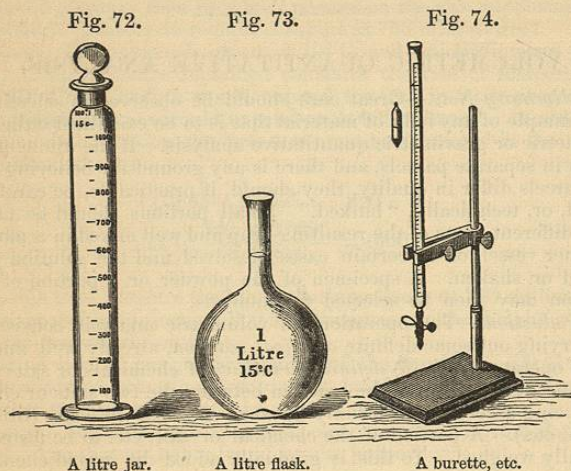of a litre. 3. A graduated tube or *burette* (Fig. 74), which, when filled to 0, holds 100 cubic centimetres (a decilitre), and is divided into 100 equal parts; it is used for accurately measuring small volumes of liquids.

Fig. 72.   Fig. 73.   Fig. 74.

A litre jar.   A litre flask.   A burette, etc.

The best form of burette is Mohr's. It consists of a glass tube, commonly about the width of a little finger and the length of an arm from the elbow, contracted at the lower extremity and graduated. The width and length of burettes, however, as well as the extent and fineness of their graduation, vary considerably. To the contracted portion is fitted a small piece of vulcanized caoutchouc tubing, into the other end of which a small spout made of narrow glass tube is tightly inserted. A strong wire clamp effectually prevents any liquid from passing out of the burette unless the knobs of the clamp are pressed by the finger and thumb of the operator, when a stream or drops flow at will. In place of the India-rubber tubing and clamp a stopcock is sometimes employed, and other modes of arresting the flow of liquid may be adopted. The accurate reading of the height of a solution in the burette is a matter of great importance; it should be taken from the bottom of the curved surface of the liquid. It may be still more exactly measured by the employment of a hollow glass float or bulb (Erdmann's float; see Fig. 74), of such a width that it can move freely in the tube without undue friction, and so adjusted in weight that it shall sink to more than half its length in any ordinary liquid. A fine line is scratched round the centre of the float; this line must always be regarded as marking the height of the fluid in the burette. In charging the burette a solution is poured in, not until its surface is coincident with 0, but until the mark on the float is coincident with 0.

ESTIMATION OF ALKALIES, ETC.

Volumetric Solution of Oxalic Acid.

(Crystallized Oxalic Acid, $H_2C_2O_4,2H_2O = 126$.)

On account of the bivalent character of the oxalic radical, and the univalent character of most of the metals contained in the salts which are estimated by oxalic acid, it is convenient that each litre of the volumetric solution should contain half a molecular weight in grammes of the acid ($H_2C_2O_4,2H_2O = 126 \div 2 = 63$).

If pure crystallized oxalic acid be at hand, the solution is made by dissolving 63 grammes in water, and making the volume up with more water to exactly one litre.

Pure oxalic acid, however, not being easy to obtain, the solution may be made from the commercial acid by dissolving 65 to 70 grammes in enough water to make a litre of solution, and then determining the strength of this solution by a titration with pure carbonate of sodium, making use of the following memoranda:—

$$\underbrace{Na_2CO_3}_{\dfrac{2)106}{53}} + \underbrace{H_2C_2O_4,2H_2O}_{\dfrac{2)126}{63}} = Na_2C_2O_4 + CO_2 + 3H_2O$$
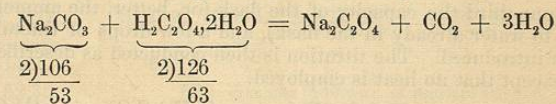
Pure anhydrous carbonate of sodium is easy to obtain, for commercial bicarbonate is usually of such purity that when a few grammes are heated to redness for a quarter of an hour the resulting carbonate is practically free from impurity. The bicarbonate should, however, be tested, and if more than traces of chlorides and sulphates are present, these may be removed by washing a few hundred grammes, first with a saturated solution of bicarbonate of sodium, and afterward with pure distilled water. After drying, the salt is ready for ignition.

About half a gramme of the carbonate of sodium is accurately weighed and placed in a half-pint flask, around the neck of which is tied calico or leather to protect the fingers when the heated vessel is shaken by the operator. The salt is dissolved in water to about one-third the capacity of the flask, and a few drops of the indicator, blue tincture of litmus, is added. The acid solution to be "set" or "standardized" is then poured into a burette, and run therefrom into the flask until the reddened litmus indicates the presence of free acid. This will be due in the first place to carbonic acid liberated and remaining dissolved in the solution. The contents of the flask are therefore boiled for several minutes, when the blue color will have returned. More acid is then run in until the mixture, after boiling, remains of a neutral color, indicating that just enough acid has been added to complete the reaction expressed in the foregoing equation.

Let it be supposed that 0.6 gramme of carbonate of sodium was taken, and that this required 11 c.c. of oxalic acid solution; how many c.c. of this solution would contain 63 grammes of oxalic acid crystals? or, what is equivalent in the reaction, how many c.c. would
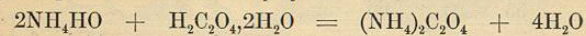
be required to neutralize 53 grammes of carbonate of sodium? As 0.6 gramme Na_2CO_3 is to 11 c.c. sol., so are 53 grammes Na_2CO_3 to x c.c. sol.; $x = 972$ c.c. 972 c.c. (nearly) are equivalent to 53 grammes of carbonate of sodium, and contain 63 grammes of oxalic acid.

This solution may either be used as it is, or may be diluted with water, every 972 c.c. to be diluted to 1000 c.c., so that 1000 c.c. shall contain 63 grammes of oxalic acid.

The following official substances are tested by this solution according to the United States Pharmacopœia:—
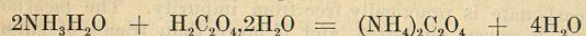
Solutions of Ammonia.—2 or 3 grammes of dilute, or about 1 gramme of strong, solution of ammonia is a convenient quantity to operate upon. The weighing is most conveniently accomplished by taking a small stoppered bottle containing half an ounce or so of the substance, and, having ascertained its total weight, transfer about the quantity desired to the flask in which the estimation is to be conducted, and again weigh the bottle with what remains in it. The difference is the exact quantity taken. The weighing of the ammonia solution having been accomplished, water is added to about one-third the capacity of the flask (or, better, the ammonia is added to water already in the flask), and a few drops of tincture of litmus introduced. The titration is then conducted as described before, except that no heat is employed.

$$2NH_4HO \;\; + \;\; H_2C_2O_4,2H_2O \;\; = \;\; (NH_4)_2C_2O_4 \;\; + \;\; 4H_2O$$

$$\underbrace{}\qquad\qquad \underbrace{}$$

2)70   2)126

35   63 = grammes in 1000 c.c. of standard solution.

$$2NH_3H_2O \;\; + \;\; H_2C_2O_4,2H_2O \;\; = \;\; (NH_4)_2C_2O_4 \;\; + \;\; 4H_2O$$

2)34   2)126

17   63 = grammes in 1000 c.c. of standard solution.

1000 c.c. of standard solution, or its equivalent of a solution of any other strength, would, according to this reaction, neutralize 17 grammes of ammonia gas (NH_3) or 35 grammes of hydrate of ammonium (NH_4HO). If 3 grammes of ammonia solution had been taken, and it had required 15 c.c. of standard oxalic acid solution, then the amount of ammonia gas or hydrate of ammonium it contained would be seen by the following calculations:—

1000 c.c. : $17NH_3$: : 15 c.c. : $x = .255$ grammes NH_3
1000 c.c. : $35NH_4HO$: : 15 c.c. : $x = .525$ grammes NH_4HO

Three grammes, then, would contain .255 grammes of the gas or .525 grammes of hydrate of ammonium. Or, in percentage,

3 gr. sol. : .255 gr. NH_3 : : 100 gr. sol. : x gr. NH_3 = 8.5 % NH_3
3 gr. sol. : .525 gr. NH_4HO : : 100 gr. sol. : x gr. NH_4HO = 17.5 % NH_4HO

The solution would therefore contain 8.5 per cent. of ammonia gas (NH_3) or 17.5 per cent. of hydrate of ammonium (NH_4HO). If the oxalic acid solution was not of full standard, the number of c.c. which contained 63 grammes of oxalic acid—which was, in fact, equivalent

to 1000 c.c. of standard solution—would be substituted for 1000 c.c. in the preceding proportions.

A comparison should now be made with the requirements of the Pharmacopœia. It is useful to express results as percentage of substance of pharmacopœial strength in the material examined. Thus the U. S. Pharmacopœia requires dilute ammonia solution (both *Aqua Ammoniæ* and *Spiritus Ammoniæ*) to contain 10 per cent. of the gas (NH_3). The solution supposed to have been operated on contained 8.5 per cent. NH_3 ($10 : 8.5 : : 100 : x = 85$). Therefore it contains 85 per cent. of the dilute ammonia of the U. S. Pharmacopœia.*

Strong Solution of Ammonia, U. S. P., contains 28 per cent. of ammonia gas (NH_3).

Note.—The calculations just described for ammonia are similar to those employed throughout volumetric analysis; they will not be repeated, therefore, in the case of every substance.

Carbonate of Ammonium.—The reactions indicated by the following equations occur between commercial carbonate of ammonium and oxalic acid:—

$$2N_3H_{11}C_2O_5 \;\; + \;\; 3H_2C_2O_4,2H_2O \;\; = \;\; 3(NH_4)_2C_2O_4 \;\; + \;\; 8H_2O \;\; + \;\; 4CO_2$$

6)314   6)378
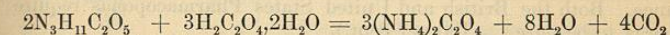
52.33   63 = grammes in 1000 c.c. of standard solution.

About 1 gramme is a convenient quantity to operate upon. Tincture of litmus is the indicator, and the titration is conducted at a temperature just short of boiling. The estimation is not very satisfactory, because the heat employed, while scarcely sufficient to expel the carbonic acid gas, is enough to occasion loss of ammoniacal salt. Practised analysts usually add excess of the standard acid, and thus

* Extremely minute quantities of ammonia—1 part in many millions of water—may be estimated volumetrically by adding excess of a colorless, strongly alkaline solution of red iodide of mercury (Nessler's test), then in a similar vessel, containing an equal amount of pure water with excess of the Nessler reagent, imitating the depth of yellow or reddish-yellow color thus produced by adding an ammoniacal solution *of known strength*. The amount of ammonia thus added represents the amount in the original liquid.

The Nessler Reagent.—A litre may be made by dissolving 30 or 40 grammes of iodide of potassium in a small quantity of hot water, adding a strong hot solution of perchloride of mercury until the precipitate of mercuric iodide ceases to redissolve even by the aid of rapid stirring and heat, slightly diluting, filtering, adding a strong solution of (120 to 140 grammes) caustic soda or (160 to 180 grammes) caustic potash, and diluting to 1 litre. A few c.c. (5 or 6 more) of a strong solution of perchloride of mercury are finally stirred in, the whole set aside till all precipitated red iodide has deposited, and the clear liquid decanted for use. The reaction of this Nessler test with ammonia is as follows:—
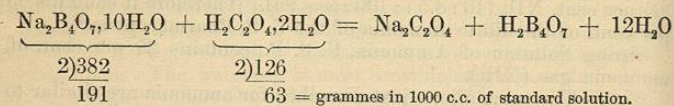
$$NH_3 + 2HgI_2 + 3KHO = NHg_2I + 3KI + 3H_2O.$$
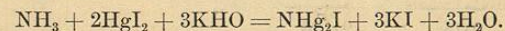
Potassio-mercuric Iodide, without alkali, is commonly known as *Mayer's Reagent*, $HgI_2 2KI$.
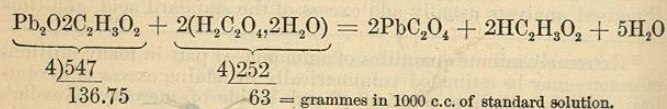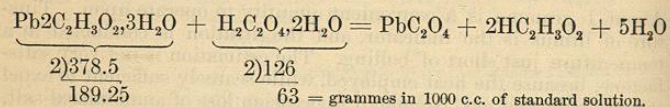
fix every trace of ammonia; then gently boil to get rid of carbonic acid gas; bring back the liquid to neutrality by an observed volume of standard alkaline solution, and deduct an equivalent volume of acid from the quantity first added. The United States Pharmacopœia requires 5.232 grammes to neutralize 100 c.c. of standard solution of oxalic acid. This corresponds to 100 per cent. of carbonate having the formula $N_3H_{11}C_2O_5$.

Borax.—Two or three grammes is a convenient quantity.

$$Na_2B_4O_7,10H_2O + H_2C_2O_4,2H_2O = Na_2C_2O_4 + H_2B_4O_7 + 12H_2O$$

$$\underline{2)382} \qquad \underline{2)126}$$
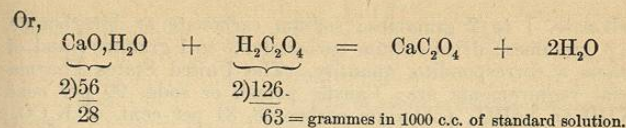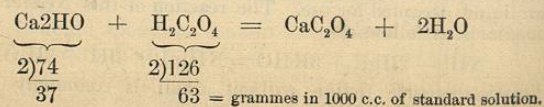$$191 \qquad 63 = \text{grammes in 1000 c.c. of standard solution.}$$

Tincture of litmus is the indicator, and the titration may be carried on without heat. The liberation of boracic acid colors the litmus wine-red. This is not regarded, the titration being continued until the bright red due to the action of free oxalic acid makes its appearance. Both the British and United States Pharmacopœias require borax to be pure (= 100 per cent.).

Lead Acetate and Solution of Subacetate.—Operate upon about three grammes of acetate of lead and from five to ten grammes of solution of subacetate.
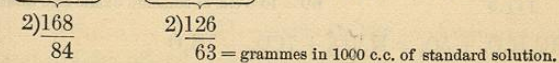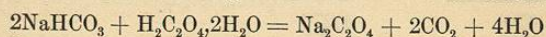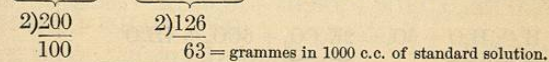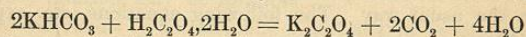
$$Pb2C_2H_3O_2,3H_2O + H_2C_2O_4,2H_2O = PbC_2O_4 + 2HC_2H_3O_2 + 5H_2O$$

$$\underline{2)378.5} \qquad \underline{2)126}$$
$$189.25 \qquad 63 = \text{grammes in 1000 c.c. of standard solution.}$$

$$Pb_2O2C_2H_3O_2 + 2(H_2C_2O_4,2H_2O) = 2PbC_2O_4 + 2HC_2H_3O_2 + 5H_2O$$

$$\underline{4)547} \qquad \underline{4)252}$$
$$136.75 \qquad 63 = \text{grammes in 1000 c.c. of standard solution.}$$

The flask in which the estimation is being conducted should contain one third of a flaskful of water. In the case of both acetate and solution of subacetate of lead a little acetic acid should be added to prevent precipitation of basic salt on dilution. The only indicator of complete reaction is cessation of production of the precipitate—oxalate of lead. The United States Pharmacopœia requires acetate of lead to be pure (100 per cent.), and solution of subacetate to contain 25 per cent.

Lime-Water and Saccharated Solution of Lime.—Measure about half a litre of lime-water for the estimation, and of saccharated solution weigh about 25 grammes. The following equations, etc. are quantitative expressions of the reactions :—

$$Ca2HO + H_2C_2O_4 = CaC_2O_4 + 2H_2O$$

$$\underline{2)74} \qquad \underline{2)126}$$
$$37 \qquad 63 = \text{grammes in 1000 c.c. of standard solution.}$$

Or,

$$CaO,H_2O + H_2C_2O_4 = CaC_2O_4 + 2H_2O$$

$$\underline{2)56} \qquad \underline{2)126}.$$
$$28 \qquad 63 = \text{grammes in 1000 c.c. of standard solution.}$$

Litmus is used as an indicator.

Caustic Potash and Soda, Potassium and Sodium Carbonates and Bicarbonates.—Litmus is the indicator throughout, and heat is used in all cases, for the caustic alkalies always contain some carbonate.

$$2KHO + H_2C_2O_4,2H_2O = K_2C_2O_4 + 4H_2O$$

$$\underline{2)112} \qquad \underline{2)126}$$
$$56 \qquad 63 = \text{grammes in 1000 c.c. of standard solution.}$$

$$2NaHO + H_2C_2O_4,2H_2O = Na_2C_2O_4 + 4H_2O$$

$$\underline{2)80} \qquad \underline{2)126}$$
$$40 \qquad 63 = \text{grammes in 1000 c.c. of standard solution.}$$

$$K_2CO_3 + H_2C_2O_4,2H_2O = K_2C_2O_4 + CO_2 + 3H_2O$$

$$\underline{2)138} \qquad \underline{2)126}$$
$$69 \qquad 63 = \text{grammes in 1000 c.c. of standard solution.}$$

Or,

$$K_2CO_3 + 16\%H_2O + H_2C_2O_4,2H_2O = K_2C_2O_4 + CO_2 + xH_2O$$

$$\underline{2)164.28} \qquad \underline{2)126}$$
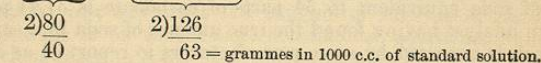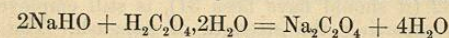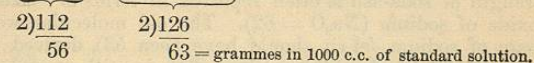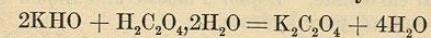$$82.14 \qquad 63 = \text{grammes in 1000 c.c. of standard solution.}$$

$$Na_2CO_3 + H_2C_2O_4,2H_2O = Na_2C_2O_4 + CO_2 + 3H_2O$$

$$\underline{2)106} \qquad \underline{2)126}$$
$$53 \qquad 63 = \text{grammes in 1000 c.c. of standard solution.}$$

Or,

$$Na_2CO_3,10H_2O + H_2C_2O_4,2H_2O = Na_2C_2O_4 + CO_2 + 13H_2O$$

$$\underline{2)286} \qquad \underline{2)126}$$
$$143 \qquad 63 = \text{grammes in 1000 c.c. of standard solution.}$$

$$2KHCO_3 + H_2C_2O_4,2H_2O = K_2C_2O_4 + 2CO_2 + 4H_2O$$

$$\underline{2)200} \qquad \underline{2)126}$$
$$100 \qquad 63 = \text{grammes in 1000 c.c. of standard solution.}$$

$$2NaHCO_3 + H_2C_2O_4,2H_2O = Na_2C_2O_4 + 2CO_2 + 4H_2O$$

$$\underline{2)168} \qquad \underline{2)126}$$
$$84 \qquad 63 = \text{grammes in 1000 c.c. of standard solution.}$$

Convenient quantities to operate with are: Of caustic potash, 1 gramme; caustic soda, .5 to 1 gramme; potassium carbonate or

bicarbonate, 1 to 2 grammes; sodium carbonate or bicarbonate, 2 to 3 grammes; dried sodium carbonate, .5 to 1 gramme; and of solutions a corresponding quantity. The United States Pharmacopœial requirements are: Caustic potash or soda, 90 per cent. of KHO or NaHO; potassium carbonate, 81 per cent. of K_2CO_3; sodium carbonate, 98 per cent. of $Na_2CO_3,10H_2O$; potassium bicarbonate, 100 per cent. of $KHCO_3$; sodium bicarbonate, 99 per cent. of $NaHCO_3$; and commercial bicarbonate, at least 95 per cent. The dried carbonate (*Sodii Carbonas Exsiccatus*, U. S. P.) is to contain 72.6 per cent. of real carbonate. *Liquor Potassæ* and *Liquor Sodæ* must contain 5 per cent. of pure hydrate.

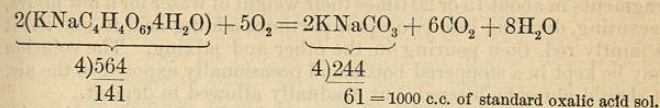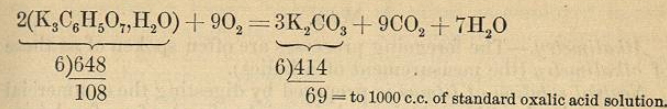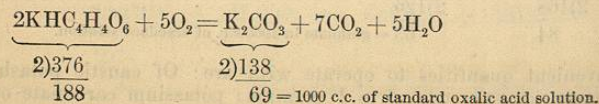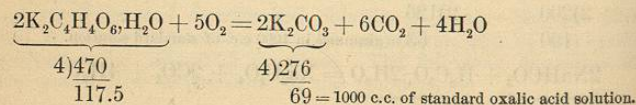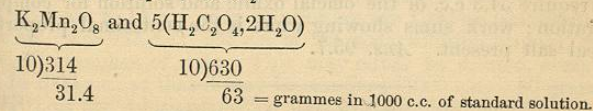The strength of soda-ash is often reported in terms of "soda"—that is, oxide of sodium ($Na_2O = 62$). The old molecular weight of carbonate of sodium, 54 (it should have been 53), derived from that of "soda," 32 (it should have been 31), is still employed in Great Britain in reporting the strength of soda-ash. The true amount of soda equivalent to 54 parts of carbonate is 31.41 parts. A modern analyst having found the true amount of soda in a sample of soda-ash is expected by some manufacturers to report 31 as 31.41 parts, or 53 of carbonate as 54, and other quantities in proportion to these figures.

Tartrates and Citrates of Potassium and Sodium and Acetate of Potassium.—When tartrates or citrates of alkali-metals are burned in the open air the whole of the metal remains in the form of carbonate. Each molecular weight of a neutral tartrate gives one molecular weight of carbonate, and every two molecular weights of an acid tartrate give one molecular weight of carbonate. Advantage is taken of these reactions to estimate indirectly the quantity of citrate or tartrate in presence of substances with which they are generally associated. One to two grammes of any of these salts is a convenient quantity to operate upon. The ignition may be conducted in a platinum or porcelain crucible. A low red heat only should be used, and the vessel removed when complete carbonization has been effected—that is to say, when nothing remains but the carbonate and free carbon. The mixture is in this case treated with hot water, and the carbon separated by filtration. If too little heat has been used and carbonization is not complete, the filtrate will be more or less colored. If this should be the case the operation must be repeated with a fresh quantity of material. The carbonate is titrated in the usual way. The following equations, etc. explain the reactions:—

$$2K_2C_4H_4O_6,H_2O + 5O_2 = 2K_2CO_3 + 6CO_2 + 4H_2O$$

$$\underbrace{4)470}_{117.5} \qquad \underbrace{4)276}_{69} = 1000 \text{ c.c. of standard oxalic acid solution.}$$

$$2KHC_4H_4O_6 + 5O_2 = K_2CO_3 + 7CO_2 + 5H_2O$$

$$\underbrace{2)376}_{188} \qquad \underbrace{2)138}_{69} = 1000 \text{ c.c. of standard oxalic acid solution.}$$

$$2(K_3C_6H_5O_7,H_2O) + 9O_2 = 3K_2CO_3 + 9CO_2 + 7H_2O$$

$$\underbrace{6)648}_{108} \qquad \underbrace{6)414}_{69} = \text{to 1000 c.c. of standard oxalic acid solution.}$$

$$2(KNaC_4H_4O_6,4H_2O) + 5O_2 = 2KNaCO_3 + 6CO_2 + 8H_2O$$

$$\underbrace{4)564}_{141} \qquad \underbrace{4)244}_{61} = 1000 \text{ c.c. of standard oxalic acid sol.}$$

$$2KC_2H_3O_2 + 4O_2 = K_2CO_3 + 3CO_2 + 3H_2O$$

$$\underbrace{2)196}_{98} \qquad \underbrace{2)133}_{69} = 1000 \text{ c.c. of standard oxalic acid solution.}$$

It will be readily understood that in the first (for example) of the reactions just expressed 113 weights of tartrate of potassium are equivalent to 69 weights of carbonate of potassium; and as in a previous reaction it has been shown that 69 weights of carbonate of potassium are equivalent to 63 weights of oxalic acid, it follows that 113 weights of tartrate of potassium are equivalent to 63 weights of oxalic acid. Let these weights be grammes, and then 113 grammes of tartrate of potassium are equivalent to 63 grammes of oxalic acid, or to 1000 c.c. of the standard solution of oxalic acid. If the substance estimated be a crude sample of tartrate of potassium, and the number of c.c. of oxalic acid used has been 15 c.c., then as 1000 c.c. of the acid solution are to 113 grammes of tartrate of potassium, so are 15 c.c. of the solution to 1.695 grammes of tartrate of potassium. Now, if the weight of the sample taken was 2 grammes, then as 2 grammes of the sample contain 1.695 of real tartrate of potassium, 100 will contain $x = 84.75$ per cent. of real tartrate. These salts are required to be 100 per cent. pure by the United States Pharmacopœia, except acetate of potassium, which is to have 98 per cent. of real acetate. Trade samples are practically pure as a rule. If sulphate of calcium be present in tartrates or citrates, loss of carbonate of potassium will ensue, sulphate of potassium being formed. In estimating acid tartrate of potassium, which is the salt most likely to contain sulphate of calcium, direct titration without ignition may be followed.

Permanganate of Potassium.—The reaction is shown in the following equation: $K_2Mn_2O_8 + 3H_2SO_4 + 5(H_2C_2O_4,2H_2O) = K_2SO_4 + 2MnSO_4 + 18H_2O + 10CO_2.$

$$\underbrace{K_2Mn_2O_8}_{} \text{ and } \underbrace{5(H_2C_2O_4,2H_2O)}_{}$$

$$\underbrace{10)314}_{31.4} \qquad \underbrace{10)630}_{63} = \text{grammes in 1000 c.c. of standard solution.}$$

The salt satisfies official requirements if it contains 98.8 per cent. of real permanganate of potassium.

Notes.

Alkalimetry.—The foregoing processes are often spoken of as those of *alkalimetry* (the measurement of alkalies).

Neutral solution of litmus is prepared by digesting the commercial fragments in about 15 or 20 times their weight of water for a few hours, decanting, dividing into two equal portions, adding acid to one till it is faintly red, then pouring in the other and mixing. The solution may be kept in a stoppered bottle and occasionally exposed to the air. It should never be filtered, but gradually allowed to deposit.

Standard sulphuric acid may be used in the place of oxalic acid, 1000 c.c. of the liquid containing half of the molecular weight of the pure acid in grammes. It is prepared by diluting oil of vitriol with from 3 to 4 times its bulk of distilled water, ascertaining how much of the acid liquid is required to exactly neutralize $\frac{1}{20}$ of the molecular weight of pure carbonate of sodium, taken in grammes (5.3), and adding water until the observed volume of acid is increased to 100 c.c., the whole of the fluid being similarly diluted.

Weighing.—In the case of substances which are liable to alter by exposure to air it is important that a selected quantity should be quickly weighed, rather than selected weights be accurately balanced by material, the former operation occupying much the shorter time.

Salts other than the official may be quantitatively analyzed by the volumetric solutions of the Pharmacopœia, slight modifications of manipulation even enabling the processes to be adapted to fresh classes of salts. Ample instructions for extending operations in this manner will be found in Sutton's *Handbook of Volumetric Analysis.*

QUESTIONS AND EXERCISES.

1007. Describe the various pieces of apparatus used in volumetric determinations.

1008. One hundred cubic centimetres of solution of oxalic acid contain 6.3 grammes of the crystallized acid; work sums showing what weights of bicarbonate of potassium and anhydrous carbonate of sodium that volume will saturate. *Ans.* 10 grammes and 5.3 grammes.

1009. Show what weight of hydrate of potassium is contained in solution of potash, 48.02 grammes of which are saturated by 50 c.c. of the standard solution of oxalic acid. *Ans.* 5.83 per cent.

1010. Calculate the percentage of hydrate of calcium in lime-water, 438 grammes of which are neutralized by 20 c.c. of the volumetric solution of oxalic acid. *Ans.* 0.1689.

1011. Eight grammes of a sample of Rochelle salt, after ignition, etc., require 54.3 c.c. of the official oxalic acid solution for complete saturation; work sums showing what is the centesimal proportion of real salt present. *Ans.* 95.7.
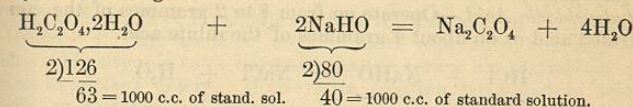
ESTIMATION OF ACIDS.

In the previous experiments a known amount of an acid has been used in determining unknown amounts of alkalies. In those about

to be described a known amount of an alkali is employed in estimating unknown amounts of acids. The alkaline salt selected may be either a hydrate or a carbonate; but the former is to be preferred, for the carbonic acid set free when a strong acid is added to a carbonate interferes to some extent with the indications of alkalinity, acidity, or neutrality afforded by litmus. The alkali most convenient for use is soda, a solution of which has probably already been made the subject of experiment in operations with the standard solution of oxalic acid. It should be kept in a stoppered bottle and exposed to air as little as possible.

VOLUMETRIC SOLUTION OF SODA.

(Hydrate of Sodium, NaHO = 40.)

This aqueous solution of soda is most conveniently made of such a strength that each 1000 c.c. contains one molecular weight in grammes of the alkali (NaHO = 40). It will be seen from the following equation that 40 grammes of soda convert 63 grammes of oxalic acid into neutral oxalate of sodium. Therefore, 1 litre of this solution, containing 40 grammes of soda, will form a neutral solution of oxalate with 1 litre of standard oxalic acid solution, or with a chemically equivalent quantity of oxalic acid solution of any other strength.

$$H_2C_2O_4, 2H_2O \quad + \quad 2NaHO \quad = \quad Na_2C_2O_4 \quad + \quad 4H_2O$$

$$\underbrace{2)126}_{63 = 1000 \text{ c.c. of stand. sol.}} \qquad \underbrace{2)80}_{40 = 1000 \text{ c.c. of standard solution.}}$$

If pure soda were at hand, it would only be necessary to weigh 40 grammes, dissolve this in water, and dilute to 1 litre. But pure soda cannot readily be produced. Therefore weigh about 45 grammes of hydrate of sodium of trade, and add water to 1 litre. When dissolved take, say, 14 c.c., dilute with more water in a flask, add a few drops of tincture of litmus, and titrate with oxalic acid solution of known strength. Suppose that the volume of standard acid solution required to neutralize the 14 c.c. of soda solution the strength of which is to be estimated has been 15 c.c., or an equivalent amount of acid solution of another strength; then, how many c.c. of soda solution is equivalent to 1000 c.c. of standard acid solution? or, what comes to the same thing, how many c.c. of soda solution contain 40 grammes of real soda (NaHO)? As 15 c.c. standard acid are to 14 c.c. soda, so are 1000 c.c. standard acid to x c.c. $x = 933$ c.c. 933 c.c. of the soda solution contain, therefore, 40 grammes of soda. This may either be diluted, every 933 c.c. to 1000 c.c., so that it may be standard (1000 c.c. = 40 grammes NaHO), or the solution may be used without dilution (933 c.c. = 40 grammes NaHO). It has already been mentioned that soda nearly always contains carbonate. To remove resulting carbonic acid, therefore, gentle heat should be employed toward the close of each
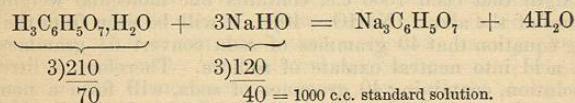
titration in all the estimations with this solution. Litmus is used throughout as an indicator of completion of the reaction. The following substances are officially estimated with this solution. The list admits of considerable extension (see Sutton's *Volumetric Analysis*).

Acetic Acid.—Operate upon about 1 gramme of glacial acid, about 20 grammes of dilute acid, or about 3 grammes of ordinary acetic acid.

$$\underbrace{HC_2H_3O_2}_{60} + \underbrace{NaHO}_{40} = NaC_2H_3O_2 + H_2O$$
40 = 1000 c.c. standard solution.
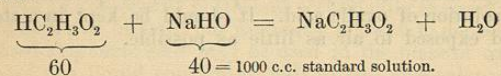
Acetic Acid, U. S. P., should contain 36 per cent of real acid ($HC_2H_3O_2$); Dilute Acetic Acid, U. S. P., 6 per cent; Glacial Acetic Acid, U. S. P., 99 per cent.

*Citric Acid.*—Operate on about 1 gramme. The reaction is expressed by the following equation, etc. :—

$$\underbrace{H_3C_6H_5O_7,H_2O}_{3)210} + \underbrace{3NaHO}_{3)120} = Na_3C_6H_5O_7 + 4H_2O$$
$$\quad\quad 70 \quad\quad\quad\quad 40 = 1000 \text{ c.c. standard solution.}$$

Citric Acid, U. S. P., should be pure (= 100 per cent. $H_3C_6H_5O_7,H_2O$).

Hydrochloric Acid.—Operate on from 1 to 2 grammes of the concentrated acid or on about 4 grammes of the dilute acid.

$$\underbrace{HCl}_{36.4} + \underbrace{NaHO}_{40} = NaCl + H_2O$$
40 = 1000 c.c. standard solution.
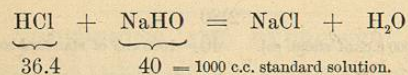
Hydrochloric Acid, U. S. P., should contain 31.9 per cent. of real acid (HCl), and Dilute Hydrochloric, U. S. P., 10 per cent.

Dilute Hydrobromic Acid.—Operate on from 8 to 12 c.c.

$$\underbrace{HBr}_{80.8} + \underbrace{NaHO}_{40} = NaBr + H_2O$$
40 = 1000 c.c. standard solution.
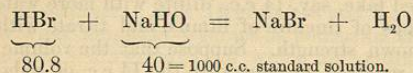
Dilute Hydrobromic Acid, U. S. P., should contain 10 per cent. of real acid (HBr).

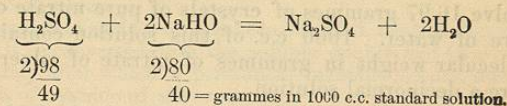*Lactic Acid.*—Operate on 1.5 to 2 grammes. The reaction is expressed by the following equation :—

$$\underbrace{HC_3H_5O_3}_{90} + \underbrace{NaHO}_{40} = NaC_3H_5O_3 + H_2O$$
40 = 1000 c.c. of standard solution.
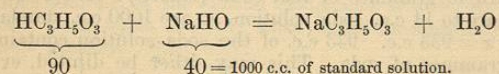
Lactic Acid, U. S. P., should represent 75 per cent. of absolute lactic acid ($HC_3H_5O_3$).

Nitric Acid.—Operate on from 1 to 2 grammes of concentrated or on from 4 to 5 grammes of dilute acid.

$$\underbrace{HNO_3}_{63} + \underbrace{NaHO}_{40} = NaNO_3 + H_2O$$
40 = grammes in 1000 c.c. standard solution.
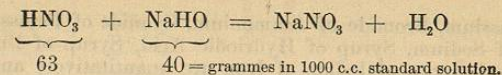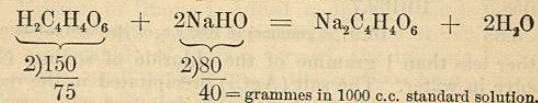
Nitric Acid, U. S. P., should contain 69.4 per cent., and Dilute Nitric Acid, U. S. P., 10 per cent., of real acid (HNO_3).

Sulphuric Acid.—Operate upon from .5 to 1 gramme of concentrated acid or from 4 to 5 grammes of either Dilute or Aromatic Sulphuric Acid.

$$\underbrace{H_2SO_4}_{\genfrac{}{}{0pt}{}{2)98}{49}} + \underbrace{2NaHO}_{\genfrac{}{}{0pt}{}{2)80}{40}} = Na_2SO_4 + 2H_2O$$
40 = grammes in 1000 c.c. standard solution.

Sulphuric Acid, U. S. P., should contain not less than 96 per cent., Dilute, U. S. P., 10 per cent. of real acid, and Aromatic, U. S. P., 18 per cent., of sulphuric acid (H_2SO_4), partly as ethyl-sulphuric acid.

Tartaric Acid.—Operate upon about 1 gramme of the acid. The following equation, etc. represents the reaction :—

$$\underbrace{H_2C_4H_4O_6}_{\genfrac{}{}{0pt}{}{2)150}{75}} + \underbrace{2NaHO}_{\genfrac{}{}{0pt}{}{2)80}{40}} = Na_2C_4H_4O_6 + 2H_2O$$
40 = grammes in 1000 c.c. standard solution.

Tartaric Acid, U. S. P., should contain 100 per cent. of $H_2C_4H_4O_6$.

Notes.—1. Pure acetates, citrates, more especially, tartrates, and some other organic salts have an alkaline action on litmus, but not to an important extent. If the soda solution be added to acetic, citric, or tartaric acid containing litmus until the liquid is fairly blue, the operator will obtain trustworthy results. In delicate experiments turmeric, "methyl-orange," "phenolphthalein," etc. may be used instead of litmus.

2. The operations for the quantitative analysis or measurement of acids are often collectively spoken of under the name of *acidimetry*.

QUESTIONS AND EXERCISES.

1012. Calculate the percentage of real acid present in diluted sulphuric acid, 30 grammes of which are neutralized by 84 c.c. of the official volumetric solution of soda. *Ans.* 13.72.

1013. Show how much real nitric acid is contained in a solution 36 grammes of which are saturated by 94 c.c. of the standard solution of soda. *Ans.* 16.45 per cent.

ESTIMATION OF ACIDULOUS RADICALS PRECIPITATED BY NITRATE OF SILVER.

The purity of many salts and the strength of their solutions may be determined by this process. Diluted Hydrocyanic Acid, Bromide