield 1.5 grammes of ferric oxide.

From other compounds of iron, soluble in water or acid, the metal is precipitated in the form of hydrate ($Fe_2 6HO$) by solution of ammonia, and converted into oxide ($Fe_2 6O_3$) by ignition. Dissolve a piece (about 0.2 grm.) of the purest iron obtainable (piano wire), accurately weighed, in water acidulated with hydrochloric acid; add a few drops of nitric acid and gently boil; pour in excess of ammonia, stir, set aside till the ferric hydrate has deposited, pass the supernatant liquid through a filter, treat the precipitate three or four times with boiling water; transfer to the filter, wash till the filtrate yields no trace of chlorine (for chloride of ammonium will decompose ignited ferric oxide, with volatilization of ferric chloride), dry and ignite as usual, and weigh. Iron in the official solutions (*Liquor Ferri Perchloridi Fortior*, *Liquor Ferri Nitratis*, and *Liquor Ferri Tersulphatis*) may be estimated by this general process.

The proportion of metallic iron in a mixture of iron and oxides of iron may be determined by digestion in a strong solution of iodine in iodide of potassium, which attacks the metal only. The reduced iron of pharmacy (*Ferrum Redactum*) is in good condition so long as it contains, as shown by this method, half its weight of free metal.

Another Method.—Reduced iron is converted into ferrous chloride by a hot, strong solution of corrosive sublimate, while the oxides are not affected. The filtrate may be treated gravimetrically or volumetrically (Wilner).

Proportional Weights of Equivalent Quantities of Iron and its Salts.

Metal	Fe_2	111.8
Ferric oxide	Fe_2O_3	159.8
Ferric hydrate . . .	$Fe_2 6HO$	213.8
Ferric chloride . . .	Fe_2Cl_6	324.2
Ferric sulphate . . .	$Fe_2 3SO_4$	399.8
Ferrous sulphate . .	$2(FeSO_4,7H_2O)$ . .	555.8

ARSENICUM.

Arsenic (As_2O_3) is usually estimated volumetrically (*vide* p. 573). With certain precautions arsenicum may also be precipitated and weighed as sulphide (As_2S_3).

Process 1.—The pure, white, massive arsenic (about 0.2 grm.) is dissolved in a flask in a small quantity of water containing bicarbonate of sodium or potassium, the liquid being heated. A slight excess of hydrochloric acid is then added, and sulphuretted hydrogen gas passed through the solution so long as a precipitate falls, the mouth of the flask being stopped by a plug of cotton-wool (to prevent undue access of air and consequent decomposition of the gas, resulting in precipitation of sulphur). The mixture is warmed in the flask, and carbonic acid gas passed through it until the odor of sulphuretted hydrogen has nearly disappeared; the precipitate collected on a tared filter, washed as quickly as possible with hot water containing a little sulphuretted hydrogen, dried in a water-oven, and weighed. 197.8 parts of arsenic should yield 245.8 of sulphide of arsenicum.

Process 2.—The arsenicum must be present in the arsenic condition. If the operator is not certain that this is the case, the solution must be warmed with a little hydrochloric acid and a few grains of chlorate of potassium added until a distinct odor of chlorous vapor is evolved, which is then allowed to escape by continued application of heat. To the solution thus obtained ammonia, which must produce no turbidity, is added in excess, and then magnesia mixture (see p. 665). The solution is set aside for twenty-four or forty-eight hours. The precipitate is collected on a filter and washed with as little ammonia-water (1 to 3) as possible until the filtrate ceases to give a reaction for chlorides. The precipitate is then dried on the filter, the precipitate and filter-paper burned, and the whole gently ignited in a crucible and weighed. The residue is represented by the formula ($Mg_2As_2O_7$).

ANTIMONY.

The metal is precipitated in the form of sulphide (Sb_2S_3), with the precautions observed in estimating arsenicum, a small quantity of tartaric acid, as well as hydrochloric, being added to prevent the precipitation of an oxysalt. If the sulphuretted hydrogen be passed through a hot solution, the particles of precipitate aggregate better, and the latter may be more quickly filtered out and washed. Tha experiment may be performed on about half a gramme of pure tartar-emetic: the salt should yield slightly more than half its weight (50.6 per cent.) of sulphide. According to Fresenius, the sulphide dried at 100° C. still contains 2 per cent. of water, and must be heated in a current of carbonic acid gas until it turns from an orange to a black color before all moisture is expelled. In the United States Pharmacopœia the purity of tartar-emetic (*Antimonium Tartaratum*) and the strength of solution of chloride of antimony (*Liquor Antimonii Chloridi*) are determined by the

above process. *Sulphurated Antimony* of official quality, when dissolved in hydrochloric acid and the solution boiled and poured into a considerable volume of water, should yield a precipitate of oxychloride, which, after washing and drying, should weigh 85 per cent. of the sulphurated antimony.

(For the volumetric estimation of antimony in antimonious salts, see p. 573.)

COPPER.

Copper is precipitated from its solutions and weighed (1) as metal (Cu_2) or (2) as oxide (CuO).

Process 1.—Dissolve about half a gramme of dry crystallized sulphate of copper in a small quantity of water in a tared porcelain crucible or beaker, acidulate with hydrochloric acid, introduce a fragment or two of pure zinc, cover the vessel with a watch-glass, and set aside till evolution of hydrogen has ceased and the still acid liquid is colorless. The copper is then washed with hot water by decantation until no trace of acid remains, the precipitate drained, rinsed with strong spirit of wine, dried in the water-oven, and weighed.

Process 2.—About three-fourths of a gramme of sulphate of copper is accurately weighed, dissolved in half a litre of water, the liquid boiled; dilute solution of potash or soda is then added till no more precipitate falls, ebullition continued for a short time, and the beaker set aside; the supernatant liquid is decanted, the precipitate boiled with water, twice or thrice collected on a filter, washed, dried, transferred to a crucible, the filter incinerated, and its ash moistened with a drop of nitric acid; the whole is finally heated strongly, cooled, and weighed.

Process 3.—From a solution acidulated by sulphuric acid and placed in a platinum crucible copper may be entirely deposited in a coherent form by a weak current of electricity, the crucible being connected with the zinc pole of the battery, a platinum spatula suspended in the solution forming the positive pole. The crucible may afterward be freed from the deposited copper by nitric acid.

249.2 parts of sulphate of copper yield 79.2 of oxide or 63.2 of metal.

Other processes are occasionally employed.

BISMUTH.

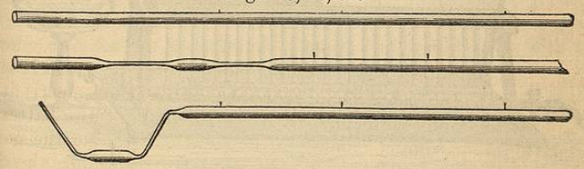
Dissolve 0.3 or 0.4 grm. of pure oxycarbonate of bismuth ($2Bi_2O_2CO_3,H_2O$) (*Bismuthi Subcarbonas*, U. S. P.) in a small quantity of hydrochloric acid, dilute with water slightly acidulated by hydrochloric acid, pass excess of sulphuretted hydrogen through the liquid, collect the precipitate on a tared filter, wash, dry at 100° C., and weigh. The sulphide must not be exposed too long in the water-oven, or it will increase in weight, owing to absorption of oxygen; hence it should be tested in the balance every half hour during desiccation. 521 of oxycarbonate should yield 516 of sulphide (Bi_2S_3). The atomic weight of bismuth is 210.

MERCURY.

This element may be (1) isolated and estimated in the form of metal, or precipitated and weighed as (2) mercurous chloride, or (3) mercuric sulphide.

Process 1.—The process by which the metal itself is separated is one of distillation into a bulb surrounded by water. About half a metre of the difficultly fusible German glass known as *combustion-tubing* is sealed at one end after the manner of a test-tube (Fig. 79); a mixture of bicarbonate of sodium and dry chalk is then dropped into the tube to the height of 2 or 3 centimetres, and, next, several small fragments of quicklime so as to occupy another centimetre: a mixture of about a gramme of pure calomel or corrosive sublimate with enough powdered quicklime to occupy 10 or 12 centimetres of the tube is added; then the lime-rinsings of the mixing-mortar, a layer of a few centimetres of powdered quicklime, and finally a plug of *asbestos* (a fibrous mineral unaffected by heat), The whole powder should occupy two-thirds of the length of the tube. The part of the tube just above the asbestos is now softened in the blowpipe-flame and drawn out about a decimetre to the diameter of a narrow quill; it is again drawn out to the same extent at a point about two or three centimetres nearer the mouth, and any excess of tubing cut off. The bulb thus formed may be enlarged by softening and blowing. The tube is next softened at a point close

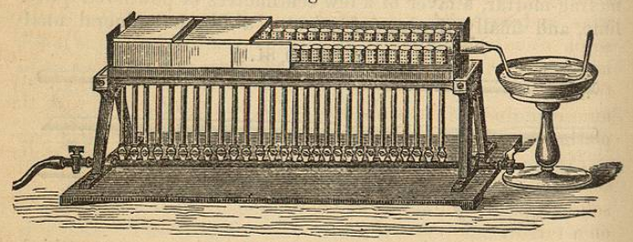
Figs. 79, 80, 81.



to but anterior to the asbestos, and bent to form an obtuse angle; the tube is then softened close to the bulb and slightly bent, so that the bulb may be parallel with the large tube; then softened on the other side of the bulb, and the terminal tube bent to an obtuse angle, so that, the tube being held in a horizontal position, the bulb may be sunk in water and the terminal tube point upward (Fig. 81). The long tube is now laid in the gas-furnace found in most laboratories (Fig. 82), a basin so placed that the bulb of the apparatus may be cooled by being surrounded by water, the part of the tube occupied by asbestos heated to redness, and the flame slowly lengthened until the whole tube is red hot. Under the circumstances just described the mercurial compound volatilizes, is decomposed by the lime, and its acidulous radical fixed, the mercury carried to and condensed in the bulb, the carbonic acid gas evolved from the bicarbonate of sodium and chalk washing out the last portions of mercury vapor from the tube. When the distillation is considered to be complete, the dish of water is removed, the bulb dried, and then detached by help of a file at a point beyond any sublimate of mercury. The bulb is lastly weighed, the mercury shaken or dissolved out, and the tube again dried and weighed.

Process 2.—The process by which mercury is separated in the form of calomel consists in adding hydrochloric and phosphorous acids (*vide* p. 348) to an aqueous or even acid solu-

Fig. 82.



Distillation of Mercury for Quantitative Purposes.

tion of a weighed quantity of the mercurial compound, setting the mixture aside for twelve hours, collecting the precipitate on a tared filter, washing, drying at 100° C., and weighing (Rose). The experiment may be tried on half a gramme to a gramme of corrosive sublimate.

Process 3.—Two or three decigrammes of corrosive sublimate are dissolved in water, the solution acidulated with hydrochloric acid, excess of sulphuretted hydrogen passed through it, the precipitate collected on a tared filter, washed with cold water, dried at 100° C., and weighed.

Proportional Weights of Equivalent Quantities of Mercury and its Salts.

Metal	Hg	199.7
Mercurous chloride	HgCl	235.1
Mercuric chloride	$HgCl_2$	270.5
Mercuric sulphide	HgS	231.7

LEAD.

Lead is generally estimated either as (1) oxide, (2) sulphate, (3) chromate, or (4) metal.

Process 1.—Weigh out 1 or 2 grammes of pure acetate of lead in a covered crucible previously tared, and heat slowly until no more vapors are evolved. Remove the lid, stir down the carbonaceous mass with a clean iron wire, and keep the crucible in the flame so long as any carbon remains unconsumed. Introduce some fragments of fused nitrate of ammonium, and again ignite until no metallic lead remains and all excess of the nitrate has been decomposed. Cool and weigh the resulting oxide (PbO).

Process 2.—Dissolve 0.4 or 0.5 of a gramme of acetate of lead in a small quantity of water, drop in diluted sulphuric acid, add to the mixture twice its bulk of methylated spirit of wine, and set aside. Decant the supernatant liquid, collect the sulphate on a filter, wash with spirit, dry, transfer to a porcelain crucible, removing as much of the sulphate as possible from the paper, incinerate on the crucible-lid (not in the platinum coil, for the particles of reduced lead would unite with the platinum by fusion), ignite, cool, and weigh.

Process 3.—About half a gramme of acetate of lead is dissolved in 200 or 300 c.c. of water, acetic acid added, and then solution of red chromate of potassium. Collect the precipitate on a tared filter, wash, dry at 100° C., and weigh.

Process 4.—In certain cases, notably in that of commercial white lead, the lead may be estimated in the metallic state by means of cyanide of potassium. The lead paint (about 20 grammes) is weighed and carefully incinerated. The residue, a mixture of metallic lead and oxide of lead, is then mixed with several times its bulk of cyanide of potassium and the whole heated to fusion. With careful manipulation the lead collects in one globule, which, after cooling, may readily be

separated from the mixed cyanide and cyanate and weighed. White lead, commercially pure, should contain 74 per cent. of lead.

Proportionate Weights of Equivalent Quantities of Lead and its Salts.

Metal	Pb	206.5
Acetate	$Pb2C_2H_3O_2,2H_2O$.	378.5
Oxide	PbO	222.5
Sulphate . . .	$PbSO_4$	302.5
Chromate . . .	$PbCrO_4$	322.9

SILVER.

Compounds of silver which are readily decomposed by heat are estimated in the form of (1) metal, others usually as (2) chloride (AgCl), but sometimes as (3) cyanide (AgNC).

Process 1.—Heat about a gramme of oxide of silver (Ag_2O) in a tared crucible, cool, and weigh. 231.4 of oxide yield 215.4 of metal. "29 grains heated to redness yield 27 grains of metallic silver."—*Brit. Pharm.*

Process 2.—Dissolve 0.4 or 0.5 grm. of pure dry crystals of nitrate of silver in water, acidulate with two or three drops of nitric acid, slowly add hydrochloric acid, stirring rapidly, until no more precipitate falls. Pour off the supernatant liquid through a filter, wash the chloride of silver once or twice with hot water, transfer to the filter, complete the washing, and dry. After removing as much as possible of the precipitate from the paper to the crucible, burn the filter, letting its ash fall on the inverted lid of the crucible, moisten with a drop of nitric acid, warm, add a drop of hydrochloric acid, evaporate to dryness, replace the lid on the crucible, unite the whole until the edges of the mass of chloride begin to fuse; cool and weigh. 169.7 of nitrate yield 143.1 of chloride. According to the United States Pharmacopœia, 10 parts of nitrate should thus yield 8.4 of chloride, while 20 parts of "moulded nitrate of silver" should yield 16 of chloride, and the filtrate from the chloride evaporated to dryness should leave no residue, indicating absence of nitrates of potassium or sodium and other similar adulterants. 20 parts of "diluted nitrate of silver" should yield 8.4 of chloride; 10 parts of "oxide of silver" should yield 12.36 of chloride.

Process 3.—Cyanide of silver may be collected on a tared filter and dried at 100° C. 169.7 of nitrate yield 133.7 of cyanide.

Silver and its salts may be volumetrically estimated by a standard solution of chloride of sodium.

Cupellation.—The amount of silver in an alloy may be also determined by a dry method. The metal is folded in a piece of thin sheet lead, placed on a *cupel* (*cupella*, little cup, made of compressed bone-earth), and heated in a furnace, the cupel being protected from the direct action of flame by a muff-shaped or, rather, oven-shaped, case termed a muffle. The metals melt, the baser become oxidized, the oxide of lead fusing and dissolving the other oxides; the fluid oxides are absorbed by the porous cupel, a button of pure silver remaining. An alloy supposed to contain 95 per cent. of silver requires about three times its weight of lead for successful cupellation; if 92½ per cent. (English silver coin), between five and six times its weight of lead is necessary.

QUESTIONS AND EXERCISES.

1048. Explain the gravimetric process by which the strength of the official solutions of ferric chloride, nitrate, and sulphate is determined.

1049. Mention the various amounts of ferrous and ferric salts equivalent to 100 parts of metal.

1050. State the precautions necessary to be observed in estimating arsenicum or antimony in the form of sulphide.

1051. In what form are the official compounds of bismuth weighed for quantitative purposes?

1052. Give an outline of the process by which mercury may be isolated from its official preparations and weighed in the metallic condition.

1053. Describe three methods for the quantitative analysis of salts of lead, and the weights of the respective precipitates, supposing 0.56 of crystallized acetate to have been operated on in each case.

1054. Describe the process by which silver is estimated in the forms of metal, chloride, and cyanide.

1055. What proportions of nitrate of silver are indicated, respectively, by 15 of metal, 9.8 of chloride, and 8.1 of cyanide?

1056. Describe cupellation.

GRAVIMETRIC ESTIMATION OF THE ACIDULOUS RADICALS OF SALTS.

CHLORIDES.

Free chlorine (chlorine-water) and compounds which by action of acids yield free chlorine (Chlorinated Lime, Chlorinated Soda, and their official solutions) are estimated volumetrically by a standard solution of hyposulphite of sodium (*vide* p. 636). The amount of combined chlorine in pure chlorides

(HCl, NaCl) may also be determined by volumetric analysis with a standard solution of nitrate of silver (p. 624).

Combined chlorine is gravimetrically estimated in the form of chloride of silver, the operation being identical with that just described for silver salts (p. 657). 58.4 parts of pure, colorless, crystallized chloride of sodium (rock-salt) yield 143.1 of chloride of silver.

IODIDES.

Free iodine is estimated volumetrically by solutions of hyposulphite of sodium (*vide* p. 579).

Combined iodine is determined gravimetrically in the form of iodide of silver, the operations being conducted as with chloride of silver. Iodide of potassium may be used for an experimental determination: KI=165.1 should yield AgI=234.3. Of iodide of cadmium (*Cadmii Iodidum*, B. P., 1867) it is stated that "10 grains dissolved in water, and nitrate of silver added in excess, give a precipitate which, when washed with water and afterward with half an ounce of solution of ammonia, and dried, weighs 12.5 grains."

In presence of chlorides and bromides the iodine in iodides may be precipitated and weighed as iodide of palladium.

Moisture in iodine is estimated by loss on exposing a weighed quantity of iodine in a capsule over a dish of sulphuric acid under a small bell-jar, or by adding to a weighed sample five or six times as much mercury or twice as much zinc, and a little water, drying and weighing. The product is the amount of metal employed plus that of the *dry* iodine in the sample.

BROMIDES.

Free bromine may be estimated by shaking with excess of solution of iodide of potassium, and then determining the equivalent quantity of liberated iodine by a standard solution of hyposulphite of sodium (p. 636).

The bromine in bromides may be precipitated and weighed as bromide of silver, the manipulations being the same as those for chloride of silver: 0.2 to 0.3 of pure bromide of potassium may be used for an experimental analysis.

Ammonii Bromidum, U. S. P.: "1 gm. of the powdered and dry salt, when completely precipitated by nitrate of silver, yields, if perfectly pure, 1.917 gm. of dry bromide of silver." *Calcii Bromidum*, U. S. P.: "1 gm of the dry salt, when completely precipitated by nitrate of silver, yields, if perfectly pure, 1.878 gm. of dry bromide of silver."

CYANIDES.

The hydrogen cyanide (hydrocyanic acid) is usually estimated volumetrically (*vide* p. 624).

From all soluble cyanides cyanogen may be precipitated by nitrate of silver after acidulating with nitric acid, the cyanide of silver collected on a tared filter, dried at 100° C., and weighed.

Of the official Diluted Hydrocyanic Acid it is stated that 100 grains (or 110 minims), precipitated by solution of nitrate of silver, yield 10 grains of dry cyanide of silver.

Cyanide of Silver.

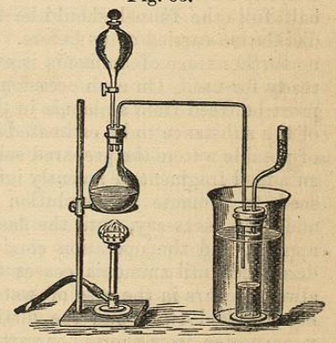
		In 1 molec. wt.	In 100 parts.
Silver	Ag	107.7	80.55
Cyanogen	CN	26.00	19.45
		133.7	100.00

NITRATES.

Nitrates cannot be estimated by direct gravimetric analysis, none of the basylous radicals yielding a definite nitrate insoluble in water. With some difficulty they may be determined by indirect volumetric methods.

Process.—The following (Thorpe's) method depends upon the fact (Gladstone and Tribe) that when zinc upon which copper is deposited in a spongy form is boiled with water hydrogen is evolved. Thorpe found that in a solution containing nitrates the nascent hydrogen converts the whole of the nitrogen of the nitrates into ammonia, which may be collected and estimated. (The oxygen of the nitrate is simultaneously converted into water, the nitrate-metal into hydrate, and the zinc into hydrate of zinc. The power of the copper-zinc couple is considered to depend largely on the hydrogen absorbed by the finely-divided metal.)

Fig. 83.



Estimation of Nitrates.