CHAPTER 10
TITRIMETRIC ANALYSIS

THEORETICAL CONSIDERATIONS

10.1 TITRIMETRIC ANALYSIS

The term 'titrimetric analysis' refers to quantitative chemical analysis carried out by determining the volume of a solution of accurately known concentration which is required to react quantitatively with a measured volume of a solution of the substance to be determined. The solution of accurately known strength is called the **standard solution**, see Section 10.3. The weight of the substance to be determined is calculated from the volume of the standard solution used and the chemical equation and relative molecular masses of the reacting compounds.

The term 'volumetric analysis' was formerly used for this form of quantitative determination but it has now been replaced by **titrimetric analysis**. It is considered that the latter expresses the process of titration rather better, and the former is likely to be confused with measurements of volumes, such as those involving gases. In titrimetric analysis the reagent of known concentration is called the **titrant** and the substance being titrated is termed the **titrand**. The alternative name has not been extended to apparatus used in the various operations; so the terms volumetric glassware and volumetric flasks are still common, but it is better to employ the expressions graduated glassware and graduated flasks and these are used throughout this book.

The standard solution is usually added from a long graduated tube called a burette. The process of adding the standard solution until the reaction is just complete is termed a **titration**, and the substance to be determined is **titrated**. The point at which this occurs is called the **equivalence point** or the **theoretical** (or **stoichiometric**) **end point**. The completion of the titration is detected by some physical change, produced by the standard solution itself (e.g. the faint pink colour formed by potassium permanganate) or, more usually, by the addition of an auxiliary reagent, known as an indicator; alternatively some other physical measurement may be used. After the reaction between the substance and the standard solution is practically complete, the indicator should give a clear visual change (either a colour change or the formation of turbidity) in the liquid being titrated. The point at which this occurs is called the **end point of the titration**. In the ideal titration the visible end point will coincide with the stoichiometric or theoretical end point. In practice, however, a very small difference usually occurs; this represents the titration error. The indicator and the experimental conditions should be so selected that the difference between the visible end point and the equivalence point is as small as possible.

For use in titrimetric analysis a reaction must fulfil the following conditions.

1. There must be a simple reaction which can be expressed by a chemical equation; the substance to be determined should react completely with the reagent in stoichiometric or equivalent proportions.
2. The reaction should be relatively fast. (Most ionic reactions satisfy this condition.) In some cases the addition of a catalyst may be necessary to increase the speed of a reaction.
3. There must be an alteration in some physical or chemical property of the solution at the equivalence point.
4. An indicator should be available which, by a change in physical properties (colour or formation of a precipitate), should sharply define the end point of the reaction. [If no visible indicator is available, the detection of the equivalence point can often be achieved by following the course of the titration by measuring (*a*) the potential between an indicator electrode and a reference electrode (**potentiometric titration**, see Chapter 15); (*b*) the change in electrical conductivity of the solution (**conductimetric titration**, see Chapter 13); (*c*) the current which passes through the titration cell between an indicator electrode and a depolarised reference electrode at a suitable applied e.m.f. (**amperometric titration**, see Chapter 16); or (*d*) the change in absorbance of the solution (**spectrophotometric titration**, see Section 17.48).]

Titrimetric methods are normally capable of high precision (1 part in 1000) and wherever applicable possess obvious advantages over gravimetric methods. They need simpler apparatus, and are, generally, quickly performed; tedious and difficult separations can often be avoided. The following apparatus is required for titrimetric analysis: (i) calibrated measuring vessels, including burettes, pipettes, and measuring flasks (see Chapter 3); (ii) substances of known purity for the preparation of standard solutions; (iii) a visual indicator or an instrumental method for detecting the completion of the reaction.

10.2 CLASSIFICATION OF REACTIONS IN TITRIMETRIC ANALYSIS

The reactions employed in titrimetric analysis fall into four main classes. The first three of these involve no change in oxidation state as they are dependent upon the combination of ions. But the fourth class, oxidation–reduction reactions, involves a change of oxidation state or, expressed another way, a transfer of electrons.

1. Neutralisation reactions, or acidimetry and alkalimetry. These include the titration of free bases, or those formed from salts of weak acids by hydrolysis, with a standard acid (**acidimetry**), and the titration of free acids, or those formed by the hydrolysis of salts of weak bases, with a standard base (**alkalimetry**). The reactions involve the combination of hydrogen and hydroxide ions to form water.

Also under this heading must be included titrations in non-aqueous solvents, most of which involve organic compounds.

2. Complex formation reactions. These depend upon the combination of ions, other than hydrogen or hydroxide ions, to form a soluble, slightly dissociated ion or compound, as in the titration of a solution of a cyanide with silver nitrate

($2CN^- + Ag^+ \rightleftharpoons [Ag(CN)_2]^-$) or of chloride ion with mercury(II) nitrate solution ($2Cl^- + Hg^{2+} \leftrightharpoons HgCl_2$).

Ethylenediaminetetra-acetic acid, largely as the disodium salt of EDTA, is a very important reagent for complex formation titrations and has become one of the most important reagents used in titrimetric analysis. Equivalence point detection by the use of metal-ion indicators has greatly enhanced its value in titrimetry.

3. Precipitation reactions. These depend upon the combination of ions to form a simple precipitate as in the titration of silver ion with a solution of a chloride (Section 10.74). No change in oxidation state occurs.

4. Oxidation–reduction reactions. Under this heading are included all reactions involving change of oxidation number or transfer of electrons among the reacting substances. The standard solutions are either oxidising or reducing agents. The principal oxidising agents are potassium permanganate, potassium dichromate, cerium(IV) sulphate, iodine, potassium iodate, and potassium bromate. Frequently used reducing agents are iron(II) and tin(II) compounds, sodium thiosulphate, arsenic(III) oxide, mercury(I) nitrate, vanadium(II) chloride or sulphate, chromium(II) chloride or sulphate, and titanium(III) chloride or sulphate.

10.3 STANDARD SOLUTIONS

The word 'concentration' is frequently used as a general term referring to a quantity of substance in a defined volume of solution. But for quantitative titrimetric analysis use is made of standard solutions in which the base unit of quantity employed is the mole. This follows the definition given by the International Union of Pure and Applied Chemistry[1] in which:

> 'The mole is the amount of substance which contains as many elementary units as there are atoms in 0.012 kilogram of carbon-12. The elementary unit must be specified and may be an atom, a molecule, an ion, a radical, an electron or other particle or a specified group of such particles.'

As a result standard solutions are now commonly expressed in terms of molar concentrations or molarity (M). Such standard solutions are specified in terms of the number of moles of solute dissolved in 1 litre of solution; for any solution,

$$\text{Molarity } (M) = \frac{\text{Moles of solute}}{\text{Volume of solution in litres}}$$

As the term 'mole' refers to an amount of substance with reference to the specified mass of carbon-12, it is possible to express the relative molecular mass (the basis for the mole) for any substance as the additive sum of the relative atomic masses (R.A.M.s) of its component elements, for example:

The relative molecular mass for sulphuric acid, H_2SO_4, is calculated from the relative atomic masses as follows:

Element	R.A.M.
Hydrogen	1.0079 × 2 = 2.0158
Sulphur	32.06 × 1 = 32.06
Oxygen	15.9994 × 4 = 63.9986
Relative Molecular Mass	= 98.0744

This approach can be used to obtain the R.A.M. of any compound, so that

1 mole of Hg_2Cl_2 has a mass of 0.472 09 kg
1 mole of Na_2CO_3, $10H_2O$ has a mass of 0.286 141 kg
1 mole of H_2SO_4 has a mass of 0.098 074 kg

It follows from this, that a molar solution of sulphuric acid will contain 98.074 grams of sulphuric acid in 1 litre of solution, or 49.037 grams in 500 mL of solution. Similarly, a 0.1 *M* solution will contain 9.8074 grams of sulphuric acid in 1 litre of solution, and a 0.01 *M* solution will have 0.980 74 gram in the same volume. So that the concentration of any solution can be expressed in terms of the molar concentration so long as the weight of substance in any specified volume is known.

10.4 EQUIVALENTS, NORMALITIES AND OXIDATION NUMBERS

Although molar concentrations are now commonly used in determinations of reacting quantities in titrimetric analysis, it has been traditional to employ other concepts involving what are known as 'equivalent weights' and 'normalities' for this purpose. In neutralisation reactions the equivalent weight/normality concept is relatively straightforward, but for reduction–oxidation titrations it often requires an understanding of what are known as 'oxidation numbers' of the substances involved in the redox reaction. Although the modern approach is to discard this form of calculation and quantitation, the authors of this book fully appreciate that there are many scientists who do prefer to use it, and some who claim it has clear advantages over the molar concept. Because of this, a full explanation of this approach to titrimetry is retained as Appendix 17 but all other quantitative aspects in this book are in terms of moles per litre.

10.5 PREPARATION OF STANDARD SOLUTIONS

If a reagent is available in the pure state, a solution of definite molar strength is prepared simply by weighing out a mole, or a definite fraction or multiple thereof, dissolving it in an appropriate solvent, usually water, and making up the solution to a known volume. It is not essential to weigh out exactly a mole (or a multiple or sub-multiple thereof); in practice it is more convenient to prepare the solution a *little* more concentrated than is ultimately required, and then to dilute it with distilled water until the desired molar strength is obtained. If M_1 is the required molarity, V_1 the volume after dilution, M_2 the molarity originally obtained, and V_2 the original volume taken, $M_1V_1 = M_2V_2$, or $V_1 = M_2V_2/M_1$. The volume of water to be added to the volume V_2 is $(V_1 - V_2)$ mL.

The following is a list of some of the substances which can be obtained in a

state of high purity and are therefore suitable for the preparation of standard solutions: sodium carbonate, potassium hydrogenphthalate, benzoic acid, sodium tetraborate, sulphamic acid, potassium hydrogeniodate, sodium oxalate, silver, silver nitrate, sodium chloride, potassium chloride, iodine, potassium bromate, potassium iodate, potassium dichromate, lead nitrate and arsenic(III) oxide.

When the reagent is not available in the pure form as in the cases of most alkali hydroxides, some inorganic acids and various deliquescent substances, solutions corresponding approximately to the molar strength required are first prepared. These are then standardised by titration against a solution of a pure substance of known concentration. It is generally best to standardise a solution by a reaction of the same type as that for which the solution is to be employed, and as nearly as possible under identical experimental conditions. The titration error and other errors are thus considerably reduced or are made to cancel out. This indirect method is employed for the preparation of, for instance, solutions of most acids (the constant boiling point mixture of definite composition of hydrochloric acid can be weighed out directly, if desired), sodium hydroxide, potassium hydroxide and barium hydroxide, potassium permanganate, ammonium and potassium thiocyanates, and sodium thiosulphate.

10.6 PRIMARY AND SECONDARY STANDARDS

In titrimetry certain chemicals are used frequently in defined concentrations as reference solutions. Such substances are referred to as **primary standards** or **secondary standards**. A primary standard is a compound of sufficient purity from which a standard solution can be prepared by direct weighing of a quantity of it, followed by dilution to give a defined volume of solution. The solution produced is then a primary standard solution. A primary standard should satisfy the following requirements.

1. It must be easy to obtain, to purify, to dry (preferably at 110–120 °C), and to preserve in a pure state. (This requirement is not usually met by hydrated substances, since it is difficult to remove surface moisture completely without effecting partial decomposition.)
2. The substance should be unaltered in air during weighing; this condition implies that it should not be hygroscopic, oxidised by air, or affected by carbon dioxide. The standard should maintain an unchanged composition during storage.
3. The substance should be capable of being tested for impurities by qualitative and other tests of known sensitivity. (The total amount of impurities should not, in general, exceed 0.01–0.02 per cent.)
4. It should have a high relative molecular mass so that the weighing errors may be negligible. (The precision in weighing is ordinarily 0.1–0.2 mg; for an accuracy of 1 part in 1000, it is necessary to employ samples weighing at least about 0.2 g.)
5. The substance should be readily soluble under the conditions in which it is employed.
6. The reaction with the standard solution should be stoichiometric and practically instantaneous. The titration error should be negligible, or easy to determine accurately by experiment.

In practice, an ideal primary standard is difficult to obtain, and a compromise between the above ideal requirements is usually necessary. The substances commonly employed as primary standards are indicated below:

(*a*) **Acid-base reactions** — sodium carbonate Na_2CO_3, sodium tetraborate $Na_2B_4O_7$, potassium hydrogenphthalate $KH(C_8H_4O_4)$, constant boiling point hydrochloric acid, potassium hydrogeniodate $KH(IO_3)_2$, benzoic acid (C_6H_5COOH).

(*b*) **Complex formation reactions** — silver, silver nitrate, sodium chloride, various metals (e.g. spectroscopically pure zinc, magnesium, copper, and manganese) and salts, depending upon the reaction used.

(*c*) **Precipitation reactions** — silver, silver nitrate, sodium chloride, potassium chloride, and potassium bromide (prepared from potassium bromate).

(*d*) **Oxidation–reduction reactions** — potassium dichromate $K_2Cr_2O_7$, potassium bromate $KBrO_3$, potassium iodate KIO_3, potassium hydrogeniodate $KH(IO_3)_2$, sodium oxalate $Na_2C_2O_4$, arsenic(III) oxide As_2O_3, and pure iron.

Hydrated salts, as a rule, do not make good standards because of the difficulty of efficient drying. However, those salts which do not effloresce, such as sodium tetraborate $Na_2B_4O_7$, $10H_2O$, and copper sulphate $CuSO_4,5H_2O$, are found by experiment to be satisfactory secondary standards.[2]

A secondary standard is a substance which may be used for standardisations, and whose content of the active substance has been found by comparison against a primary standard. It follows that a secondary standard solution is a solution in which the concentration of dissolved solute has not been determined from the weight of the compound dissolved but by reaction (titration) of a volume of the solution against a measured volume of a primary standard solution.

NEUTRALISATION TITRATIONS

10.7 NEUTRALISATION INDICATORS

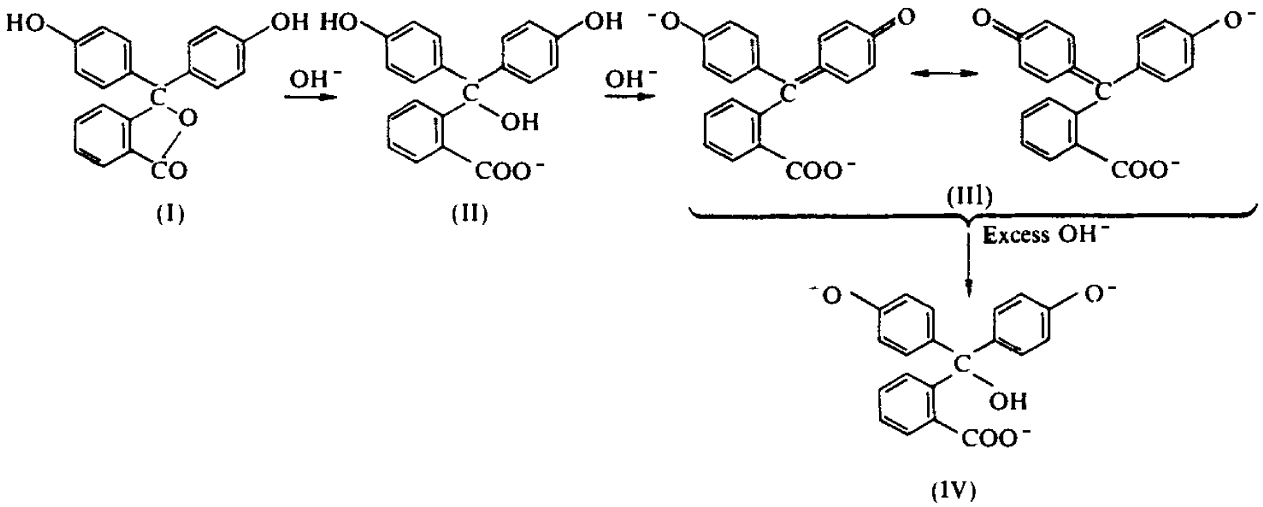
The object of titrating, say, an alkaline solution with a standard solution of an acid is the determination of the amount of acid which is exactly equivalent chemically to the amount of base present. The point at which this is reached is the **equivalence point**, **stoichiometric point**, or **theoretical end point**; the resulting aqueous solution contains the corresponding salt. If both the acid and base are strong electrolytes, the solution at the end-point will be neutral and have a pH of 7 (Section 2.17); but if either the acid or the base is a weak electrolyte, the salt will be hydrolysed to a certain degree, and the solution at the equivalence point will be either slightly alkaline or slightly acid. The exact pH of the solution at the equivalence point can readily be calculated from the ionisation constant of the weak acid or the weak base and the concentration of the solution (see Section 2.19). For any actual titration the correct end-point will be characterised by a definite value of the hydrogen-ion concentration of the solution, the value depending upon the nature of the acid and the base and the concentration of the solution.

A large number of substances, called **neutralisation** or **acid–base indicators**, change colour according to the hydrogen-ion concentration of the solution. The

chief characteristic of these indicators is that the change from a predominantly 'acid' colour to a predominantly 'alkaline' colour is not sudden and abrupt, but takes place within a small interval of pH (usually about two pH units) termed the **colour-change interval** of the indicator. The position of the colour-change interval in the pH scale varies widely with different indicators. For most acid–base titrations it is possible to select an indicator which exhibits a distinct colour change at a pH close to that corresponding to the equivalence point.

The first useful theory of indicator action was suggested by W. Ostwald[3] based upon the concept that indicators in general use are very weak organic acids or bases.

The simple Ostwald theory of the colour change of indicators has been revised, and the colour changes are believed to be due to structural changes, including the production of quinonoid and resonance forms; these may be illustrated by reference to phenolphthalein, the changes of which are characteristic of all phthalein indicators: see the formulae I–IV given below. In the presence of dilute alkali the lactone ring in I opens to yield II, and the triphenylcarbinol structure (II) undergoes loss of water to produce the resonating ion III which is red. If phenolphthalein is treated with excess of concentrated alcoholic alkali the red colour first produced disappears owing to the formation of IV.



The Brønsted–Lowry concept of acids and bases[4] makes it unnecessary to distinguish between acid and base indicators: emphasis is placed upon the charge types of the acid and alkaline forms of the indicator. The equilibrium between the acidic form In_A and the basic form In_B may be expressed as:

$$In_A \rightleftharpoons H^+ + In_B \tag{1}$$

and the equilibrium constant as:

$$\frac{a_{H^+} \times a_{In_B}}{a_{In_A}} = K_{In} \tag{2}$$

The observed colour of an indicator in solution is determined by the ratio of the concentrations of the acidic and basic forms. This is given by:

$$\frac{[In_A]}{[In_B]} = \frac{a_{H^+} \times y_{In_B}}{K_{In} \times y_{In_A}} \tag{3}$$

where y_{In_A} and y_{In_B} are the activity coefficients of the acidic and basic forms of the indicator. Equation (3) may be written in the logarithmic form:

$$pH = -\log a_{H^+} = pK_{In} + \log\frac{[In_B]}{[In_A]} + \log\frac{y_{In_B}}{y_{In_A}} \quad (4)$$

The pH will depend upon the ionic strength of the solution (which is, of course, related to the activity coefficient — see Section 2.5). Hence, when making a colour comparison for the determination of the pH of a solution, not only must the indicator concentration be the same in the two solutions but the ionic strength must also be equal or approximately equal. The equation incidentally provides an explanation of the so-called salt and solvent effects which are observed with indicators. The colour-change equilibrium at any particular ionic strength (constant activity-coefficient term) can be expressed by a condensed form of equation (4):

$$pH = pK'_{In} + \log\frac{[In_B]}{[In_A]} \quad (5)$$

where pK'_{In} is termed the **apparent indicator constant.**

The value of the ratio $[In_B]/[In_A]$ (i.e. [Basic form]/[Acidic form]) can be determined by a visual colour comparison or, more accurately, by a spectrophotometric method. Both forms of the indicator are present at any hydrogen-ion concentration. It must be realised, however, that the human eye has a limited ability to detect either of two colours when one of them predominates. Experience shows that the solution will appear to have the 'acid' colour, i.e. of In_A, when the ratio of $[In_A]$ to $[In_B]$ is above approximately 10, and the 'alkaline' colour, i.e. of In_B, when the ratio of $[In_B]$ to $[In_A]$ is above approximately 10. Thus only the 'acid' colour will be visible when $[In_A]/[In_B] > 10$; the corresponding limit of pH given by equation (5) is:

$$pH = pK'_{In} - 1$$

Only the alkaline colour will be visible when $[In_B]/[In_A] > 10$, and the corresponding limit of pH is:

$$pH = pK'_{In} + 1$$

The colour-change interval is accordingly $pH = pK'_{In} \pm 1$, i.e. over approximately two pH units. Within this range the indicator will appear to change from one colour to the other. The change will be gradual, since it depends upon the ratio of the concentrations of the two coloured forms (acidic form and basic form). When the pH of the solution is equal to the apparent dissociation constant of the indicator pK'_{In}, the ratio $[In_A]$ to $[In_B]$ becomes equal to 1, and the indicator will have a colour due to an equal mixture of the 'acid' and 'alkaline' forms. This is sometimes known as the 'middle tint' of the indicator. This applies strictly only if the two colours are of equal intensity. If one form is more intensely coloured than the other or if the eye is more sensitive to one colour than the other, then the middle tint will be slightly displaced along the pH range of the indicator.

Table 10.1 contains a list of indicators suitable for titrimetric analysis and for the colorimetric determination of pH. The colour-change intervals of most of the various indicators listed in the table are represented graphically in Fig. 10.1.

Table 10.1 Colour changes and pH range of certain indicators

Indicator	Chemical name	pH range	Colour in acid solution	Colour in alkaline solution	pK'_{In}
Brilliant cresyl blue (acid)	Aminodiethylaminomethyldiphenazonium chloride	0.0–1.0	Red–orange	Blue	—
Cresol red (acid)	1-Cresolsulphonphthalein	0.2–1.8	Red	Yellow	—
m-Cresol purple	*m*-Cresolsulphonphthalein	0.5–2.5	Red	Yellow	—
Quinaldine red	1-(*p*-Dimethylaminophenylethylene)quinoline ethiodide	1.4–3.2	Colourless	Red	—
Thymol blue (acid)	Thymolsulphonphthalein	1.2–2.8	Red	Yellow	1.7
Tropaeolin OO	*p*-Anilinophenylazobenzenesulphonic acid sodium salt	1.3–2.8	Red	Yellow	—
Bromophenol blue	Tetrabromophenolsulphonphthalein	2.8–4.6	Yellow	Blue	4.1
Ethyl orange		3.0–4.5	Red	Orange	—
Methyl orange	Dimethylaminophenylazobenzenesulphonic acid sodium salt	2.9–4.6	Red	Orange	3.7
Congo red	Diphenyldiazobis-1-naphthylaminesulphonic acid disodium salt	3.0–5.0	Blue	Red	—
Bromocresol green	Tetrabromo-*m*-cresolsulphonphthalein	3.6–5.2	Yellow	Blue	4.7
Methyl red	1-Carboxybenzeneazodimethylaniline	4.2–6.3	Red	Yellow	5.0
Ethyl red		4.5–6.5	Red	Orange	—
Chlorophenol red	Dichlorophenolsulphonphthalein	4.6–7.0	Yellow	Red	6.1
4-Nitrophenol	4-Nitrophenol	5.0–7.0	Colourless	Yellow	7.1
Bromocresol purple	Dibromo-*o*-cresolsulphonphthalein	5.2–6.8	Yellow	Purple	6.1
Bromophenol red	Dibromophenolsulphonphthalein	5.2–7.0	Yellow	Red	—
Azolitmin (litmus)	—	5.0–8.0	Red	Blue	—
Bromothymol blue	Dibromothymolsulphonphthalein	6.0–7.6	Yellow	Blue	7.1
Neutral red	Aminodimethylaminotoluphenazonium chloride	6.8–8.0	Red	Orange	—
Phenol red	Phenolsulphonphthalein	6.8–8.4	Yellow	Red	7.8
Cresol red (base)	1-Cresolsulphonphthalein	7.2–8.8	Yellow	Red	8.2
1-Naphtholphthalein	1-Naphtholphthalein	7.3–8.7	Yellow	Blue	8.4
m-Cresol purple	*m*-Cresolsulphonphthalein	7.6–9.2	Yellow	Purple	—
Thymol blue (base)	Thymolsulphonphthalein	8.0–9.6	Yellow	Blue	8.9
o-Cresolphthalein	Di-*o*-cresolphthalide	8.2–9.8	Colourless	Red	—
Phenolphthalein	Phenolphthalein	8.3–10.0	Colourless	Red	9.6
Thymolphthalein	Thymolphthalein	9.3–10.5	Colourless	Blue	9.3
Alizarin yellow R	*p*-Nitrobenzeneazosalicylic acid	10.1–12.1	Yellow	Orange–red	—
Brilliant cresyl blue (base)	Aminodiethylaminomethyldiphenazonium chloride	10.8–12.0	Blue	Yellow	—
Tropaeolin O	*p*-Sulphobenzeneazoresorcinol	11.1–12.7	Yellow	Orange	—
Nitramine	2,4,6-Trinitrophenylmethylnitroamine	10.8–13.0	Colourless	Orange–brown	—

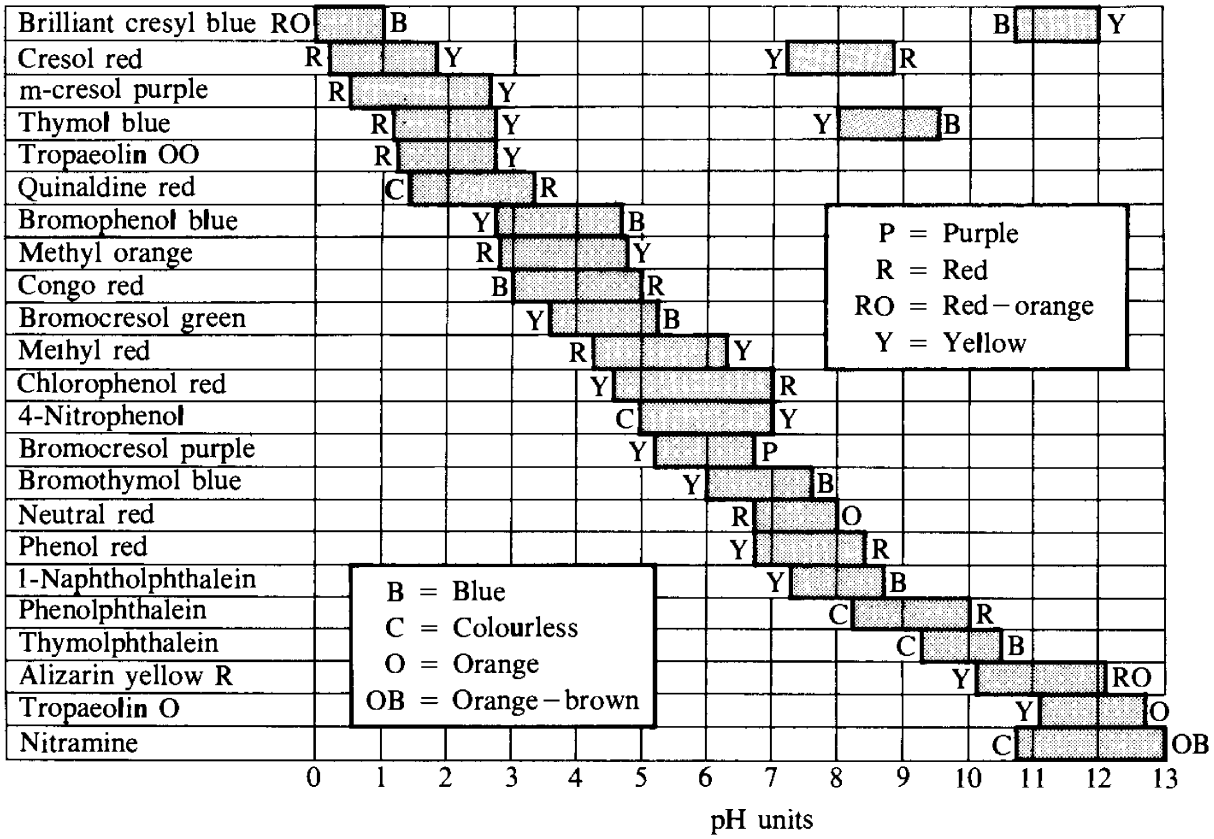


Fig. 10.1

It is necessary to draw attention to the variable pH of water which may be encountered in quantitative analysis. Water in equilibrium with the normal atmosphere which contains 0.03 per cent by volume of carbon dioxide has a pH of about 5.7; very carefully prepared conductivity water has a pH close to 7; water saturated with carbon dioxide under a pressure of one atmosphere has a pH of about 3.7 at 25 °C. The analyst may therefore be dealing, according to the conditions that prevail in the laboratory, with water having a pH between the two extremes pH 3.7 and pH 7. Hence for indicators which show their alkaline colours at pH values above 4.5, the effect of carbon dioxide introduced during a titration, either from the atmosphere or from the titrating solutions, must be seriously considered. This subject is discussed again later (Section 10.12).

10.8 PREPARATION OF INDICATOR SOLUTIONS

As a rule laboratory solutions of the indicators contain 0.5–1 g of indicator per litre of solvent. If the substance is soluble in water, e.g. a sodium salt, water is the solvent; in most other cases 70–90 per cent ethanol is employed.

Methyl orange. This indicator is available either as the free acid or as the sodium salt.

Dissolve 0.5 g of the free acid in 1 litre of water. Filter the cold solution to remove any precipitate which separates.

Dissolve 0.5 g of the sodium salt in 1 litre of water, add 15.2 mL of 0.1 *M* hydrochloric acid, and filter, if necessary, when cold.

Methyl red. Dissolve 1 g of the free acid in 1 litre of hot water, or dissolve in 600 mL of ethanol and dilute with 400 mL of water.

1-Naphtholphthalein. Dissolve 1 g of the indicator in 500 mL of ethanol and dilute with 500 mL of water.

Phenolphthalein. Dissolve 5 g of the reagent in 500 mL of ethanol and add 500 mL of water with constant stirring. Filter, if a precipitate forms.

Alternatively, dissolve 1 g of the dry indicator in 60 mL of 2-ethoxyethanol (Cellosolve), b.p. 135 °C, and dilute to 100 mL with distilled water: the loss by evaporation is less with this preparation.

Thymolphthalein. Dissolve 0.4 g of the reagent in 600 mL of ethanol and add 400 mL of water with stirring.

Sulphonphthaleins. These indicators are usually supplied in the acid form. They are rendered water-soluble by adding sufficient sodium hydroxide to neutralise the sulphonic acid group. One gram of the indicator is triturated in a clean glass mortar with the appropriate quantity of 0.1 *M* sodium hydroxide solution, and then diluted with water to 1 L. The following volumes of 0.1 *M* sodium hydroxide are required for 1 g of the indicators: bromophenol blue, 15.0 mL; bromocresol green, 14.4 mL; bromocresol purple, 18.6 mL; chlorophenol red, 23.6 mL; bromothymol blue, 16.0 mL; phenol red, 28.4 mL; thymol blue, 21.5 mL; cresol red, 26.2 mL; metacresol purple, 26.2 mL.

Quinaldine red. Dissolve 1 g in 100 mL of 80 per cent ethanol.

Methyl yellow, neutral red, and Congo red. Dissolve 1 g of the indicator in 1 L of 80 per cent ethanol. Congo red may also be dissolved in water.

4-Nitrophenol. Dissolve 2 g of the solid in 1 L of water.

Alizarin yellow R. Dissolve 0.5 g of the indicator in 1 L of 80 per cent ethanol.

Tropaeolin O and tropaeolin OO. Dissolve 1 g of the solid in 1 L of water.

Many of the indicator solutions are available from commercial suppliers already prepared for use.

10.9 MIXED INDICATORS

For some purposes it is desirable to have a sharp colour change over a narrow and selected range of pH; this is not easily seen with an ordinary acid–base indicator, since the colour change extends over two units of pH. The required result may, however, be achieved by the use of a suitable mixture of indicators; these are generally selected so that their pK'_{In} values are close together and the overlapping colours are complementary at an intermediate pH value. A few examples will be given in some detail.

(*a*) A mixture of equal parts of neutral red (0.1 per cent solution in ethanol) and methylene blue (0.1 per cent solution in ethanol) gives a sharp colour change from violet–blue to green in passing from acid to alkaline solution at pH 7. This indicator may be employed to titrate acetic acid (ethanoic acid) with ammonia solution or vice versa. Both acid and base are approximately of the same strength, hence the equivalence point will be at a pH $\approx$ 7 (Section 10.15); owing to the extensive hydrolysis and the flat nature of the titration curve, the titration cannot be performed except with an indicator of very narrow range.

(*b*) A mixture of phenolphthalein (3 parts of a 0.1 per cent solution in ethanol) and 1-naphtholphthalein (1 part of a 0.1 per cent solution in ethanol) passes from pale rose to violet at pH = 8.9. The mixed indicator is suitable for the titration of phosphoric acid to the diprotic stage ($K_2 = 6.3 \times 10^{-8}$; the equivalence point at pH ≈ 8.7).

(*c*) A mixture of thymol blue (3 parts of a 0.1 per cent aqueous solution of the sodium salt) and cresol red (1 part of a 0.1 per cent aqueous solution of the sodium salt) changes from yellow to violet at pH = 8.3. It has been recommended for the titration of carbonate to the hydrogencarbonate stage.

Other examples are included in Table 10.2.

Table 10.2 Some mixed indicators

Indicator mixture	pH	Colour change	Composition*
Bromocresol green; methyl orange	4.3	Orange → blue–green	1 p 0.1% (Na) in w; 1 p 0.2% in w
Bromocresol green; chlorophenol red	6.1	Pale green → blue violet	1 p 0.1% (Na) in w; 1 p 0.1% (Na) in w
Bromothymol blue; neutral red	7.2	Rose pink → green	1 p 0.1% in e; 1 p 0.1% in e
Bromothymol blue; phenol red	7.5	Yellow → violet	1 p 0.1% (Na) in w; 1 p 0.1% (Na) in w
Thymol blue; cresol red	8.3	Yellow → violet	3 p 0.1% (Na) in w; 1 p 0.1% (Na) in w
Thymol blue; phenolphthalein	9.0	Yellow → violet	1 p 0.1% in 50% e; 3 p 0.1% in 50% e
Thymolphthalein; phenolphthalein	9.9	Colourless → violet	1 p 0.1% in e; 1 p 0.1% in w

* Abbreviations: p = part, w = water, e = ethanol, Na = Na salt

The colour change of a single indicator may also be improved by the addition of a pH-sensitive dyestuff to produce the complement of one of the indicator colours. A typical example is the addition of xylene cyanol FF to methyl orange (1.0 g of methyl orange and 1.4 g of xylene cyanol FF in 500 mL of 50 per cent ethanol): here the colour change from the alkaline to the acid side is green → grey → magenta, the middle (grey) stage being at pH = 3.8. The above is an example of a **screened indicator**, and the mixed indicator solution is sometimes known as 'screened' methyl orange. Another example is the addition of methyl green (2 parts of a 0.1 per cent solution in ethanol) to phenolphthalein (1 part of a 0.1 per cent solution in ethanol); the former complements the red–violet basic colour of the latter, and at a pH of 8.4–8.8 the colour change is from grey to pale blue.

10.10 UNIVERSAL OR MULTIPLE-RANGE INDICATORS

By mixing suitable indicators together changes in colour may be obtained over a considerable portion of the pH range. Such mixtures are usually called '**universal indicators**'. They are not suitable for quantitative titrations, but may be employed for the determination of the approximate pH of a solution by the colorimetric method. One such universal indicator is prepared by dissolving 0.1 g of phenolphthalein, 0.2 g of methyl red, 0.3 g of methyl yellow, 0.4 g of

bromothymol blue, and 0.5 g of thymol blue in 500 mL of absolute ethanol, and adding sodium hydroxide solution until the colour is yellow. The colour changes are: pH 2, red; pH 4, orange; pH 6, yellow; pH 8, green; pH 10, blue.

Another recipe for a universal indicator is as follows: 0.05 g of methyl orange, 0.15 g of methyl red, 0.3 g of bromothymol blue, and 0.35 g of phenolphthalein in 1 L of 66 per cent ethanol. The colour changes are: pH up to 3, red; pH 4, orange–red; pH 5, orange; pH 6, yellow; pH 7, yellowish–green; pH 8, greenish–blue; pH 9, blue; pH 10, violet; pH 11, reddish–violet. Several 'universal indicators' are available commercially as solutions and as test papers.

10.11 NEUTRALISATION CURVES

The mechanism of neutralisation processes can be understood by studying the changes in the hydrogen ion concentration during the course of the appropriate titration. The change in pH in the neighbourhood of the equivalence point is of the greatest importance, as it enables an indicator to be selected which will give the smallest titration error. The curve obtained by plotting pH as the ordinate against the percentage of acid neutralised (or the number of mL of alkali added) as abscissa is known as the neutralisation (or, more generally, the titration) curve. This may be evaluated experimentally by determination of the pH at various stages during the titration by a potentiometric method (Sections 15.15 and 15.20), or it may be calculated from theoretical principles.

10.12 NEUTRALISATION OF A STRONG ACID WITH A STRONG BASE

For this calculation it is assumed that both the acid and the base are completely dissociated and the activity coefficients of the ions are unity in order to obtain the pH values during the course of the neutralisation of the strong acid and the strong base, or vice versa, at the laboratory temperature. For simplicity of calculation consider the titration of 100 mL of 1 *M* hydrochloric acid with 1 *M* sodium hydroxide solution. The pH of 1 *M* hydrochloric acid is 0. When 50 mL of the 1 *M* base have been added, 50 mL of unneutralised 1 *M* acid will be present in a total volume of 150 mL.

$[H^+]$ will therefore be $50 \times 1/150 = 3.33 \times 10^{-1}$, or pH = 0.48
For 75 mL of base, $[H^+] = 25 \times 1/175 = 1.43 \times 10^{-1}$, pH = 0.84
For 90 mL of base, $[H^+] = 10 \times 1/190 = 5.26 \times 10^{-2}$, pH = 1.3
For 98 mL of base, $[H^+] = 2 \times 1/198 = 1.01 \times 10^{-2}$, pH = 2.0
For 99 mL of base, $[H^+] = 1 \times 1/199 = 5.03 \times 10^{-3}$, pH = 2.3
For 99.9 mL of base, $[H^+] = 0.1 \times 1/199.9 = 5.00 \times 10^{-4}$, pH = 3.3

Upon the addition of 100 mL of base, the pH will change sharply to 7, i.e. the theoretical equivalence point. The resulting solution is simply one of sodium chloride. Any sodium hydroxide added beyond this will be in excess of that needed for neutralisation.

With 100.1 mL of base, $[OH^-] = 0.1/200.1 = 5.00 \times 10^{-4}$, pOH = 3.3 and pH = 10.7
With 101 mL of base, $[OH^-] = 1/201 = 5.00 \times 10^{-3}$, pOH = 2.3, and pH = 11.7

These results show that as the titration proceeds, initially the pH rises slowly, but between the addition of 99.9 and 100.1 mL of alkali, the pH of the solution

rises from 3.3 to 10.7, i.e. in the vicinity of the equivalence point the rate of change of pH of the solution is very rapid.

The complete results, up to the addition of 200 mL of alkali, are collected in Table 10.3; this also includes the figures for 0.1 *M* and 0.01 *M* solutions of acid and base respectively. The additions of alkali have been extended in all three cases to 200 mL; it is evident that the range from 200 to 100 mL and beyond represents the reverse titration of 100 mL of alkali with the acid in the presence of the non-hydrolysed sodium chloride solution. The data in the table are presented graphically in Fig. 10.2.

Table 10.3 pH during titration of 100 mL of HCl with NaOH of equal concentration

NaOH added (mL)	1*M* solution (pH)	0.1*M* solution (pH)	0.01*M* solution (pH)
0	0.0	1.0	2.0
50	0.5	1.5	2.5
75	0.8	1.8	2.8
90	1.3	2.3	3.3
98	2.0	3.0	4.0
99	2.3	3.3	4.3
99.5	2.6	3.6	4.6
99.8	3.0	4.0	5.0
99.9	3.3	4.3	5.3
100.0	7.0	7.0	7.0
100.1	10.7	9.7	8.7
100.2	11.0	10.0	9.0
100.5	11.4	10.4	9.4
101	11.7	10.7	9.7
102	12.0	11.0	10.0
110	12.7	11.7	10.7
125	13.0	12.0	11.0
150	13.3	12.3	11.3
200	13.5	12.5	11.5

In quantitative analysis it is the changes of pH near the equivalence point which are of special interest. This part of Fig. 10.2 is accordingly shown on a larger scale in Fig. 10.3, on which are also indicated the colour-change intervals of some of the common indicators.

With 1 M *solutions*, it is evident that any indicator with an effective range between pH 3 and 10.5 may be used. The colour change will be sharp and the titration error negligible.

With 0.1 M *solutions*, the ideal pH range for an indicator is limited to 4.5–9.5. Methyl orange will exist chiefly in the alkaline form when 99.8 mL of alkali have been added, and the titration error will be 0.2 per cent, which is negligibly small for most practical purposes; it is therefore advisable to add sodium hydroxide solution until the indicator is present completely in the alkaline form. The titration error is also negligibly small with phenolphthalein.

With 0.01 *M* solutions, the ideal pH range is still further limited to 5.5–8.5; such indicators as methyl red, bromothymol blue, or phenol red will be suitable. The titration error for methyl orange will be 1–2 per cent.

The above considerations apply to solutions which do not contain carbon dioxide. In practice, carbon dioxide is usually present (compare Section 10.7)

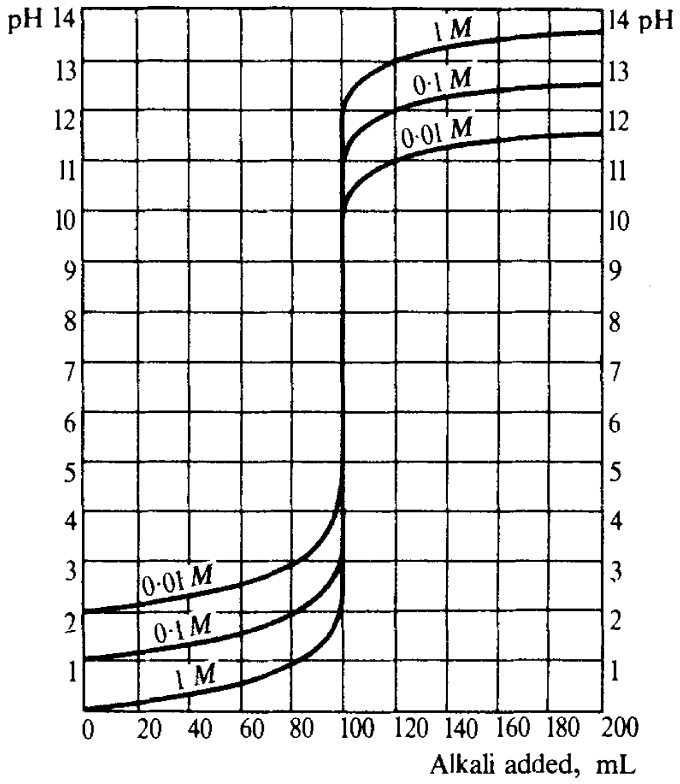


Fig. 10.2 Neutralisation curves of 100 mL of HCl with NaOH of same concentration (calculated).

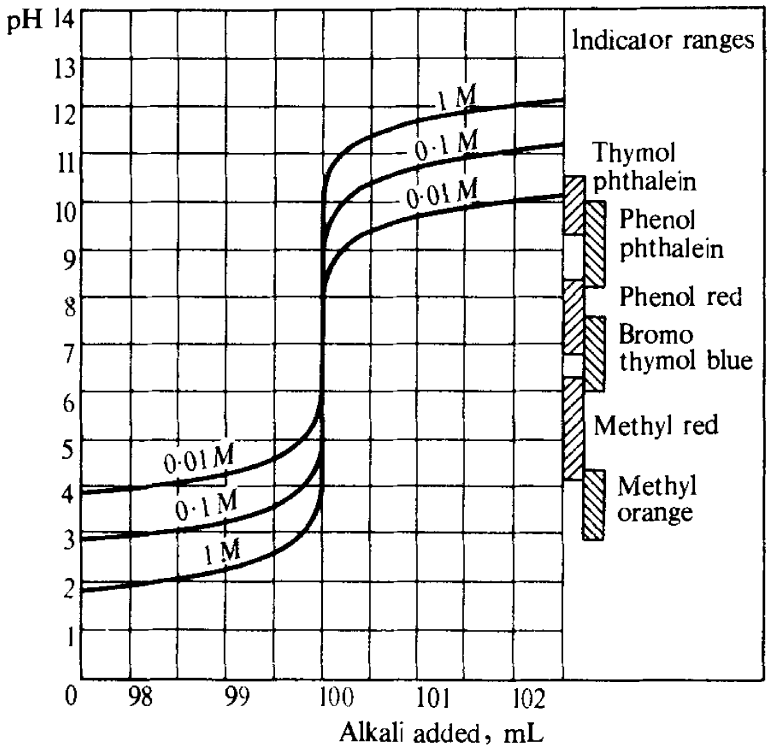


Fig. 10.3 Neutralisation curves of 100 mL of HCl with NaOH of same concentration in vicinity of equivalence point (calculated).

arising from the small quantity of carbonate in the sodium hydroxide and/or from the atmosphere. The gas is in equilibrium with carbonic acid, of which both stages of ionisation are weak. This will introduce a small error when

indicators of high pH range (above pH 5) are used, e.g. phenolphthalein or thymolphthalein. More acid indicators, such as methyl orange and methyl yellow, are unaffected by carbonic acid. The difference between the amounts of sodium hydroxide solution used with methyl orange and phenolphthalein is not greater than 0.15–0.2 mL of 0.1 *M* sodium hydroxide when 100 mL of 0.1 *M* hydrochloric acid are titrated. A method of eliminating this error, other than that of selecting an indicator with a pH range below pH 5, is to boil the solution while still acid to expel carbon dioxide and then to continue the titration with the cold solution. Boiling the solution is particularly efficacious when titrating dilute (e.g. 0.01 *M*) solutions.

10.13 NEUTRALISATION OF A WEAK ACID WITH A STRONG BASE

The neutralisation of 100 mL of 0.1 *M* acetic acid (ethanoic acid) with 0.1 *M* sodium hydroxide solution will be considered here; other concentrations can be treated similarly. The pH of the solution at the equivalence point is given by (Section 2.19)

$$\text{pH} = \tfrac{1}{2}\text{p}K_w + \tfrac{1}{2}\text{p}K_a - \tfrac{1}{2}\text{p}c = 7 + 2.37 - \tfrac{1}{2}(1.3) = 8.72$$

For other concentrations, we may employ the approximate Mass Action expression:

$$[\text{H}^+] \times [\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}] = K_a \qquad (6)$$

or $[\text{H}^+] = [\text{CH}_3\text{COOH}] \times K_a/[\text{CH}_3\text{COO}^-]$

or $\text{pH} = \log[\text{Salt}]/[\text{Acid}] + \text{p}K_a \qquad (7)$

The concentration of the salt (and of the acid) at any point is calculated from the volume of alkali added, due allowance being made for the total volume of the solution.

The initial pH of 0.1 *M* acetic acid is computed from equation (6); the dissociation of the acid is relatively so small that it may be neglected in expressing the concentration of acetic acid. Hence from equation (6):

$$[\text{H}^+] \times [\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}] = 1.82 \times 10^{-5}$$

or $[\text{H}^+]^2/0.1 = 1.82 \times 10^{-5}$

or $[\text{H}^+] = \sqrt{1.82 \times 10^{-6}} = 1.35 \times 10^{-3}$

or $\text{pH} = 2.87$

When 50 mL of 0.1 *M* alkali have been added,

$$[\text{Salt}] = 50 \times 0.1/150 = 3.33 \times 10^{-2}$$

and $[\text{Acid}] = 50 \times 0.1/150 = 3.33 \times 10^{-2}$

$$\text{pH} = \log(3.33 \times 10^{-2}/3.33 \times 10^{-2}) + 4.74 = 4.74$$

The pH values at other points on the titration curve are similarly calculated. After the equivalence point has been passed, the solution contains excess of OH^- ions which will repress the hydrolysis of the salt; the pH may be assumed, with sufficient accuracy for our purpose, to be that due to the excess of base present, so that in this region the titration curve will almost coincide with that

10.18 CHOICE OF INDICATORS IN NEUTRALISATION REACTIONS

As a general rule, for a titration to be feasible there should be a change of approximately two units of pH at or near the stoichiometric point produced by the addition of a small volume of the reagent. The pH at the equivalence point may be calculated by using the equations given in Section 2.19 (see also below), the pH at either side of the equivalence point (0.1–1 mL) may be calculated as described in the preceding sections, and the difference will indicate whether the change is large enough to permit a sharp end point to be observed. Alternatively, the pH change on both sides of the equivalence point may be obtained from the neutralisation curve determined by potentiometric titration (Sections 15.15 and 15.20). If the pH change is satisfactory, an indicator should be selected that changes at or near the equivalence point.

For convenience of reference, the conclusions already deduced from theoretical principles are summarised below.

Strong acid and strong base. For 0.1 M or more concentrated solutions, any indicator may be used which has a range between the limits pH 4.5 and pH 9.5. With 0.01 M solutions, the pH range is somewhat smaller (5.5–8.5). If carbon dioxide is present, either the solution should be boiled while still acid and the solution titrated when cold, or an indicator with a range below pH 5 should be employed.

Weak acid and a strong base. The pH at the equivalence point is calculated from the equation:

$$\mathrm{pH} = \tfrac{1}{2}\mathrm{p}K_w + \tfrac{1}{2}\mathrm{p}K_a - \tfrac{1}{2}\mathrm{p}c$$

The pH range for acids with $K_a > 10^{-5}$ is 7–10.5; for weaker acids ($K_a > 10^{-6}$) the range is reduced (8–10). The pH range 8–10.5 will cover most of the examples likely to be encountered; this permits the use of thymol blue, thymolphthalein, or phenolphthalein.

Weak base and strong acid. The pH at the equivalence point is computed from the equation:

$$\mathrm{pH} = \tfrac{1}{2}\mathrm{p}K_w - \tfrac{1}{2}\mathrm{p}K_b + \tfrac{1}{2}\mathrm{p}c$$

The pH range for bases with $K_b > 10^{-5}$ is 3–7, and for weaker bases ($K_b > 10^{-6}$) 3–5. Suitable indicators will be methyl red, methyl orange, methyl yellow, bromocresol green, and bromophenol blue.

Weak acid and weak base. There is no sharp rise in the neutralisation curve and, generally, no simple indicator can be used. The titration should therefore be avoided, if possible. The approximate pH at the equivalence point can be computed from the equation:

$$\mathrm{pH} = \tfrac{1}{2}\mathrm{p}K_w + \tfrac{1}{2}\mathrm{p}K_a - \tfrac{1}{2}\mathrm{p}K_b$$

It is sometimes possible to employ a mixed indicator (see Section 10.9) which exhibits a colour change over a very limited pH range, for example, neutral red–methylene blue for dilute ammonia solution and acetic (ethanoic) acid.

Polyprotic acids (or mixtures of acids, with dissociation constants K_1, K_2, and K_3) and strong bases. The first stoichiometric end point is given approximately

by:

$$pH = \tfrac{1}{2}(pK_1 + pK_2)$$

The second stoichiometric end point is given approximately by:

$$pH = \tfrac{1}{2}(pK_2 + pK_3)$$

Anion of a weak acid titrated with a strong acid. The pH at the equivalence point is given by:

$$pH = \tfrac{1}{2}pK_w - \tfrac{1}{2}pK_a - \tfrac{1}{2}pc$$

Cation of a weak base titrated with a strong base. The pH at the stoichiometric end point is given by:

$$pH = \tfrac{1}{2}pK_w - \tfrac{1}{2}pK_b - \tfrac{1}{2}pc$$

As a general rule, wherever an indicator does not give a sharp end point, it is advisable to prepare an equal volume of a comparison solution containing the same quantity of indicator and of the final products and other components of the titration as in the solution under test, and to titrate to the colour shade thus obtained.

In cases where it proves impossible to find a suitable indicator (and this will occur when dealing with strongly coloured solutions) then titration may be possible by an electrometric method such as conductimetric, potentiometric or amperometric titration; see Chapters 13–16. In some instances, spectrophotometric titration (Chapter 17) may be feasible. It should also be noted that if it is possible to work in a non-aqueous solution rather than in water, then acidic and basic properties may be altered according to the solvent chosen, and titrations which are difficult in aqueous solution may then become easy to perform. This procedure is widely used for the analysis of organic materials but is of very limited application with inorganic substances and is discussed in Sections 10.19–10.21.

10.19 TITRATIONS IN NON-AQUEOUS SOLVENTS

The Brønsted–Lowry theory of acids and bases referred to in Section 10.7 can be applied equally well to reactions occurring during acid–base titrations in non-aqueous solvents. This is because their approach considers an acid as any substance which will tend to donate a proton, and a base as a substance which will accept a proton. Substances which give poor end points due to being weak acids or bases in aqueous solution will frequently give far more satisfactory end points when titrations are carried out in non-aqueous media. An additional advantage is that many substances which are insoluble in water are sufficiently soluble in organic solvents to permit their titration in these non-aqueous media.

In the Brønsted–Lowry theory, any acid (HB) is considered to dissociate in solution to give a proton (H^+) and a conjugate base (B^-); whilst any base (B) will combine with a proton to produce a conjugate acid (HB^+).

$$HB \rightleftharpoons H^+ + B^- \qquad (a)$$

$$B + H^+ \rightleftharpoons HB^+ \qquad (b)$$

The ability of substances to act as acids or bases will depend very much upon

the nature of the solvent system which is employed. Non-aqueous solvents are classified into the four groups: aprotic solvents, protophilic solvents, protogenic solvents, and amphiprotic solvents.

Aprotic solvents include those substances which may be considered to be chemically neutral and virtually unreactive under the conditions employed. Carbon tetrachloride and benzene come in this group, they possess low dielectric constants, do not cause ionisation in solutes and do not undergo reactions with acids and bases. Aprotic solvents are frequently used to dilute reaction mixtures while taking no part in the overall process.

Protophilic solvents are substances such as liquid ammonia, amines and ketones which possess a high affinity for protons. The overall reaction taking place can be represented as:

$$HB + S \rightleftharpoons SH^+ + B^- \qquad (c)$$

The equilibrium in this reversible reaction will be greatly influenced by the nature of the acid and that of the solvent. Weak acids are normally used in the presence of strongly protophilic solvents as their acidic strengths are then enhanced and then become comparable to those of strong acids — this is referred to as the '**levelling effect**'.

Protogenic solvents are acidic in nature and readily donate protons. Anhydrous acids such as hydrogen fluoride and sulphuric acid fall in this category; because of their strength and ability to donate protons they enhance the strength of weak bases.

Amphiprotic solvents consist of liquids, such as water, alcohols and weak organic acids, which are slightly ionised and combine both protogenic and protophilic properties in being able to donate and to accept protons.

Thus, acetic (ethanoic) acid displays acidic properties in dissociating to produce protons:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

But in the presence of perchloric acid, which is a far stronger acid, acetic acid will accept a proton:

$$CH_3COOH + HClO_4 \rightleftharpoons CH_3COOH_2^+ + ClO_4^-$$

The $CH_3COOH_2^+$ ion so formed can very readily give up its proton to react with a base. A weak base will, therefore, have its basic properties enhanced, and as a consequence titrations between weak bases and perchloric acid can frequently be readily carried out using acetic acid as solvent.

In general, strongly protophilic solvents lead to the equilibrium of equation (*c*) being forced to the right. This effect is so powerful that in such solvents all acids act as if they were of similar strength. The converse of this occurs with strongly protogenic solvents which cause all bases to act as if they were of similar strength. Solvents which act in this way are known as 'levelling' solvents.

Determinations in non-aqueous solvents are of importance for substances which may give poor end points in normal aqueous titrations and for substances which are not soluble in water. They are also of particular value for determining the proportions of individual components in mixtures of either acids or of bases. These differential titrations are carried out in solvents which do not exert a levelling effect.

Whilst indicators may be used to establish individual end points, as in

traditional acid–base titrations, potentiometric methods of end point detection are also used extensively, especially for highly coloured solutions.

Non-aqueous titrations have been used to quantify mixtures of primary, secondary and tertiary amines,[5] for studying sulphonamides, mixtures of purines and for many other organic amino compounds and salts of organic acids.

10.20 SOLVENTS FOR NON-AQUEOUS TITRATIONS

A very large number of both inorganic and organic solvents have been used for non-aqueous determinations, but a few have been used more frequently than most. Some of the most widely applied solvent systems are discussed below. In all instances pure, dry analytical reagent quality solvents should be used to assist in obtaining sharp end points.

Glacial acetic acid (ethanoic acid) is by far the most frequently employed solvent for this purpose. Before it is used it is advisable to check the water content, which may be between 0.1 and 1.0%, and to add just sufficient acetic anhydride to convert any water to the acid. The acid may be used by itself or in conjunction with other solvents such as acetic anhydride, acetonitrile and nitromethane.

Acetonitrile (methyl cyanide, cyanomethane) is frequently used with other solvents such as chloroform and phenol, and particularly with acetic acid. It enables very sharp end points to be obtained in the titration of metal acetates[6] when titrated with perchloric acid.

Alcohols: it has been found that determinations of salts of organic acids and especially of soaps are best carried out in solvent mixtures of glycols and alcohols or of glycols and hydrocarbons. The most common combinations of this type are ethylene glycol (dihydroxyethane) with propan-2-ol or butan-1-ol. The combinations provide admirable solvent power for both the polar and non-polar ends of the molecule. Another suitable solvent mixture is methanol and benzene.

Dioxan is another popular solvent which is often used in place of glacial acetic acid when mixtures of substances are to be quantified. Unlike acetic acid, dioxan is not a levelling solvent and separate end points are normally possible corresponding to the individual components in the mixtures.

Dimethylformamide (DMF) is a protophilic solvent which is frequently employed for titrations between, for instance, benzoic acid and amides, although end points may sometimes be difficult to obtain.

10.21 INDICATORS FOR NON-AQUEOUS TITRATIONS

The various relationships concerning the interconversion between un-ionised and ionised or different resonant forms of indicators referred to in Section 10.7 apply equally well to those indicators used for non-aqueous titrations. However, in this type of titration the colour change exhibited by an indicator at the end point is not always the same for different titrations as it depends upon the nature of the titrand to which it has been added. The colour corresponding to the correct end point may be established by carrying out a potentiometric titration while simultaneously observing the colour change of the indicator. The appropriate colour corresponds to the inflexion point of the titration curve (see Section 15.18).

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.

BUFFER SOLUTIONS:

A solution of hydrochloric acid (0.0001 mol L^{-1}) should have a pH equal to 4, but the solution is extremely sensitive to traces of alkali from the glass of the containing vessel and to ammonia from the air. Likewise a solution of sodium hydroxide (0.0001 mol L^{-1}), which should have a pH of 10, is sensitive to traces of carbon dioxide from the atmosphere. Aqueous solutions of potassium chloride and of ammonium acetate have a pH of about 7. The addition to 1 L of these solutions of 1 ml of a solution of hydrochloric acid (1 mol L^{-1}) results in a change of pH to 3 in the former case and in very little change in the latter.

The resistance of a solution to changes in hydrogen ion concentration upon the addition of small amounts of acid or alkali is termed as buffer action; a solution which possesses such properties is known as a buffer solution. Buffer soln. eqn ☞

It is said to possess 'reserve acidity' and 'reserve alkalinity'. Buffer solutions usually consist of solutions containing a mixture of a weak acid HA and its sodium or potassium Salt (A^-), or of a weak base B and its Salt (BH^+). A buffer is usually a mixture of an acid and its conjugate base. In order to understand buffer action, consider first the equilibrium between a weak acid and its salt. The dissociation of a weak acid is given by:

$$HA \rightleftharpoons H^+ + A^-$$

and its magnitude is controlled by the value of the dissociation constant Ka:

$$\frac{a_{H^+} \times a_{A^-}}{a_{HA}} = K_a, \quad \text{or} \quad a_{H^+} = \frac{a_{HA}}{a_{A^-}} \times K_a \qquad (17)$$

The expression may be approximated by writing concentrations for activities:

$$[H^+] = \frac{[HA]}{[A^-]} \times K_a$$

This equilibrium applies to a mixture of an acid HA and its salt, say MA. If the concentration of the acid be C_a and that of the salt be C_s, then the concentration of the undissociated portion of the acid is $(C_a - [H^+])$. The solution is electrically neutral, hence $[A^-] = C_s + [H^+]$ (the Salt is completely dissociated). Substituting these values in the above equilibrium equation, we have:

$$[H^+] = \frac{c_a - [H^+]}{c_s + [H^+]} \times K_a \qquad (19)$$

It can be simplified by introducing the following further approximations. In a mixture of a weak acid and its salt, the dissociation of the acid is repressed by the common ion effect, and $[H^+]$ may be taken as negligibly small by comparison with C_a and C_s. Equation (19) then reduces to:

$$[H^+] = \frac{C_a}{C_s} . K_a, \quad \text{or} \quad [H^+] = \frac{[\text{Acid}]}{[\text{Salt}]} \times K_a \tag{20}$$

$$\text{or} \quad pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \tag{21}$$

The equations can be readily expressed in a somewhat more general form when applied to a Bronsted-Lowry acid A and its conjugate base B:

$$A \rightleftharpoons H^+ + B$$

(e.g. CH_3COOH and CH_3COO^-, etc.). The expression for pH is:

$$pH = pK_a + \log \frac{[B]}{[A]}$$

where $K_a = [H^+][B]/[A]$.

Similarly for a mixture of a weak base of dissociation constant K_b and its salt with a strong acid:

$$[OH^-] = \frac{[\text{Base}]}{[\text{Salt}]} \times K_b \tag{22}$$

$$\text{or} \quad pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \tag{23}$$

Confining attention to the case in which the concentrations of the acid and its Salt are equal, i.e. of a half-neutralized acid then $pH = pK_a$. Thus the pH of a half-neutralized solution of a weak acid is equal to the negative logarithm of the dissociation constant of the acid. For acetic (ethanoic) acid, $K_a = 1.75 \times 10^{-5}$ mol L^{-1}, $pK_a = 4.76$; a half-neutralized solution of, Say 0.1M acetic acid will have a pH of 4.76. If we add a small concentration of H^+ ions to such a solution, the former will combine with acetate ions to form undissociated acetic acid:

$$H^+ + CH_3COO^- \rightleftharpoons CH_3COOH$$

Similarly, if a small concentration of hydroxide ions is added, then OH-1 will combine with the hydrogen ions arising from the dissociation of the acetic acid and form water; the equilibrium will be disturbed, and more acetic acid will dissociate to replace the hydrogen ions removed in this way. In either case, the concentration of the acetic acid and acetate ion (or salt) will not be appreciably changed. It follows from equation (21) that the pH of the solution will not be materially affected.

Example 12. Calculate the pH of the solution produced by adding 10 mL of 1 *M* hydrochloric acid to 1 L of a solution which is 0.1 *M* in acetic (ethanoic) acid and 0.1 *M* in sodium acetate ($K_a = 1.75 \times 10^{-5}$ mol L^{-1}).

The pH of the acetic acid-sodium acetate buffer solution is given by the equation:

$$pH = pK_a + \log \frac{[Salt]}{[Acid]} = 4.76 + 0.0 = 4.76$$

The hydrogen ions from the hydrochloric acid react with acetate ions forming practically undissociated acetic acid, and neglecting the change in volume from 1000 mL to 1010 mL we can say

$$CH_3COO^- = 0.1 - 0.01 = 0.09$$

$$CH_3COOH = 0.1 + 0.01 = 0.11$$

$$\text{and} \quad pH = 4.76 + \log 0.09/0.11 = 4.76 - 0.09 = 4.67$$

Thus the pH of the acetic acid-sodium acetate buffer solution is only altered by 0.09 pH unit on the addition of the hydrochloric acid. The same volume of hydrochloric acid added to 1 litre of water (pH = 7) would lead to a solution with pH = -log(O.Ol) = 2; a change of 5 pH units.

STANDARDISATION OF APPROXIMATELY 0.1 M SODIUM HYDROXIDE

If the solution contains carbonate, methyl-orange, methyl orange-indigo carmine, or bromophenol blue must be used in standardization against hydrochloric acid of known molar concentration. Phenolphthalein or other indicators with a similar pH range, which are affected by carbon dioxide, cannot be used at the ordinary temperature. With carbonate-free sodium hydroxide phenolphthalein or thymol blue may be employed, and standardisation may be effected against hydrochloric acid, potassium hydrogeniodate, potassium hydrogenphthalate, benzoic acid, or other organic acids.

Procedure A: with standard hydrochloric acid.

Place the standardized (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 standardized 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 *VA* and *mA* refer to the volume and known molarity of the acid respectively, *VB* is the volume of alkali solution required for the neutralisation, and *m*, is its (unknown) molarity.

Procedure B: with potassium hydrogenphthalate.

Analytical grade potassium hydrogenphthalate has a purity of at least 99.9 percent; it is almost non-hygroscopic, but, it is advisable to dry it at 120 °C for 2 hours, and allow it to cool in a covered vessel in desiccators. Weigh out three 0.6-0.7-g portions of the salt into 250mL Pyrex conical flasks, add 75 mL of boiled-out water to each portion, stopper 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 the above calculations. The R.M.M. of potassium hydrogenphthalate is 204.22. The variation in the results should not exceed 0.1-0.2 per cent.

$$HK(C_8H_4O_4) + NaOH = NaK(C_8H_4O_4) + H_2O$$

Succinic acid {$(CH_2COOH)_2$,; R.M.M.=118.09}. The pure commercial product should be recrystallised from pure acetone and dried in a vacuum desiccator. The purity is checked by means of a melting-point determination

(185-185.5 °C). The acid is fairly soluble in water; phenolphthalein is a suitable indicator.

DETERMINATION OF THE Na_2CO_3 CONTENT OF WASHING SODA

Procedure. Weigh out accurately about 3.5 g of the washing-soda crystals,

dissolve in water, and make up to 250 mL in a graduated flask. Mix thoroughly. Titrate 25 mL of the solution with standard hydrochloric acid of approximately 0.1 M concentration using methyl orange, or, better, methyl orange-indigo carmine or bromocresol green as indicator. Two consecutive titrations should agree within 0.05 mL.

Calculation. The weight of anhydrous sodium carbonate, Na2C03, which has reacted with the standard hydrochloric acid, can be readily calculated from the equation:

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$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$$

106.01 2×36.46

The percentage of Na2C03 can then be calculated from the known weight of washing soda employed. A simpler and more general procedure is illustrated by the following example.

Weight of weighing bottle + substance = 16.7910 g

Weight of weighing bottle + residual substance = 13.0110 g

∴ Weight of sample used = 3.7800 g

This was dissolved in water and made up to 250mL. Titration of 25.00 mL of the carbonate solution with 0.1060M HCl, using methyl orange-indigo carmine as indicator.

$$1\ mL\ 1M\ HCl \equiv 0.05300\ g\ Na_2CO_3$$

$$25.93 \times 0.1060 \equiv 2.749\ mL\ 1M\ HCl$$

$2.749 \times 0.05300 = 0.1457$ g Na_2CO_3 in portion titrated.

Weight of washing soda in portion titrated $= 3.7800 \times 25.0/250 = 0.3780$ g

∴ Percentage of $Na_2CO_3 = 0.1457 \times 100/0.3780 = 38.54$ per cent

Alternative method of calculation. 25.0 mL of the carbonate solution required 25.93 mL of 0.1060*M* HCl.

But 72.92 g HCl ≡ 106.01 g Na_2CO_3

$$25.93\ mL\ of\ 0.1060M\ HCl \equiv \frac{25.93 \times 0.1060}{1000} \times 36.46\ g\ HCl \equiv 0.1002\ g\ HCl$$

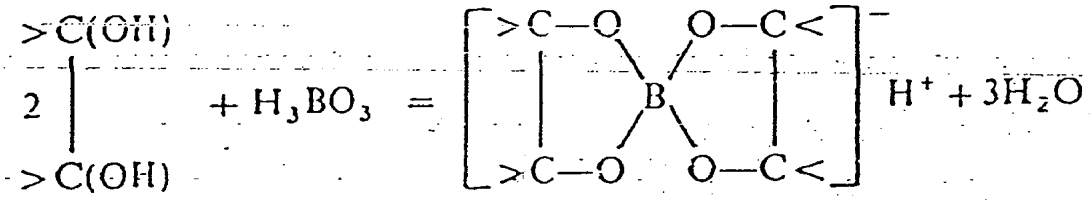
$$\therefore 25\ mL\ Na_2CO_3\ solution\ contain \frac{0.1002}{72.92} \times 106.01\ g\ Na_2CO_3$$

$$\therefore 3.78\ g\ washing\ soda\ contain \frac{0.1002 \times 106.01 \times 250\ g}{72.92 \times 25} Na_2CO_3$$

$$= 1.457\ g = 38.54\ per\ cent$$

DETERMINATION OF BORIC ACID

Discussion. Boric acid acts as a weak monoprotic acid (Ka = 6.4 x 10^{-10}); it cannot be titrated accurately with 0.1 M standard alkali. However, by the addition of certain organic poly-hydroxy compounds, such as mannitol, glucose, sorbitol, or glycerol. It acts as a much stronger acid (for mannitol Ka = 1.5 x 10^{-4}) and can be titrated to a phenolphthalein end point. The effect of poly-hydroxy compounds has been explained on the basis of the formation of 1:1 and 1 :2-mole ratio complexes between the hydrated borate ion and 1,2- or 1,3-diols:



Glycerol has been widely employed for this purpose but mannitol and sorbitol are more effective, and have the advantage that being solids they do not materially increase the volume of the solution being titrated: 0.5-0.7 g of mannitol or sorbitol in 10 mL of solution is a convenient quantity.

The method may be applied to commercial boric acid, but as this material may contain ammonium salts it is necessary to add a slight excess of sodium carbonate solution and then to boil down to expel ammonia. Any precipitate which separates is filtered off and washed thoroughly, then the filtrate is neutralised to methyl red, and after boiling, mannitol is added, and the solution titrated with standard 0.1 M sodium hydroxide solution:

$$H[\text{boric acid complex}] + NaOH = Na[\text{boric acid complex}] + H_2O$$

$$1\ mL\ 1M\ NaOH \equiv 0.06184\ g\ H_3BO_3$$

A mixture of boric acid and a strong acid can be analysed by first titrating the strong acid using methyl red indicator, and then after adding mannitol or sorbitol, the titration is continued using phenolphthalein as indicator. Mixtures of sodium tetraborate and boric acid can be similarly analysed by titrating the salt with standard hydrochloric acid and then adding mannitol and continuing the titration with standard sodium hydroxide solution: it must of course be borne in mind that in this second titration the boric acid liberated in the first titration will also react.

Procedure. To determine the purity of a sample of boric acid, weigh accurately about 0.8 g of the acid, transfer quantitatively to a 250 mL graduated flask and make up to the mark. Pipette 25 mL of the solution into a 250 mL conical flask, add an equal volume of distilled water, 2.5-3 g of mannitol or sorbitol, and titrate with standard 0.1 M sodium hydroxide solution using phenolphthalein as indicator. It is advisable to

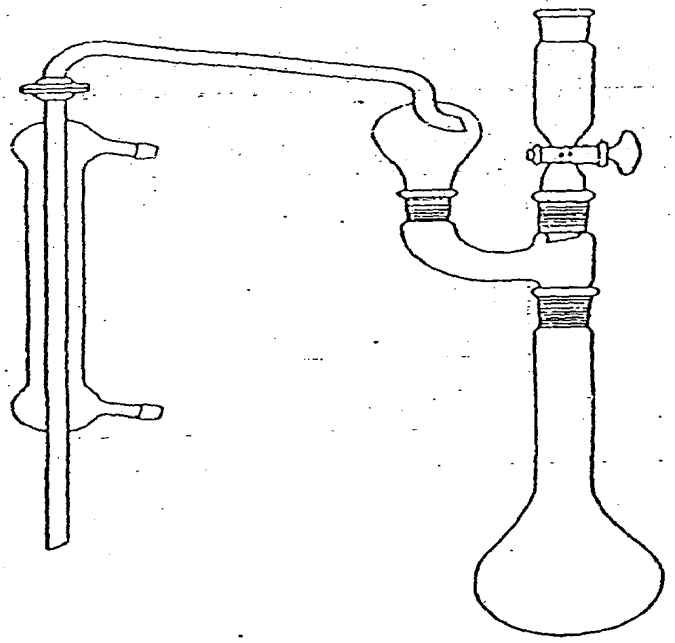
check whether any blank correction must be made: dissolve a similar weight of mannitol (sorbitol) in 50 mL of distilled water, add phenolphthalein, and ascertain how much sodium hydroxide solution must be added to produce the characteristic end point colour.

DETERMINATION OF ORGANIC NITROGEN:

(THE KJELDAHL PROCEDURE)

Discussion. Kjeldahl procedure is used very extensively as it is a highly reliable technique with well-established routines. The basic concept of the method is the digestion of organic material (containing nitrogen), e.g. proteins, using sulphuric acid and a catalyst to convert any organic nitrogen to ammonium sulphate in solution. By making the mixture alkaline any ammonia can be steam-distilled off and the resulting alkaline distillate titrated with standard acid.

Procedure. Weigh out accurately part of the organic sample, sufficient to contain about 0.04g of nitrogen, and place it in the long-necked Kjeldahl digestion flask. Add 0.7 g of mercury(II) oxide, 15 g of potassium sulphate and 40 mL of concentrated sulphuric acid. Heat the flask gently in a slightly inclined position. Some frothing is likely to occur and may be controlled by the use of an anti-foaming agent. When foaming ceases boil the reactants for 2 h.



After cooling, add 200 mL of water and 25 mL of 0.5 M sodium thiosulphate solution and mix well. To the mixture add a few anti-bumping granules, then carefully pour sufficient 10 M sodium hydroxide solution down the inside of the flask to make the mixture strongly alkaline (approximately 115mL). Before mixing the reagents, connect the flask to a distillation apparatus (Fig.) in which the tip of the delivery tube is submerged just below the surface of a measured volume of 0.1 M hydrochloric acid. Ensure that the contents of the distillation flask are well mixed, then boil until at least 150 mL of liquid have been distilled into the receiver.

Add methyl red indicator to the hydrochloric acid solution and titrate with 0.1 M sodium hydroxide (titration a mL). Carry out a blank titration on an equal measured volume of the 0.1 M hydrochloric acid (titration b mL). Using the quantities and concentrations given above, the percentage of nitrogen in the sample is given by:

$$N = \frac{(b-a) \times 0.1 \times 14 \times 100}{\text{Weight of sample (g)}} \text{ per cent}$$

DETERMINATION OF THE SAPONIFICATION VALUE OF OILS AND FATS

Discussion. For oils and fats, which are esters of long-chain fatty acids, the saponification value (or number) is defined as;

"The number of milligrams of potassium hydroxide which will neutralise the free fatty acids obtained from the hydrolysis of 1 g of the oil or fat."

This means that the saponification number is inversely proportional to the relative molecular masses of the fatty acids obtained from the esters. A typical reaction from the hydrolysis of a glyceride is:

$$\begin{array}{l} CH_2{-}O{-}CO{-}C_{17}H_{35} \\ | \\ CH{-}O{-}CO{-}C_{17}H_{35} \\ | \\ CH_2{-}O{-}CO{-}C_{17}H_{35} \end{array} + 3KOH \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3C_{17}H_{35}COOK$$

Stearin — Glycerol — Potassium stearate

Procedure. Prepare an approximately 0.5 M solution of potassium hydroxide by dissolving 30 g potassium hydroxide in 20 mL of water and make the final volume to 1 L using 95 per cent ethanol. Leave the solution to stand for 24 h before decanting and filtering the solution.

Using 25 mL aliquots, titrate the potassium hydroxide solution with 0.5 M hydrochloric acid using phenolphthalein indicator (record as titration a mL).

For the hydrolysis, accurately weigh approximately 2 g of the fat or oil into a 250 mL conical flask with a ground-glass joint and add 25 mL of the potassium hydroxide solution. Attach a reflux condenser and heat the flask contents on a steam bath for 1 h with occasional shaking. While the solution is still hot add phenolphthalein indicator and titrate the excess potassium hydroxide with the 0.5 M hydrochloric acid (record as titration b mL).

$$\text{The saponification value} = \frac{(a-b) \times 0.5 \times 56.1}{\text{Weight of sample (mg)}}$$