

The majority of non-aqueous titrations are carried out using a fairly limited range of indicators. Typical of those employed are the following.

- (a) *Crystal violet* is used as a 0.5 per cent w/v solution in glacial acetic acid. Its colour change is from violet through blue, followed by green, then to greenish-yellow, in reactions in which, for instance, bases such as pyridine are titrated with perchloric acid.
- (b) *Methyl red* is used as a 0.2 per cent w/v solution in dioxan with a yellow to red colour change.
- (c) *1-Naphthol benzein* gives a yellow to green colour change when employed as a 0.2 per cent w/v solution in acetic acid. It gives sharp end points in nitromethane containing acetic anhydride for titrations of weak bases against perchloric acid.
- (d) *Oracet blue B* is used as a 0.5 per cent w/v solution in acetic acid and is considered to be superior to crystal violet for titrations of bases in acetic acid with standard perchloric acid. The end point is a distinct change from blue to pink.
- (e) *Quinaldine red* has been used as an indicator for drug determinations in dimethylformamide solution. It is used as a 0.1 per cent w/v solution in ethanol and gives a colour change from purple/red to pale green.
- (f) *Thymol blue* is used extensively as an indicator for titrations of substances acting as acids in dimethylformamide solution. It is used as a 0.2 per cent w/v solution in methanol with a sharp colour change from yellow to blue at the end point.

10.22 PREPARATION OF A STANDARD ACID

Hydrochloric acid and sulphuric acid are widely employed in the preparation of standard solutions of acids. Both of these are commercially available as concentrated solutions; concentrated hydrochloric acid is about 10.5–12 *M*, and concentrated sulphuric acid is about 18 *M*. By suitable dilution, solutions of any desired *approximate* concentration may be readily prepared. Hydrochloric acid is generally preferred, since most chlorides are soluble in water. Sulphuric acid forms insoluble salts with calcium and barium hydroxides; for titration of hot liquids or for determinations which require boiling for some time with excess of acid, standard sulphuric acid is, however, preferable. Nitric acid is rarely employed, because it almost invariably contains a little nitrous acid, which has a destructive action upon many indicators.

For the preparation of standard solutions of hydrochloric acid, two methods are available. The first utilises the experimental fact that aqueous solutions of hydrochloric acid lose either hydrogen chloride or water upon boiling, according to whether they are more or less concentrated than the constant boiling point mixture, until they attain a practically constant composition (constant boiling point mixture), which depends upon the prevailing pressure. The composition of this constant boiling mixture, listed in Table 10.5, and its dependence upon pressure have been determined with great accuracy by Foulk and Hollingsworth.⁷

The constant boiling point acid is neither hygroscopic nor appreciably volatile, and its concentration remains unchanged if kept in a well-stoppered vessel out of direct sunlight. This acid may be employed directly in the preparation of a solution of hydrochloric acid of known concentration.

Table 10.5 Composition of constant boiling point hydrochloric acid

Pressure (Pa)	Percentage of HCl in acid (vac. wt.)	Weight of acid, weighed in air, containing 36.47 g of HCl (g)
103 991	20.173	180.621
102 658	20.197	180.407
101 325	20.221	180.193
99 992	20.245	179.979
98 659	20.269	179.766
97 325	20.293	179.555

In the second method a solution of the approximate strength required is prepared, and this is standardised against some standard alkaline substance, such as sodium tetraborate or anhydrous sodium carbonate; standard potassium iodate or pure silver may also be used (see Section 10.84). If a solution of an exact strength is required, a solution of an approximate strength somewhat greater than that desired is first prepared; this is suitably diluted with water after standardisation (for a typical calculation, see Appendix 17).

10.23 PREPARATION OF CONSTANT BOILING POINT HYDROCHLORIC ACID

Mix 400 mL of pure concentrated hydrochloric acid with 250–400 mL of distilled water so that the specific gravity of the resultant acid is 1.10 (test with a hydrometer). Insert a thermometer in the neck of a 1 L Pyrex distillation flask so that the bulb is just opposite the side tube, and attach a condenser to the side tube; use an all-glass apparatus. Place 500 mL of the diluted acid in the flask, distil the liquid at a rate of about $3\text{--}4\text{ mL min}^{-1}$ and collect the distillate in a small Pyrex flask. From time to time pour the distillate into a 500 mL measuring cylinder. When 375 mL has been collected in the measuring cylinder, collect a further 50 mL in the small Pyrex flask; watch the thermometer to see that the temperature remains constant. Remove the receiver and stopper it; this contains the pure constant boiling point acid. Note the barometric pressure to the nearest millimetre at intervals during the distillation and take the mean value. Interpolate the concentration of the acid from Table 10.5.

10.24 DIRECT PREPARATION OF 0.1 M HYDROCHLORIC ACID FROM THE CONSTANT BOILING POINT ACID

Clean and dry a small, stoppered conical flask. After weighing, do not handle the flask directly with the fingers; handle it with the aid of a tissue or a linen cloth. Add the calculated quantity of constant boiling point acid required for the preparation of 1 L of 0.1 M acid (see Table 10.5) with the aid of a pipette; make the final adjustment with a dropper pipette. Reweigh the flask to 0.001 g after replacing the stopper. Add an equal volume of water to prevent loss of acid, and transfer the contents to a 1 L graduated flask. Wash out the weighing flask several times with distilled water and add the washings to the original solution. Make up to the mark with distilled water. Insert the stopper and mix the solution thoroughly by shaking and inverting the flask repeatedly.

Note. Unless a solution of exact concentration is required, it is not necessary to weigh out the exact quantity of constant-boiling acid; the concentration may be calculated from the weight of acid. Thus if 18.305 g of acid, prepared at 101 325 Pa was diluted to 1 L, its concentration would be $18.305/180.193 = 0.101\ 58\ \text{mol L}^{-1}$.

10.25 PREPARATION OF APPROXIMATELY 0.1 M HYDROCHLORIC ACID AND STANDARDISATION

Measure out 9 mL of pure concentrated hydrochloric acid by means of a burette, pour the acid into a 1 L measuring cylinder containing about 500 mL of distilled water. Make up to the litre mark with distilled water and thoroughly mix by shaking. This will give a solution that is approximately 0.1 M.

Note. If 1 M hydrochloric acid is required, use 90 mL of the concentrated acid. If 0.01 M acid is required, dilute two 50 mL portions of the approximately 0.1 M acid, removed with a 50 mL pipette, to 1 litre in a graduated flask.

Approximately 0.05 M sulphuric acid is similarly prepared from 3 mL of pure concentrated sulphuric acid.

Two excellent methods (utilising acid–base indicators) are available for standardisation. The first is widely employed, but the second is more convenient, less time-consuming, and equally accurate. A third, back-titration, procedure is also available.

A. Standardisation with anhydrous sodium carbonate. *Pure sodium carbonate.* Analytical reagent quality sodium carbonate of 99.9 per cent purity is obtainable commercially. This contains a little moisture and must be dehydrated by heating at 260–270 °C for half an hour and allowed to cool in a desiccator before use. Alternatively, pure sodium carbonate may be prepared by heating sodium hydrogencarbonate to 260–270 °C for 60–90 minutes; the temperature must not be allowed to exceed 270 °C, for above this temperature the sodium carbonate may lose carbon dioxide. It has been recommended² that the sodium hydrogencarbonate be decomposed by adding to hot (85 °C) water, and then the hydrated sodium carbonate which crystallises out is filtered off and dehydrated by heating, first at 100 °C, and finally at 260–270 °C.

In all cases the crucible is allowed to cool in a desiccator, and, before it is quite cold, the solid is transferred to a warm, dry glass-stoppered tube or bottle, out of which, when cold, it may be weighed rapidly as required. It is important to remember that anhydrous sodium carbonate is hygroscopic and has a tendency to change into the monohydrate.

Procedure. Weigh out accurately from a weighing bottle about 0.2 g of the pure sodium carbonate into a 250 mL conical flask (Note 1), dissolve it in 50–75 mL of water, and add 2 drops of methyl orange indicator (Note 2) or preferably of methyl orange–indigo carmine indicator (Section 10.9), which gives a very much more satisfactory end point (Note 3). Rinse a clean burette three times with 5 mL portions of the acid: fill the burette to a point 2–3 cm above the zero mark and open the stopcock momentarily, in order to fill the jet with liquid. Examine the jet to see that no air bubbles are enclosed. If there are, more liquid must be run out until the jet is completely filled. Re-fill, if necessary, to bring the level above the zero mark; then slowly run out the liquid until the level is between the 0.0 and 0.5 mL marks. Read the position of the meniscus to 0.01 mL (Section 3.12).

Place the conical flask containing the sodium carbonate solution upon a piece of unglazed white paper or a white tile beneath the burette, and run in the acid slowly from the burette. During the addition of the acid, the flask must be constantly rotated with one hand while the other hand controls the stopcock. Continue the addition until the methyl orange becomes a very faint yellow or the green colour commences to become paler, when the methyl orange–indigo carmine indicator is used. Wash the walls of the flask down with a little distilled water from a wash bottle, and continue the titration very carefully by adding the acid dropwise until the colour of the methyl orange becomes orange or a faint pink, or the colour of the mixed indicator is a neutral grey. This marks the end point of the titration, and the burette-reading should be taken and recorded in a note-book. The procedure is repeated with two or three other portions of sodium carbonate. The first (or preliminary) titration will indicate the location of the true end point within 0.5 mL. With experience and care, subsequent titrations can be carried out very accurately, and should yield concordant results. From the weights of sodium carbonate and the volumes of hydrochloric acid employed, the strength of the acid may be computed for each titration. The arithmetical mean is used to calculate the strength of the solution.

Notes. (1) For *elementary students*, an approximately 0.05 M solution of sodium carbonate may be prepared by weighing out accurately about 1.3 g of pure sodium carbonate in a weighing bottle or in a small beaker, transferring it to a 250 mL graduated flask, dissolving it in water (Section 3.28), and making up to the mark. The flask is well shaken, then 25.00 mL portions are withdrawn with a pipette and titrated with the acid as described above. Individual titrations should not differ by more than 0.1 mL. Record the results as in Section 10.30.

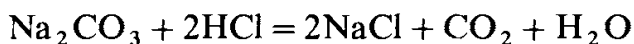
(2) To obtain the most accurate results, a comparison solution, saturated with carbon dioxide and containing the same concentration of sodium chloride (the colour of methyl orange in a saturated aqueous solution of carbon dioxide is sensitive to the concentration of sodium chloride) and indicator as the titrated solution at the end point, should be used.

(3) This indicator is prepared by dissolving 1 g of methyl orange and 2.5 g of *purified* indigo carmine in 1 L of distilled water, and filtering the solution. The colour change on passing from alkaline to acid solution is from green to magenta with a neutral-grey colour at a pH of about 4.

The mixed indicator, bromocresol green–dimethyl yellow, may be used with advantage. The indicator consists of 4 parts of a 0.2 per cent ethanolic solution of bromocresol green and 1 part of a 0.2 per cent ethanolic solution of dimethyl yellow: about 8 drops are used for 100 mL of solution. The colour change is from blue to greenish yellow at $\text{pH} = 4.0 - 4.1$; the colour is yellow at $\text{pH} = 3.9$.

Methyl red may be used as an indicator provided the carbon dioxide in solution is expelled at the end point by boiling. This indicator gives a red colour with high concentrations of carbon dioxide such as are produced during titrations involving carbonates. Add the standard hydrochloric acid to the cold sodium carbonate solution containing 3 drops of 0.1 per cent methyl red until the indicator changes colour. Boil the solution gently (preferably with a small funnel in the mouth of the flask) for 2 minutes to expel carbon dioxide: the original colour of the indicator will return. Repeat the process until the colour no longer changes on boiling. Generally, boiling and cooling must be repeated twice. Care must be taken to avoid loss of liquid by spattering during boiling. The colour change is more easily perceived than with methyl orange.

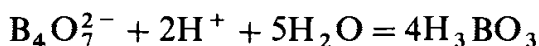
Calculation of molarity. The molarity may be calculated by using the equation:



but the best method is to derive the value entirely in terms of the primary standard substance — here, sodium carbonate. The relative molecular mass of sodium carbonate is 106.00. If the weight of the sodium carbonate is divided by the number of millilitres of hydrochloric acid to which it corresponds, as found by titration, we have the weight of primary standard equivalent to 1 mL of the acid. Thus if 0.2500 g of sodium carbonate is required for the neutralisation of 45.00 mL of hydrochloric acid, 1 mL of the acid will correspond to $0.2500/45.00 = 0.005556$ g of sodium carbonate. The weight in 1 mL of 0.5M sodium carbonate solution is 0.053 00 g. Hence the concentration of the acid is $0.005556/0.05300 = 0.1048M$.

Another method is the following: 0.2500 g of sodium carbonate required 45.00 mL of acid, hence 1 L of acid corresponds to $1000 \times 0.2500/45.00 = 5.556$ g of sodium carbonate. But 1 L of 1M acid corresponds to 53.00 g of sodium carbonate, hence the acid is $5.556/53.00 = 0.1048M$.

B. Standardisation against sodium tetraborate. The advantages of sodium tetraborate decahydrate (borax) are: (i) it has a large relative molecular mass, 381.44 (that of anhydrous sodium carbonate is 106.00); (ii) it is easily and economically purified by recrystallisation; (iii) heating to constant weight is not required; (iv) it is practically non-hygroscopic; and (v) a sharp end point can be obtained with methyl red at room temperatures, since this indicator is not affected by the very weak boric acid.



Pure sodium tetraborate. The salt is recrystallised from distilled water; 50 mL of water is used for every 15 g of solid. Care must be taken that the crystallisation does not take place above 55 °C; above this temperature there is a possibility of the formation of the pentahydrate, since the transition temperature, decahydrate $\rightleftharpoons$ pentahydrate, is 61 °C. The crystals are filtered at the pump, washed twice with water, then twice with portions of 95 per cent ethanol, followed by two portions of diethyl ether. Five-millilitre portions of water, ethanol, and ether are used for 10 g of crystals. Each washing must be followed by suction to remove the wash liquid. After the final washing, the solid is spread in a thin layer on a watch- or clock-glass and allowed to stand at room temperature for 12–18 hours. The sodium tetraborate is then dry, and may be kept in a well-stoppered tube for three to four weeks without appreciable change. An alternative method of drying is to place the recrystallised product (after having been washed twice with water) in a desiccator over a solution saturated with respect to sugar (sucrose) and sodium chloride. The substance is dry after about three days, and may be kept indefinitely in the desiccator without change. The latter method is more time-consuming; the product is identical with that obtained by the ethanol–ether process.

Procedure. Weigh out accurately from a weighing bottle 0.4–0.5 g of pure sodium tetraborate into a 250 mL conical flask (Note 1), dissolve it in about 50 mL of water and add a few drops of methyl red. Titrate with the hydrochloric acid contained in a burette (for details, see under A) until the colour changes to pink (Note 2). Repeat the titration with two other portions. Calculate the

strength of the hydrochloric acid from the weight of sodium tetraborate and the volume of acid used. The variation of these results should not exceed 1–2 parts per thousand. If it is greater, further titrations must be performed until the variation falls within these limits. The arithmetical mean is used to calculate the concentration of the solution.

Notes. (1) For *elementary students*, an approximately 0.05M solution of sodium tetraborate may be prepared by weighing out accurately 4.7–4.8 g of analytical grade material on a watchglass or in a small beaker transferring it to a 250 mL graduated flask, dissolving it in water (Section 3.28), and making up to the mark. The contents of the flask are well mixed by shaking. Portions of 25 mL are withdrawn with a pipette and titrated with the acid as detailed under A. Individual titrations should not differ by more than 0.1 mL.

(2) For work of the highest precision a comparison solution or colour standard may be prepared for detecting the equivalence point. For 0.05M solutions, this is made by adding 5 drops of methyl red to a solution containing 1.0 g of sodium chloride and 2.2 g of boric acid in 500 mL of water; the solution must be boiled to remove any carbon dioxide which may be present in the water. It is assumed that 20 mL of wash water are used in the titration.

Calculation of the molarity. This is carried out as described in A. One mole of sodium tetraborate is 381.44 g.

C. Argentimetric method. This method is described in Section 10.84.

10.26 PREPARATION OF STANDARD ALKALI

Discussion. The hydroxides of sodium, potassium, and barium are generally employed for the preparation of solutions of standard alkalis; they are water-soluble strong bases. Solutions made from aqueous ammonia are undesirable, because they tend to lose ammonia, especially if the concentration exceeds 0.5M; moreover, it is a weak base, and difficulties arise in titrations with weak acids (compare Section 10.15). Sodium hydroxide is most commonly used because of its cheapness. None of these solid hydroxides can be obtained pure, so that a standard solution cannot be prepared by dissolving a known weight in a definite volume of water. Both sodium hydroxide and potassium hydroxide are extremely hygroscopic; a certain amount of alkali carbonate and water are always present. Exact results cannot be obtained in the presence of carbonate with some indicators, and it is therefore necessary to discuss methods for the preparation of carbonate-free alkali solutions. For many purposes sodium hydroxide (which contains 1–2 per cent of sodium carbonate) is sufficiently pure.

Carbonate-free sodium hydroxide solution. One of several methods of preparation may be used:

1. Rinse sodium hydroxide pellets rapidly with deionised water; this removes the carbonate from the surface. A solution prepared from the washed pellets is satisfactory for most purposes.
2. If a concentrated solution of sodium hydroxide (equal weights of pellets and water) is prepared, covered, and allowed to stand, the carbonate remains insoluble; the clear supernatant liquid may be poured or siphoned off, and suitably diluted. (Potassium carbonate is too soluble in concentrated alkali

for this method to be applicable for the preparation of carbonate-free potassium hydroxide solution.)

3. A method which yields a product completely free from carbonate ions consists in the electrolysis of a saturated solution of analytical grade sodium chloride with a mercury cathode and a platinum anode in the apparatus shown in Fig. 10.8. About 20–30 mL of *re-distilled* mercury are placed in a 250 mL pear-shaped Pyrex separatory funnel; 100–125 mL of an almost saturated solution of sodium chloride are then carefully introduced. Two short lengths of platinum wire are sealed into Pyrex glass tubing; one of these dips into the mercury (cathode), and the other into the salt solution (anode). A little mercury is placed in the glass tubes, and electrical contact is made by means of amalgamated copper wires dipping into the mercury in the tubes. Electrolysis is carried out using 6–8 volts and 0.5–1 amp for several hours; the funnel is shaken at intervals in order to break up the amalgam crystals that form on the surface of the mercury. The weight of the sodium dissolved in the amalgam may be roughly computed from the total current passed; the current efficiency is 75–80 per cent. When sufficient amalgam has formed, the mercury is run into a Pyrex flask containing about 100 mL of boiled-out distilled water and closed with a rubber bung carrying a soda-lime guard tube. Decomposition of the amalgam, to give the sodium hydroxide solution, is complete after several days; after 12–18 hours about 75 per cent of the amalgam is decomposed.

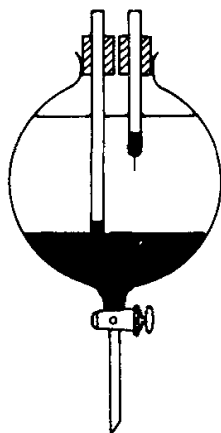


Fig. 10.8

4. In the anion exchange method, which is the preferred method, carbonate may be removed from either sodium hydroxide or potassium hydroxide. The solution is passed through a strong base anion exchange column (e.g. Duolite A113 or Amberlite IRA 400) in the chloride form (see Chapter 7). Initially the alkali hydroxide converts the resin into the hydroxide form; the carbonate ion has a greater affinity for the resin than has the hydroxide ion, and hence is retained on the resin: the first portions of the effluent contain chloride ion. If it is desired not to dilute the standard base appreciably and if chloride ion is objectionable, the effluent is discarded until it shows no test for chloride. Thus if a column containing one of the above resins, 35 cm long, is prepared in a 50 mL burette, about 150 mL of 4 per cent sodium hydroxide solution must be passed through the column of resin at a flow rate of $5\text{--}6\text{ mL min}^{-1}$ before the effluent is chloride-free; subsequently the effluent

may be collected in a 500 mL filter flask with the side arm carrying a soda-lime guard tube. When about 125 mL of liquid have been collected, 105 mL are measured out and diluted with boiled-out distilled water to 1 L. The resulting sodium hydroxide solution is carbonate-free and is about 0.1M. When the column becomes saturated with carbonate ion it is readily reconverted to the chloride form by passing dilute hydrochloric acid through it, followed by water to remove the excess acid.

Strong base anion exchangers in the hydroxide form may be used to prepare standard solutions of sodium or potassium hydroxide using weighed amounts of pure sodium chloride or potassium chloride. The resin, after conversion into the hydroxide form by passage of 1M sodium hydroxide (prepared from 18M sodium hydroxide so as to be carbonate-free) is washed with freshly boiled distilled water until the effluent contains no chloride ions and is neutral: about two litres of 1M sodium hydroxide are required for 40 g of resin, and washing is with about two litres of water. About 2.92 g of sodium chloride, accurately weighed, are dissolved in 100 mL of water. The solution is passed through the column at the rate of 4 mL min⁻¹; this is followed by about 300 mL of freshly boiled distilled water. The eluate is collected in a 500 mL graduated flask by means of an adapter permitting the use of a soda-lime guard tube. Towards the end the flow rate is decreased to permit careful adjustment to volume. An approximately 0.1M solution of sodium hydroxide results.

A number of firms supplying laboratory chemicals offer solutions of specified concentration which can be employed for titrimetric analysis. Amongst these, some manufacturers catalogue sodium hydroxide solutions 'free from carbonate', as for example BDH Ltd 'AVS' range of solutions; if only occasional need for carbonate-free sodium hydroxide solutions arises, this is the simplest way of satisfying this need. The merits of barium hydroxide solution (Section 10.29) as a carbonate-free alkali should also be borne in mind, but this suffers from the disadvantage that the maximum concentration available is between 0.025M and 0.05M. Whenever carbonate-free alkali is employed, it is essential that all the water used in the analyses should also be carbon-dioxide-free. With de-ionised water, there will be little cause for worry provided that the water is protected from atmospheric carbon dioxide, and with ordinary distilled water, dissolved carbon dioxide is readily removed by slowly aspirating a current of air which has been passed through a tube containing soda-asbestos or soda-lime through the water for 5–6 hours.

Attention must be directed to the fact that alkaline solutions, particularly if concentrated, attack glass. They may be preserved, if required, in polythene bottles, which are resistant to alkali. Furthermore, solutions of the strong bases absorb carbon dioxide from the air. If such solutions are exposed to the atmosphere for any appreciable time they become contaminated with carbonate. This may be prevented by the use of a storage vessel such as is shown in Fig. 3.9; the guard tube should be filled with soda-lime. A short exposure of an alkali hydroxide solution to the air will not, however, introduce any serious error. If such solutions are quickly transferred to a burette and the latter fitted with a soda-lime guard tube, the error due to contamination by carbon dioxide may be neglected.

The solution of alkali hydroxide prepared by any of the above methods must be standardised. Alkaline solutions that are subsequently to be used in the

presence of carbon dioxide or with strong acids are best standardised against solutions prepared from constant boiling point hydrochloric acid or potassium hydrogeniodate or sulphamic acid, or against hydrochloric acid which has been standardised by means of sodium tetraborate or sodium carbonate. If the alkali solution is to be used in the titration of weak acids, it is best standardised against organic acids or against acid salts of organic diprotic acids, such as benzoic acid or potassium hydrogenphthalate, respectively. These substances are commercially available in a purity exceeding 99.9 per cent; potassium hydrogenphthalate is preferable, since it is more soluble in water and has a greater relative molecular mass.

Procedure A. Weigh out rapidly about 4.2 g of sodium hydroxide on a watchglass or into a small beaker, dissolve it in water, make up to 1 L with boiled-out distilled water, mix thoroughly by shaking, and pour the resultant solution into the stock bottle, which should be closed by a rubber stopper.

Procedure B (carbonate-free sodium hydroxide). Dissolve 50 g of sodium hydroxide in 50 mL of distilled water in a Pyrex flask, transfer to a 75 mL test-tube of Pyrex glass, and insert a well-fitting stopper covered with tin foil. Allow it to stand in a vertical position until the supernatant liquid is clear. For a 0.1 M sodium hydroxide solution *carefully* withdraw, using a pipette fitted with a filling device, 6.5 mL of the concentrated clear solution into a 1 L bottle or flask, and dilute quickly with 1 L of recently boiled-out water.

A clear solution can be obtained more quickly, and incidentally the transfer can be made more satisfactorily, by rapidly filtering the solution through a sintered glass funnel with exclusion of carbon dioxide with the aid of the apparatus shown in Fig. 10.9. It is advisable to calibrate the test-tube in approximately 5 mL intervals and to put the graduations on a thin slip of paper gummed to the outside of the tube.

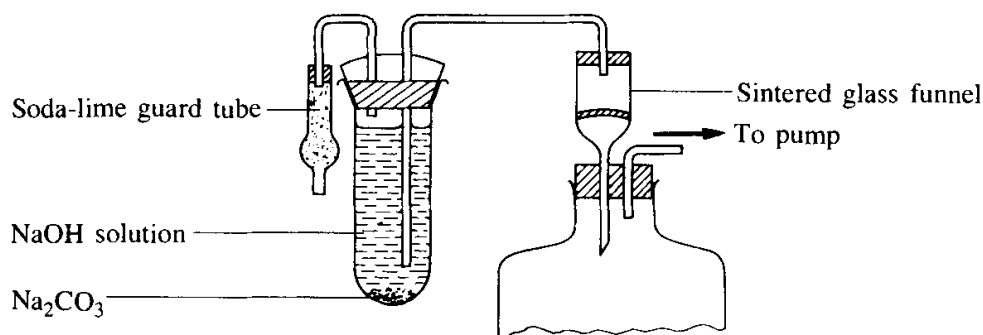


Fig. 10.9

10.27 STANDARDISATION OF APPROXIMATELY 0.1 M SODIUM HYDROXIDE

If the solution contains carbonate (Procedure A), methyl orange, methyl orange-indigo carmine, or bromophenol blue must be used in standardisation against hydrochloric acid of known molar concentration. Phenolphthalein or indicators with a similar pH range, which are affected by carbon dioxide, cannot

be used at the ordinary temperature (compare Section 10.7). With carbonate-free sodium hydroxide (Procedure B, above) phenolphthalein or thymol blue (Section 10.13) may be employed, and standardisation may be effected against hydrochloric acid, potassium hydrogeniodate, potassium hydrogenphthalate, benzoic acid, or other organic acids (Section 10.28).

Procedure A: with standard hydrochloric acid. Place the standardised (approx. 0.1 M) hydrochloric acid in the burette. Transfer 25 mL of the sodium hydroxide solution into a 250 mL conical flask with the aid of a pipette, dilute with a little water, add 1–2 drops of methyl orange or 3–4 drops of methyl orange–indigo carmine indicator, and titrate with the previously standardised hydrochloric acid. Repeat the titrations until duplicate determinations agree within 0.05 mL of each other.

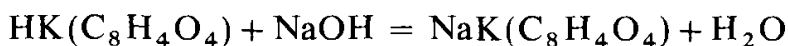
Calculation of the molarity. In this particular case the molar concentration is readily calculated from the simple relationship:

$$V_A \times m_A = V_B \times m_B$$

where V_A and m_A refer to the volume and known molarity of the acid respectively, V_B is the volume of alkali solution required for the neutralisation, and m_B is its (unknown) molarity.

Procedure B: with potassium hydrogenphthalate. Analytical grade potassium hydrogenphthalate has a purity of at least 99.9 per cent; it is almost non-hygroscopic, but, unless a product of guaranteed purity is purchased, it is advisable to dry it at 120 °C for 2 hours, and allow it to cool in a covered vessel in a desiccator. Weigh out three 0.6–0.7-g portions of the salt into 250 mL Pyrex conical flasks (Note), add 75 mL of boiled-out water to each portion, stopper each flask and shake gently until the solid has dissolved. Titrate each solution with the sodium hydroxide solution contained in a burette, using phenolphthalein or thymol blue as indicator.

Calculation of molar concentration. This is similar to that described in Section 10.25. The R.M.M. of potassium hydrogenphthalate is 204.22. The variation in the results should not exceed 0.1–0.2 per cent.



Note. For *elementary students*, an approximately 0.1 M solution is prepared by weighing out accurately about 5.1 g of the pure material, dissolving it in water, and making it up to 250 mL in a graduated flask. Volumes of 25 mL are employed in the titrations with the sodium hydroxide solution. Individual titrations should not differ by more than 0.1 mL.

10.28 OTHER STANDARD SUBSTANCES FOR ACIDIMETRY AND ALKALIMETRY

In addition to the standard substances already detailed for use in standardising acids and alkalis, numerous others have been proposed. A number of these will be briefly described.

A. Benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$; R.M.M. = 122.12). Analytical grade material has a purity of at least 99.9 per cent. For work demanding the highest accuracy, the acid should be dried before use by careful fusion in a platinum crucible placed in an oven at about 130 °C, and then powdered in an agate mortar.