مقرر الكيمياء التحليلية (I)

لطلاب الفرقة الثالثة بكلية التربية تعليم عام

شعبة الكيمياء (برنامج اللغة الانجليزية)

القائم بالتدريس

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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The term 'volumetric analysis' was formerly used for this form of quantitative determination but it has now been replaced by **titrimetric analysis**.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 ($2Cl^- + Hg^{2+} \leftrightarrows HgCl_2$).

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

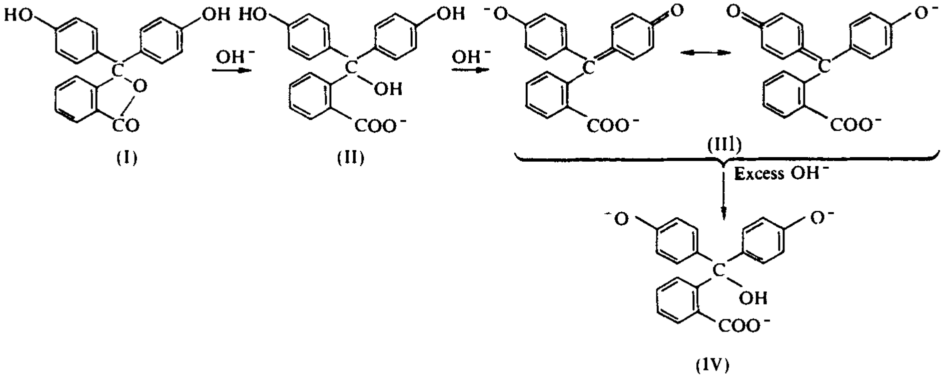
10.7 NEUTRALISATION INDICATORS

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 $\mathrm{In_A}$ and the basic form $\mathrm{In_B}$ may be expressed as:

$$\mathrm{In_A} \rightleftharpoons \mathrm{H^+} + \mathrm{In_B} \qquad (1)$$

and the equilibrium constant as:

$$\frac{a_{\mathrm{H^+}} \times a_{\mathrm{In_B}}}{a_{\mathrm{In_A}}} = K_{\mathrm{In}} \qquad (2)$$

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:

$$\frac{[\mathrm{In_A}]}{[\mathrm{In_B}]} = \frac{a_{\mathrm{H^+}} \times y_{\mathrm{In_B}}}{K_{\mathrm{In}} \times y_{\mathrm{In_A}}} \qquad (3)$$

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:

$$\text{pH} = -\log a_{\text{H}^+} = \text{pK}_{\text{In}} + \log\frac{[\text{In}_B]}{[\text{In}_A]} + \log\frac{y_{\text{In}_B}}{y_{\text{In}_A}} \tag{4}$$

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):

$$\text{pH} = \text{p}K'_{\text{In}} + \log\frac{[\text{In}_B]}{[\text{In}_A]} \tag{5}$$

where $\text{p}K'_{\text{In}}$ is termed the **apparent indicator constant**.

The value of the ratio $[\text{In}_B]/[\text{In}_A]$ (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 $[\text{In}_A]$ to $[\text{In}_B]$ is above approximately 10, and the 'alkaline' colour, i.e. of In_B, when the ratio of $[\text{In}_B]$ to $[\text{In}_A]$ is above approximately 10. Thus only the 'acid' colour will be visible when $[\text{In}_A]/[\text{In}_B] > 10$; the corresponding limit of pH given by equation (5) is:

$$\text{pH} = \text{p}K'_{\text{In}} - 1$$

Only the alkaline colour will be visible when $[\text{In}_B]/[\text{In}_A] > 10$, and the corresponding limit of pH is:

$$\text{pH} = \text{p}K'_{\text{In}} + 1$$

The colour-change interval is accordingly $\text{pH} = \text{p}K'_{\text{In}} \pm 1$, 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 $\text{p}K'_{\text{In}}$, the ratio $[\text{In}_A]$ to $[\text{In}_B]$ 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	—

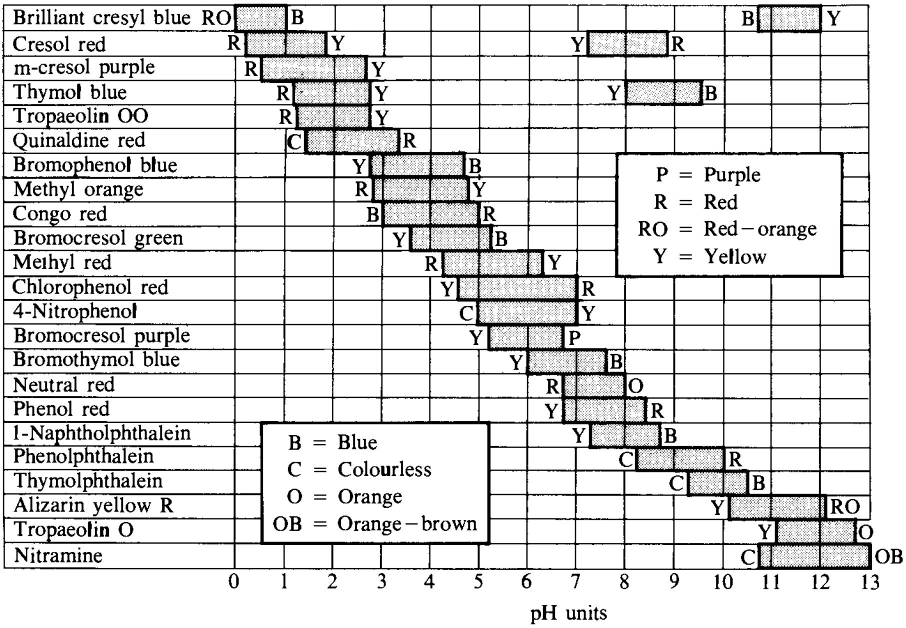


Fig. 10.1

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 $\mathrm{pH} \approx 7$ (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)

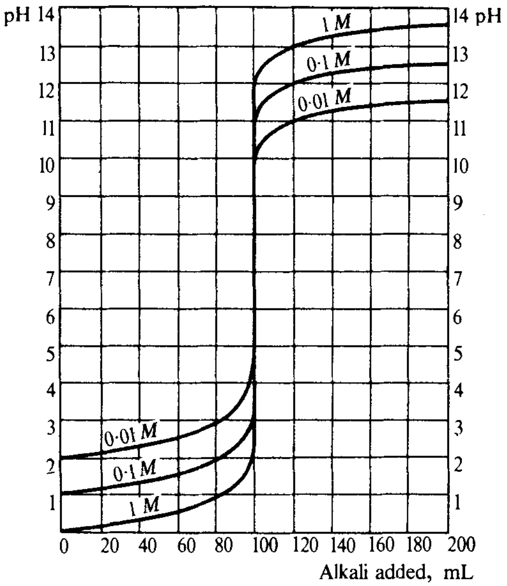


Fig. 10.2 Neutralisation curves of 100 mL of HCl with NaOH of same concentration (calculated).

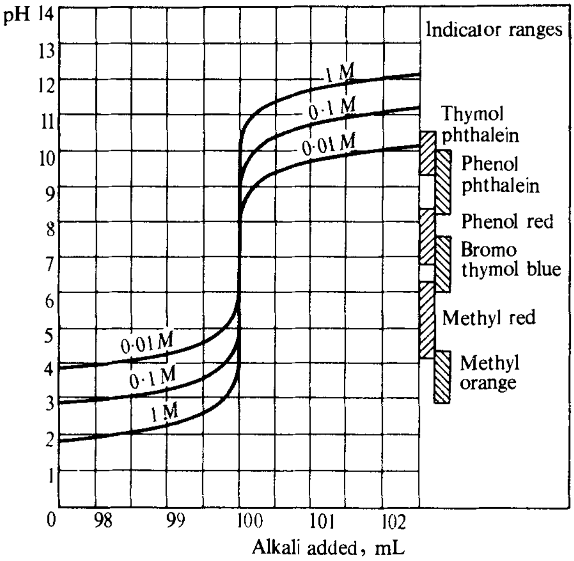


Fig. 10.3 Neutralisation curves of 100 mL of HCl with NaOH of same concentration in vicinity of equivalence point (calculated).

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)

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

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

$$[\mathrm{H^+}] \times [\mathrm{CH_3COO^-}]/[\mathrm{CH_3COOH}] = K_a \qquad (6)$$

$$\text{or} \quad [\mathrm{H^+}] = [\mathrm{CH_3COOH}] \times K_a/[\mathrm{CH_3COO^-}]$$

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

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):

$$[\mathrm{H^+}] \times [\mathrm{CH_3COO^-}]/[\mathrm{CH_3COOH}] = 1.82 \times 10^{-5}$$

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

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

$$\text{or} \quad \mathrm{pH} = 2.87$$

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

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

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

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

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 $\mathrm{OH^-}$ 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 for 0.1 M hydrochloric acid (Fig. 10.2 and Table 10.3). All the results are collected in Table 10.4, and are depicted graphically in Fig. 10.4. The results for the titration of 100 mL of 0.1 M solution of a weaker acid ($K_a = 1 \times 10^{-7}$) with 0.1 M sodium hydroxide at the laboratory temperature are also included.

Table 10.4 Neutralisation of 100 mL of 0.1M acetic acid ($K_a = 1.82 \times 10^{-5}$) and of 100 mL of 0.1$M$ HA ($K_a = 1 \times 10^{-7}$) with 0.1M sodium hydroxide

Vol. of 0.1M NaOH used (mL)	0.1M acetic acid (pH)	0.1M HA ($K_a = 1 \times 10^{-7}$) (pH)
0	2.9	4.0
10	3.8	6.0
25	4.3	6.5
50	4.7	7.0
90	5.7	8.0
99.0	6.7	9.0
99.5	7.0	9.3
99.8	7.4	9.7
99.9	7.7	9.8
100.0	8.7	9.9
100.2	10.0	10.0
100.5	10.4	10.4
101	10.7	10.7
110	11.7	11.7
125	12.0	12.0
150	12.3	12.3
200	12.5	12.5

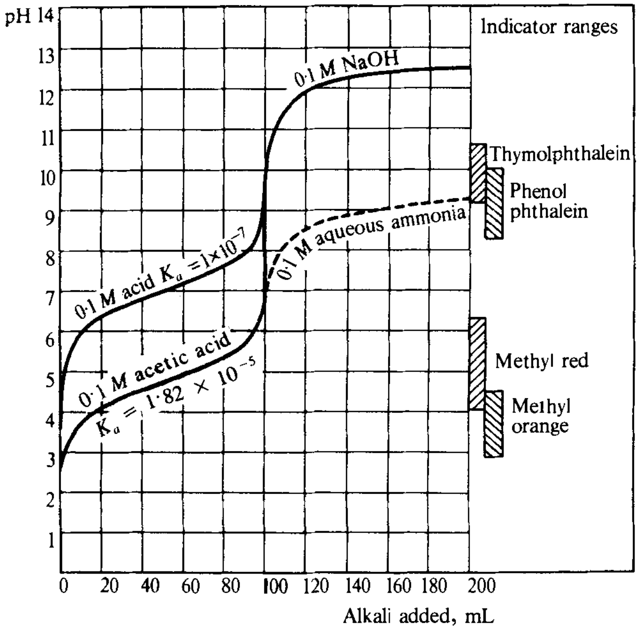


Fig. 10.4 Neutralisation curves of 100 mL of 0.1M acetic acid ($K_a = 1.82 \times 10^{-5}$) and of 0.1$M$ acid ($K_a = 1 \times 10^{-7}$) with 0.1M sodium hydroxide (calculated).

For 0.1M acetic acid and 0.1M sodium hydroxide, it is evident from the titration curve that neither methyl orange nor methyl red can be used as indicators. The equivalence point is at pH 8.7, and it is necessary to use an indicator with a pH range on the slightly alkaline side, such as phenolphthalein, thymolphthalein, or thymol blue (pH range, as base, 8.0–9.6). For the acid with $K_a = 10^{-7}$, the equivalence point is at pH = 10, but here the rate of change of pH in the neighbourhood of the stoichiometric point is very much less pronounced, owing to considerable hydrolysis. Phenolphthalein will commence to change colour after about 92 mL of alkali have been added, and this change will occur to the equivalence point; thus the end point will not be sharp and the titration error will be appreciable. With thymolphthalein, however, the colour change covers the pH range 9.3–10.5; this indicator may be used, the end point will be sharper than for phenolphthalein, but nevertheless somewhat gradual, and the titration error will be about 0.2 per cent. Acids that have dissociation constants less than 10^{-7} cannot be satisfactorily titrated in 0.1M solution with a simple indicator.

In general, it may be stated that weak acids ($K_a > 5 \times 10^{-6}$) should be titrated with phenolphthalein, thymolphthalein, or thymol blue as indicators.

10.14 NEUTRALISATION OF A WEAK BASE WITH A STRONG ACID

This may be illustrated by the titration of 100 mL of 0.1M aqueous ammonia ($K_b = 1.85 \times 10^{-5}$) with 0.1$M$ hydrochloric acid at the ordinary laboratory temperature. The pH of the solution at the equivalence point is given by the equation (Section 2.19):

$$\mathrm{pH} = \tfrac{1}{2}\mathrm{p}K_w - \tfrac{1}{2}\mathrm{p}K_b + \tfrac{1}{2}\mathrm{p}c = 7 - 2.37 + \tfrac{1}{2}(1.3) = 5.28$$

For other concentrations, the pH may be calculated with sufficient accuracy as follows (compare previous section):

$$[\mathrm{NH_4^+}] \times [\mathrm{OH^-}]/[\mathrm{NH_3}] = K_b \qquad (8)$$

$$\text{or} \quad [\mathrm{OH^-}] = [\mathrm{NH_3}] \times K_b/[\mathrm{NH_4^+}] \qquad (9)$$

$$\text{or} \quad \mathrm{pOH} = \log[\mathrm{Salt}]/[\mathrm{Base}] + \mathrm{p}K_b \qquad (10)$$

$$\text{or} \quad \mathrm{pH} = \mathrm{p}K_w - \mathrm{p}K_b - \log[\mathrm{Salt}]/[\mathrm{Base}] \qquad (11)$$

After the equivalence point has been reached, the solution contains excess of H^+ ions, hydrolysis of the salt is suppressed, and the subsequent pH changes may be assumed, with sufficient accuracy, to be those due to the excess of acid present.

The results computed in the above manner are represented graphically in Fig. 10.5; the results for the titration of 100 mL of a 0.1M solution of a weaker base ($K_b = 1 \times 10^{-7}$) are also included.

It is clear that neither thymolphthalein nor phenolphthalein can be employed in the titration of 0.1M aqueous ammonia. The equivalence point is at pH 5.3, and it is necessary to use an indicator with a pH range on the slightly acid side (3–6.5), such as methyl orange, methyl red, bromophenol blue, or bromocresol green. The last-named indicators may be utilised for the titration of all weak bases ($K_b > 5 \times 10^{-6}$) with strong acids.

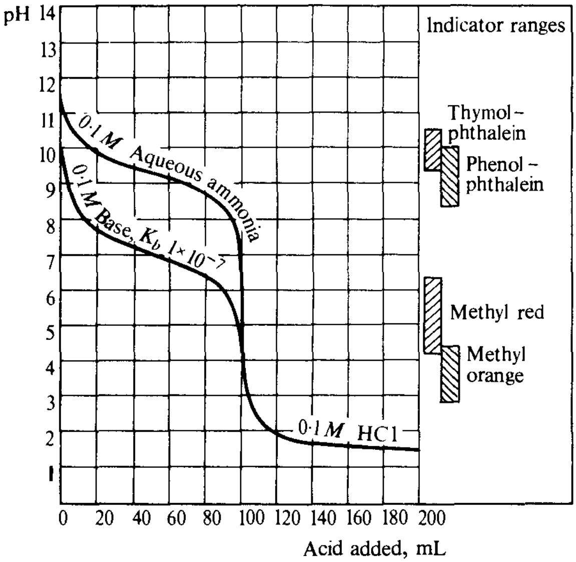


Fig. 10.5 Neutralisation curves of 100 mL 0.1*M* aqueous ammonia ($K_a = 1.8 \times 10^{-5}$) and of 0.1*M* base ($K_a = 1 \times 10^{-7}$) with 0.1*M* hydrochloric acid.

For the weak base ($K_b = 1 \times 10^{-7}$), bromophenol blue or methyl orange may be used; no sharp colour change will be obtained with bromocresol green or with methyl red, and the titration error will be considerable.

10.15 NEUTRALISATION OF A WEAK ACID WITH A WEAK BASE

This case is exemplified by the titration of 100 mL of 0.1 *M* acetic acid ($K_a = 1.82 \times 10^{-5}$) with 0.1 *M* aqueous ammonia ($K_b = 1.8 \times 10^{-5}$). The pH at the equivalence point is given by (Section 2.19)

$$\mathrm{pH} = \tfrac{1}{2}\mathrm{p}K_w + \tfrac{1}{2}\mathrm{p}K_a - \tfrac{1}{2}\mathrm{p}K_b = 7.0 + 2.38 - 2.37 = 7.1$$

The neutralisation curve up to the equivalence point is almost identical with that using 0.1 *M* sodium hydroxide as the base; beyond this point the titration is virtually the addition of 0.1 *M* aqueous ammonia solution to 0.1 *M* ammonium acetate solution and equation (11) (Section 10.14) is applicable to the calculation of the pH. The titration curve for the neutralisation of 100 mL of 0.1 *M* acetic acid with 0.1 *M* aqueous ammonia at the laboratory temperature is shown by the broken line in Fig. 10.4. The chief feature of the curve is that the change of pH near the equivalence point and, indeed, during the whole of the neutralisation curve is very gradual. There is no sudden change in pH, and hence no sharp end point can be found with any simple indicator. A mixed indicator, which exhibits a sharp colour change over a very limited pH range, may sometimes be found which is suitable. Thus for acetic acid–ammonia solution titrations, neutral red–methylene blue mixed indicator may be used (see Section 10.9), but on the whole, it is best to avoid the use of indicators in titrations involving *both* a weak acid and a weak base.

10.16 NEUTRALISATION OF A POLYPROTIC ACID WITH A STRONG BASE

The shape of the titration curve will depend upon the relative magnitudes of the various dissociation constants. It is assumed that titrations take place at the ordinary laboratory temperature in solutions of concentration of 0.1 *M* or stronger. For a diprotic acid, if the difference between the primary and secondary dissociation constants is very large ($K_1/K_2 > 10\,000$), the solution behaves like a mixture of two acids with constants K_1 and K_2 respectively; the considerations given previously may be applied. Thus for sulphurous acid, $K_1 = 1.7 \times 10^{-2}$ and $K_2 = 1.0 \times 10^{-7}$, it is evident that there will be a sharp change of pH near the first equivalence point, but for the second stage the change will be less pronounced, yet just sufficient for the use of, say, thymolphthalein as indicator (see Fig. 10.4). For carbonic acid, however, for which $K_1 = 4.3 \times 10^{-7}$ and $K_2 = 5.6 \times 10^{-11}$, only the first stage will be just discernible in the neutralisation curve (see Fig. 10.4); the second stage is far too weak to exhibit any point of inflexion and there is no suitable indicator available for direct titration. As indicator for the primary stage, thymol blue may be used (see Section 10.13), although a mixed indicator of thymol blue (3 parts) and cresol red (1 part) (see Section 10.9) is more satisfactory; with phenolphthalein the colour change will be somewhat gradual and the titration error may be several per cent.

It can be shown that the pH at the first equivalence point for a diprotic acid is given by

$$[H^+] = \sqrt{\frac{K_1 K_2 c}{K_1 + c}}$$

Provided that the first stage of the acid is weak and that K_1 can be neglected by comparison with c, the concentration of salt present, this expression reduces to

$$[H^+] = \sqrt{K_1 K_2}, \text{ or pH } = \tfrac{1}{2}\mathrm{p}K_1 + \tfrac{1}{2}\mathrm{p}K_2.$$

With a knowledge of the pH at the stoichiometric point and also of the course of the neutralisation curve, it should be an easy matter to select the appropriate indicator for the titration of any diprotic acid for which K_1/K_2 is at least 10^4. For many diprotic acids, however, the two dissociation constants are too close together and it is not possible to differentiate between the two stages. If K_2 is not less than about 10^{-7}, all the replaceable hydrogen may be titrated, e.g. sulphuric acid (primary stage — a strong acid), oxalic acid, malonic, succinic, and tartaric acids.

Similar remarks apply to triprotic acids. These may be illustrated by reference to phosphoric(V) acid (orthophosphoric acid), for which $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$, and $K_3 = 5 \times 10^{-13}$. Here $K_1/K_2 = 1.2 \times 10^5$ and $K_2/K_3 = 1.2 \times 10^5$, so that the acid will behave as a mixture of three monoprotic acids with the dissociation constants given above. Neutralisation proceeds almost completely to the end of the primary stage before the secondary stage is appreciably affected, and the secondary stage proceeds almost to completion before the tertiary stage is apparent. The pH at the first equivalence point is given approximately by $(\tfrac{1}{2}\mathrm{p}K_1 + \tfrac{1}{2}\mathrm{p}K_2) = 4.6$, and at the second equivalence point by $(\tfrac{1}{2}\mathrm{p}K_2 + \tfrac{1}{2}\mathrm{p}K_3) = 9.7$; in the very weak third stage, the curve is very flat and no indicator is available for direct titration. The third equivalence point may be calculated approximately from the equation (Section 10.13):

$$\mathrm{pH} = \tfrac{1}{2}\mathrm{p}K_w + \tfrac{1}{2}\mathrm{p}K_a - \tfrac{1}{2}\mathrm{p}c = 7.0 + 6.15 - \tfrac{1}{2}(1.6) = 12.35 \text{ for } 0.1M\ \mathrm{H_3PO_4}.$$

For the primary stage (phosphoric(V) acid as a monoprotic acid), methyl orange, bromocresol green, or Congo red may be used as indicators. The secondary stage of phosphoric(V) acid is very weak (see acid $K_a = 1 \times 10^{-7}$ in Fig. 10.4) and the only suitable simple indicator is thymolphthalein (see Section 10.14); with phenolphthalein the error may be several per cent. A mixed indicator composed of phenolphthalein (3 parts) and 1-naphtholphthalein (1 part) is very satisfactory for the determination of the end point of phosphoric(V) acid as a diprotic acid (see Section 10.9). The experimental neutralisation curve of 50 mL of 0.1*M* phosphoric(V) acid with 0.1*M* potassium hydroxide, determined by potentiometric titration, is shown in Fig. 10.6.

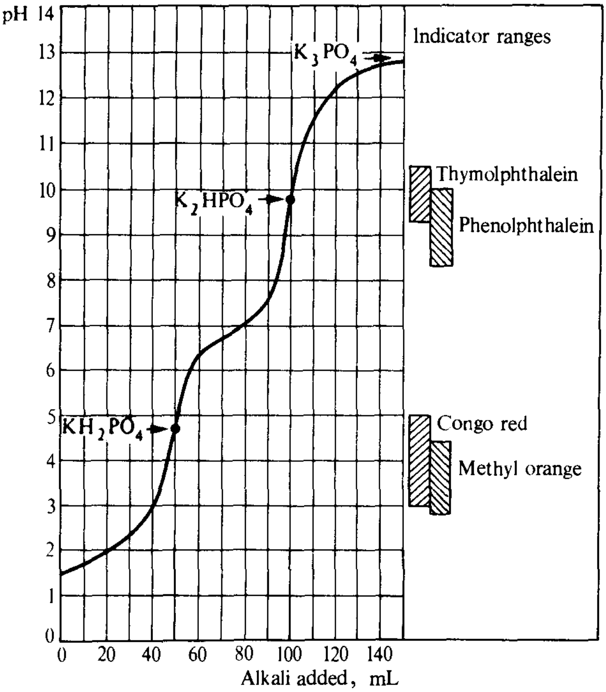


Fig. 10.6 Titration of 50 mL of 0.1*M* H_3PO_4 with 0.1*M* KOH.

There are a number of triprotic acids, e.g. citric acid with $K_1 = 9.2 \times 10^{-4}$, $K_2 = 2.7 \times 10^{-5}$, $K_3 = 1.3 \times 10^{-6}$, the three dissociation constants of which are too close together for the three stages to be differentiated easily. If $K_3 >$ *ca* 10^{-7}, all the replaceable hydrogen may be titrated; the indicator will be determined by the value of K_3.

10.17 TITRATION OF ANIONS OF WEAK ACIDS WITH STRONG ACIDS: 'DISPLACEMENT TITRATIONS'

So far the titrations considered have involved a strong base, the hydroxide ion, but titrations are also possible with weaker bases, such as the carbonate ion, the borate ion, the acetate ion, etc. Formerly titrations involving these ions were regarded as titrations of solutions of hydrolysed salts, and the net result was that the weak acid was displaced by the stronger acid. Thus in the titration of sodium acetate solution with hydrochloric acid the following equilibria were considered:

$CH_3.COO^- + H_2O \rightleftharpoons CH_3.COOH + OH^-$ (hydrolysis)

$H^+ + OH^- = H_2O$ (strong acid reacts with OH^- produced by hydrolysis).

The net result thus appeared to be:

$H^+ + CH_3COO^- = CH_3.COOH$

or $CH_3.COONa + HCl = CH_3.COOH + NaCl$

i.e. the weak acetic acid was apparently displaced by the strong hydrochloric acid, and the process was referred to as a **displacement titration**. According to the Brønsted–Lowry theory the so-called titration of solutions of hydrolysed salts is merely the titration of a weak base with a strong (highly ionised) acid. When the anion of a weak acid is titrated with a strong acid the titration curve is identical with that observed in the reverse titration of a weak acid itself with a strong base (compare Section 10.13).

A few examples encountered in practice include the following.

Titration of borate ion with a strong acid. The titration of the tetraborate ion with hydrochloric acid is similar to that described above. The net result of the displacement titration is given by:

$B_4O_7^{2-} + 2H^+ + 5H_2O = 4H_3BO_3$

Boric acid behaves as a weak monoprotic acid with a dissociation constant of 6.4×10^{-10}. The pH at the equivalence point in the titration of 0.2*M* sodium tetraborate with 0.2*M* hydrochloric acid is that due to 0.1*M* boric acid, i.e. 5.6. Further addition of hydrochloric acid will cause a sharp decrease of pH and any indicator covering the pH range 3.7–5.1 (and slightly beyond this) may be used; suitable indicators are bromocresol green, methyl orange, bromophenol blue, and methyl red.

Titration of carbonate ion with a strong acid. A solution of sodium carbonate may be titrated to the hydrogencarbonate stage (i.e. with one mole of hydrogen ions), when the net reaction is:

$CO_3^{2-} + H^+ = HCO_3^-$

The equivalence point for the primary stage of ionisation of carbonic acid is at $pH = (\frac{1}{2}pK_1 + \frac{1}{2}pK_2) = 8.3$, and we have seen (Section 10.14) that thymol blue and, less satisfactorily, phenolphthalein, or a mixed indicator (Section 10.9) may be employed to detect the end point.

Sodium carbonate solution may also be titrated until all the carbonic acid is displaced. The net reaction is then:

$CO_3^{2-} + 2H^+ = H_2CO_3$

The same end point is reached by titrating sodium hydrogencarbonate solution with hydrochloric acid:

$$HCO_3^- + H^+ = H_2CO_3$$

The end point with 100 mL of 0.2*M* sodium hydrogencarbonate and 0.2*M* hydrochloric acid may be deduced as follows from the known dissociation constant and concentration of the weak acid. The end point will obviously occur when 100 mL of hydrochloric acid has been added, i.e. the solution now has a total volume of 200 mL. Consequently since the carbonic acid liberated from the sodium hydrogencarbonate (0.02 moles) is now contained in a volume of 200 mL, its concentration is 0.1*M*. K_1 for carbonic acid has a value of 4.3×10^{-7}, and hence we can say:

$$[H^+] \times [HCO_3^-]/[H_2CO_3] = K_1 = 4.3 \times 10^{-7} \text{ mol L}^{-1}$$

and since

$$[H^+] = [HCO_3^-]$$

$$[H^+] = \sqrt{4.3 \times 10^{-7} \times 0.1} = 2.07 \times 10^{-4}$$

The pH at the equivalence point is thus approximately 3.7; the secondary ionisation and the loss of carbonic acid, due to any escape of carbon dioxide, have been neglected. Suitable indicators are therefore methyl yellow, methyl orange, Congo red, and bromophenol blue. The experimental titration curve, determined with the hydrogen electrode, for 100 mL of 0.1 *M* sodium carbonate and 0.1 *M* hydrochloric acid is shown in Fig. 10.7.

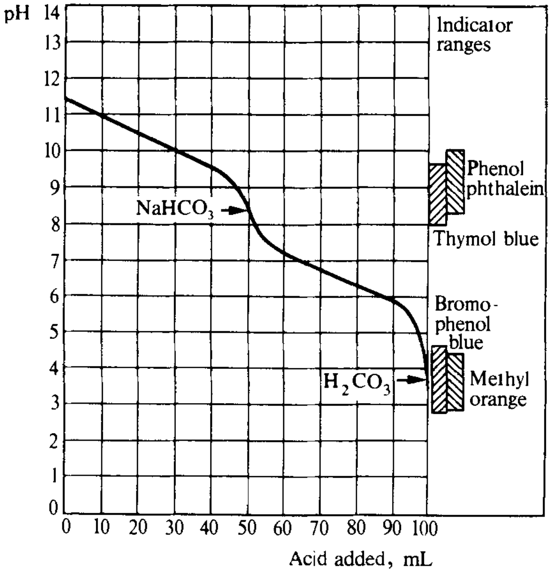


Fig. 10.7 Titration of 100 mL of 0.1*M* Na_2CO_3 with 0.1*M* HCl.

Cations of weak bases (i.e. Brønsted acids such as the phenylammonium ion $C_6H_5NH_3^+$) may be titrated with strong bases, and the treatment is similar. These were formerly regarded as salts of weak bases (e.g. aniline (phenylamine), $K_b = 4.0 \times 10^{-10}$) and strong acids: an example is aniline hydrochloride (phenylammonium chloride).

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:

$$\mathrm{pH} = \tfrac{1}{2}(\mathrm{p}K_1 + \mathrm{p}K_2)$$

The second stoichiometric end point is given approximately by:

$$\mathrm{pH} = \tfrac{1}{2}(\mathrm{p}K_2 + \mathrm{p}K_3)$$

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

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

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

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

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^+).

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

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

The ability of substances to act as acids or bases will depend very much upon concentrations. Substituting in the above equation, we obtain:

$$\frac{y_{A^+}.[A^+] \times y_{B^-}.[B^-]}{y_{AB}.[AB]} = \frac{[A^+].[B^-]}{[AB]} \times \frac{y_{A^+} \times y_{B^-}}{y_{AB}} = K_t$$

This is the rigorously correct expression for the Law of Mass Action as applied to weak electrolytes.

The activity coefficient varies with the concentration. For ions it also varies with the ionic charge, and is the same for all dilute solutions having the same **ionic strength**, the latter being a measure of the electrical field existing in the solution. The term ionic strength, designated by the symbol I, is defined as equal to one half of the sum of the products of the concentration of each ion multiplied by the square of its charge number, or $I = 0.5\Sigma c_i z_i^2$, where c_i is the ionic concentration in moles per litre of solution and z_i is the charge number of the ion concerned. An example will make this clear. The ionic strength of 0.1 M HNO_3 solution containing 0.2M $Ba(NO_3)_2$ is given by:

$$0.5\{0.1 \text{ (for } H^+) + 0.1 \text{ (for } NO_3^-)$$
$$+ 0.2 \times 2^2 \text{ (for } Ba^{2+}) + 0.2 \times 2 \text{ (for } NO_3^-)\} = 0.5\{1.4\} = 0.7$$

It can be shown on the basis of the Debye–Hückel theory that for aqueous solutions at room temperature:

$$\log y_i = -\frac{0.505 z_i^2 . I^{0.5}}{1 + 3.3 \times 10^7 a . I^{0.5}}$$

where y_i is the activity coefficient of the ion, z_i is the charge number of the ion concerned, I is the ionic strength of the solution, and a is the average 'effective diameter' of all the ions in the solution. For very dilute solutions ($I^{0.5} < 0.1$) the second term of the denominator is negligible and the equation reduces to:

$$\log y_i = -0.505 z_i^2 . I^{0.5}$$

For more concentrated solutions ($I^{0.5} > 0.3$) an additional term BI is added to the equation; B is an empirical constant. For a more detailed treatment of the Debye–Hückel theory a textbook of physical chemistry should be consulted.[1]

2.6 SOLUBILITY PRODUCT

For sparingly soluble salts (i.e. those of which the solubility is less than 0.01 mol per L) it is an experimental fact that the mass action product of the concentrations of the ions is a constant at constant temperature. This product K_s is termed the 'solubility product'. For a binary electrolyte:

$$AB \rightleftharpoons A^+ + B^-$$

$$K_{s(AB)} = [A^+] \times [B^-]$$

In general, for an electrolyte A_pB_q, which ionises into pA^{q+} and qB^{p-} ions:

$$A_pB_q = pA^{q+} + qB^{p-}$$

$$K_{s(A_pB_q)} = [A^{q+}]^p \times [B^{p-}]^q$$

A plausible deduction of the solubility product relation is the following. When excess of a sparingly soluble electrolyte, say silver chloride, is shaken up with water, some of it passes into solution to form a saturated solution of the salt and the process appears to cease. The following equilibrium is actually present (the silver chloride is completely ionised in solution):

$$\mathrm{AgCl(solid)} \rightleftharpoons \mathrm{Ag^+} + \mathrm{Cl^-}$$

The rate of the forward reaction depends only upon the temperature, and at any given temperature:

$$r_1 = k_1$$

where k_1 is a constant. The rate of the reverse reaction is proportional to the activity of each of the reactants; hence at any given temperature:

$$r_2 = k_2 \times a_{\mathrm{Ag^+}} \times a_{\mathrm{Cl^-}}$$

where k_2 is another constant. At equilibrium the two rates are equal, i.e.

$$k_1 = k_2 \times a_{\mathrm{Ag^+}} \times a_{\mathrm{Cl^-}}$$

or

$$a_{\mathrm{Ag^+}} \times a_{\mathrm{Cl^-}} = k_1/k_2 = K_{s(\mathrm{AgCl})}$$

In the very dilute solutions with which we are concerned, the activities may be taken as practically equal to the concentrations so that $[\mathrm{Ag^+}] \times [\mathrm{Cl^-}] = \mathrm{const.}$

It is important to note that the solubility product relation applies with sufficient accuracy for purposes of quantitative analysis only to saturated solutions of slightly soluble electrolytes and with *small* additions of other salts. In the presence of moderate concentrations of salts, the ionic concentration, and therefore the ionic strength of the solution, will increase. This will, in general, lower the activity coefficients of both ions, and consequently the ionic concentrations (and therefore the solubility) must increase in order to maintain the solubility product constant. This effect, which is most marked when the added electrolyte does not possess an ion in common with the sparingly soluble salt, is termed the **salt effect**.

It will be clear from the above short discussion that two factors may come into play when a solution of a salt containing a common ion is added to a saturated solution of a slightly soluble salt. At moderate concentrations of the added salt, the solubility will generally decrease, but with higher concentrations of the soluble salt, when the ionic strength of the solution increases considerably and the activity coefficients of the ions decrease, the solubility may actually increase. This is one of the reasons why a very large excess of the precipitating agent is avoided in quantitative analysis.

The following examples illustrate the method of calculating solubility products from solubility data and also the reverse procedure.

Example 1. The solubility of silver chloride is 0.0015 g per L. Calculate the solubility product.

The relative molecular mass of silver chloride is 143.3. The solubility is therefore $0.0015/143.3 = 1.05 \times 10^{-5}$ mol per L. In a saturated solution, 1 mole of AgCl will give 1 mole each of $\mathrm{Ag^+}$ and $\mathrm{Cl^-}$. Hence $[\mathrm{Ag^+}] = 1.05 \times 10^{-5}$ and $[\mathrm{Cl^-}] = 1.05 \times 10^{-5}\ \mathrm{mol\,L^{-1}}$.

$$\begin{aligned} K_{s(\mathrm{AgCl})} &= [\mathrm{Ag^+}] \times [\mathrm{Cl^-}] = (1.05 \times 10^{-5}) \times (1.05 \times 10^{-5}) \\ &= 1.1 \times 10^{-10}\ \mathrm{mol^2\,L^{-2}} \end{aligned}$$

Example 2. Calculate the solubility product of silver chromate, given that its solubility is $2.5 \times 10^{-2}\ \mathrm{g\,L^{-1}}$.

$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

The relative molecular mass of Ag_2CrO_4 is 331.7; hence the solubility $= 2.5 \times 10^{-2}/331.7 = 7.5 \times 10^{-5}\ \mathrm{mol\,L^{-1}}$.

Now 1 mole of Ag_2CrO_4 gives 2 moles of Ag^+ and 1 mole of CrO_4^{2-}; therefore

$$\begin{aligned} K_{s(Ag_2CrO_4)} &= [Ag^+]^2 \times [CrO_4^{2-}] = (2 \times 7.5 \times 10^{-5})^2 \times (7.5 \times 10^{-5}) \\ &= 1.7 \times 10^{-12}\ \mathrm{mol^3\,L^{-3}} \end{aligned}$$

Example 3. The solubility product of magnesium hydroxide is $3.4 \times 10^{-11}\ \mathrm{mol^3\,L^{-3}}$. Calculate its solubility in grams per L.

$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

$[Mg^{2+}] \times [OH^-]^2 = 3.4 \times 10^{-11}$

The relative molecular mass of magnesium hydroxide is 58.3. Each mole of magnesium hydroxide, when dissolved, yields 1 mole of magnesium ions and 2 moles of hydroxyl ions. If the solubility is $x\ \mathrm{mol\,L^{-1}}$, $[Mg^{2+}] = x$ and $[OH^-] = 2x$. Substituting these values in the solubility product expression:

$$x \times (2x)^2 = 3.4 \times 10^{-11}$$

$$\begin{aligned} \text{or}\quad x &= 2.0 \times 10^{-4}\ \mathrm{mol\,L^{-1}} \\ &= 2.0 \times 10^{-4} \times 58.3 \\ &= 1.2 \times 10^{-2}\ \mathrm{g\,L^{-1}} \end{aligned}$$

The great importance of the solubility product concept lies in its bearing upon precipitation from solution, which is, of course, one of the important operations of quantitative analysis. The solubility product is the ultimate value which is attained by the ionic concentration product when equilibrium has been established between the solid phase of a difficultly soluble salt and the solution. If the experimental conditions are such that the ionic concentration product is different from the solubility product, then the system will attempt to adjust itself in such a manner that the ionic and solubility products are equal in value. Thus if, for a given electrolyte, the product of the concentrations of the ions in solution is arbitrarily made to exceed the solubility product, as for example by the addition of a salt with a common ion, the adjustment of the system to equilibrium results in precipitation of the solid salt, provided supersaturation conditions are excluded. If the ionic concentration product is less than the solubility product or can arbitrarily be made so, as (for example) by complex salt formation or by the formation of weak electrolytes, then a further quantity of solute can pass into solution until the solubility product is attained, or, if this is not possible, until all the solute has dissolved.

2.7 QUANTITATIVE EFFECTS OF A COMMON ION

An important application of the solubility product principle is to the calculation of the solubility of sparingly soluble salts in solutions of salts with a common ion. Thus the solubility of a salt MA in the presence of a relatively large amount of the common M^+ ions,* supplied by a second salt MB, follows from the definition of solubility products:

$$[M^+] \times [A^-] = K_{s(MA)}$$

or $$[A^-] = K_{s(MA)}/[M^+]$$

The solubility of the salt is represented by the $[A^-]$ which it furnishes in solution. It is clear that the addition of a common ion will *decrease* the solubility of the salt.

Example 4. Calculate the solubility of silver chloride in (*a*) $0.001\,M$ and (*b*) $0.01\,M$ sodium chloride solutions respectively ($K_{s(AgCl)} = 1.1 \times 10^{-10}\,\text{mol}^2\,\text{L}^{-2}$).

In a saturated solution of silver chloride $[Cl^-] = \sqrt{1.1 \times 10^{-10}} = 1.05 \times 10^{-5}\,\text{mol L}^{-1}$; this may be neglected in comparison with the excess of Cl^- ions added.

For (*a*) $[Cl^-] = 1 \times 10^{-3}$, $[Ag^+] = 1.1 \times 10^{-10}/1 \times 10^{-3}$

$$= 1.1 \times 10^{-7}\,\text{mol L}^{-1}$$

For (*b*) $[Cl^-] = 1 \times 10^{-2}$, $[Ag^+] = 1.1 \times 10^{-10}/1 \times 10^{-2}$

$$= 1.1 \times 10^{-8}\,\text{mol L}^{-1}$$

Thus the solubility is decreased 100 times in $0.001M$ sodium chloride and 1000 times in $0.01\,M$ sodium chloride. Similar results are obtained for $0.001\,M$ and $0.01\,M$ silver nitrate solutions.

Example 5. Calculate the solubilities of silver chromate in $0.001\,M$ and $0.01\,M$ silver nitrate solutions, and in $0.001\,M$ and $0.01\,M$ potassium chromate solutions (Ag_2CrO_4: $K_s = 1.7 \times 10^{-12}\,\text{mol}^3\,\text{L}^{-3}$, solubility in water $= 7.5 \times 10^{-5}\,\text{mol L}^{-1}$).

$$[Ag^+]^2 \times [CrO_4^{2-}] = 1.7 \times 10^{-12}$$

or $$[CrO_4^{2-}] = 1.7 \times 10^{-12}/[Ag^+]^2$$

For $0.001\,M$ silver nitrate solution: $[Ag^+] = 1 \times 10^{-3}$

$\therefore [CrO_4^{2-}] = 1.7 \times 10^{-12}/1 \times 10^{-6} = 1.7 \times 10^{-6}\,\text{mol L}^{-1}$.

For $0.01\,M$ silver nitrate solution: $[Ag^+] = 1 \times 10^{-2}$

$[CrO_4^{2-}] = 1.7 \times 10^{-12}/1 \times 10^{-4} = 1.7 \times 10^{-8}\,\text{mol L}^{-1}$.

The solubility product equation gives:

$$[Ag^+] = \sqrt{1.7 \times 10^{-12}/[CrO_4^{2-}]}$$

For $[CrO_4^{2-}] = 0.001$, $[Ag^+] = \sqrt{1.7 \times 10^{-12}/1 \times 10^{-3}}$

$$= 4.1 \times 10^{-5}\,\text{mol L}^{-1}$$

---

*This enables us to neglect the concentration of M^+ ions supplied by the sparingly soluble salt itself, and thus to simplify the calculation.

$$\text{For } [\mathrm{CrO_4^{2-}}] = 0.01,\ [\mathrm{Ag^+}] = \sqrt{1.7 \times 10^{-12}/1 \times 10^{-2}}$$
$$= 1.3 \times 10^{-5}\ \mathrm{mol\ L^{-1}}$$

This decrease in solubility by the common ion effect is of fundamental importance in gravimetric analysis. By the addition of a suitable excess of a precipitating agent, the solubility of a precipitate is usually decreased to so small a value that the loss from solubility influences is negligible. Consider a specific case — the determination of silver as silver chloride. Here the chloride solution is added to the solution of the silver salt. If an exactly equivalent amount is added, the resultant saturated solution of silver chloride will contain 0.0015 g per L (Example 1). If 0.2 g of silver chloride is produced and the volume of the solution and washings is 500 mL, the loss, owing to solubility, will be 0.000 75 g or 0.38 per cent of the weight of the salt; the analysis would then be 0.38 per cent too low. By using an excess of the precipitant, say, to a concentration of 0.01 *M*, the solubility of the silver chloride is reduced to $1.5 \times 10^{-5}\ \mathrm{g\ L^{-1}}$ (Example 4), and the loss will be $1.5 \times 10^{-5} \times 0.5 \times 100/0.2 = 0.0038$ per cent. Silver chloride is therefore very suitable for the quantitative determination of silver with high accuracy.

It should, however, be noted that as the concentration of the excess of precipitant increases, so too does the ionic strength of the solution. This leads to a decrease in activity coefficient values with the result that to maintain the value of K_s *more* of the precipitate will dissolve. In other words there is a limit to the amount of precipitant which can be safely added in excess. Also, addition of excess precipitant may sometimes result in the formation of soluble complexes causing some precipitate to dissolve.

2.8 FRACTIONAL PRECIPITATION

In the previous section the solubility product principle has been used in connection with the precipitation of one sparingly soluble salt. It is now necessary to examine the case where two slightly soluble salts may be formed. For simplicity, consider the situation which arises when a precipitating agent is added to a solution containing two anions, both of which form slightly soluble salts with the same cation, e.g. when silver nitrate solution is added to a solution containing both chloride and iodide ions. The questions which arise are: which salt will be precipitated first, and how completely will the first salt be precipitated before the second ion begins to react with the reagent?

The solubility products of silver chloride and silver iodide are respectively $1.2 \times 10^{-10}\ \mathrm{mol^2\ L^{-2}}$ and $1.7 \times 10^{-16}\ \mathrm{mol^2\ L^{-2}}$; i.e.

$$[\mathrm{Ag^+}] \times [\mathrm{Cl^-}] = 1.2 \times 10^{-10} \tag{1}$$

$$[\mathrm{Ag^+}] \times [\mathrm{I^-}] = 1.7 \times 10^{-16} \tag{2}$$

It is evident that silver iodide, being less soluble, will be precipitated first since its solubility product will be first exceeded. Silver chloride will be precipitated when the $\mathrm{Ag^+}$ ion concentration is greater than

$$\frac{K_{s(\mathrm{AgCl})}}{[\mathrm{Cl^-}]} = \frac{1.2 \times 10^{-10}}{[\mathrm{Cl^-}]}$$

and then both salts will be precipitated simultaneously. When silver chloride commences to precipitate, silver ions will be in equilibrium with both salts, and equations (1) and (2) will be simultaneously satisfied, or

$$[\mathrm{Ag}^+] = \frac{K_{\mathrm{s(AgI)}}}{[\mathrm{I}^-]} = \frac{K_{\mathrm{s(AgCl)}}}{[\mathrm{Cl}^-]} \tag{3}$$

$$\text{and} \quad \frac{[\mathrm{I}^-]}{[\mathrm{Cl}^-]} = \frac{K_{\mathrm{s(AgI)}}}{K_{\mathrm{s(AgCl)}}} = \frac{1.7 \times 10^{-16}}{1.2 \times 10^{10}} = 1.4 \times 10^{-6} \tag{4}$$

Hence when the concentration of the iodide ion is about one-millionth part of the chloride ion concentration, silver chloride will be precipitated. If the initial concentration of both chloride and iodide ions is 0.1 M, then silver chloride will be precipitated when

$$[\mathrm{I}^-] = 0.1 \times 1.4 \times 10^{-6} = 1.4 \times 10^{-7} M = 1.8 \times 10^{-5}\,\mathrm{g\,L^{-1}}$$

Thus an almost complete separation is theoretically possible. The separation is feasible in practice if the point at which the iodide precipitation is complete can be detected. This may be done: (*a*) by the use of an adsorption indicator (see Section 10.75(c)), or (*b*) by a potentiometric method with a silver electrode (see Chapter 15).

For a mixture of bromide and iodide:

$$\frac{[\mathrm{I}^-]}{[\mathrm{Br}^-]} = \frac{K_{\mathrm{s(AgI)}}}{K_{\mathrm{s(AgBr)}}} = \frac{1.7 \times 10^{-16}}{3.5 \times 10^{-13}} = \frac{1}{2.0 \times 10^3}$$

Precipitation of silver bromide will occur when the concentration of the bromide ion in the solution is 2.0×10^3 times the iodide concentration. The separation is therefore not so complete as in the case of chloride and iodide, but can nevertheless be effected with fair accuracy with the aid of adsorption indicators (Section 10.75(*c*)).

2.9 EFFECT OF ACIDS ON THE SOLUBILITY OF A PRECIPITATE

For sparingly soluble salts of a strong acid the effect of the addition of an acid will be similar to that of any other indifferent electrolyte but if the sparingly soluble salt MA is the salt of a weak acid HA, then acids will, in general, have a solvent effect upon it. If hydrochloric acid is added to an aqueous suspension of such a salt, the following equilibrium will be established:

$$\mathrm{M}^+ + \mathrm{A}^- + \mathrm{H}^+ \rightleftharpoons \mathrm{HA} + \mathrm{M}^+$$

If the dissociation constant of the acid HA is very small, the anion A^- will be removed from the solution to form the undissociated acid HA. Consequently more of the salt will pass into solution to replace the anions removed in this way, and this process will continue until equilibrium is established (i.e. until $[\mathrm{M}^+] \times [\mathrm{A}^-]$ has become equal to the solubility product of MA) or, if sufficient hydrochloric acid is present, until the sparingly soluble salt has dissolved completely. Similar reasoning may be applied to salts of acids, such as phosphoric(V) acid ($K_1 = 7.5 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$; $K_2 = 6.2 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$; $K_3 = 5 \times 10^{-13}\,\mathrm{mol\,L^{-1}}$), oxalic acid ($K_1 = 5.9 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$; $K_2 = 6.4 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$), and arsenic(V) acid. Thus the solubility of, say, silver phosphate(V) in dilute nitric acid is due to the removal of the PO_4^{3-} ion as

HPO_4^{2-} and/or $H_2PO_4^-$:

$$PO_4^{3-} + H^+ \rightleftharpoons HPO_4^{2-}; \quad HPO_4^{2-} + H^+ \rightleftharpoons H_2PO_4^-$$

With the salts of certain weak acids, such as carbonic, sulphurous, and nitrous acids, an additional factor contributing to the increased solubility is the actual disappearance of the acid from solution either spontaneously, or on gentle warming. An explanation is thus provided for the well-known solubility of the sparingly soluble sulphites, carbonates, oxalates, phosphates(V), arsenites(III), arsenates(V), cyanides (with the exception of silver cyanide, which is actually a salt of the strong acid $H[Ag(CN)_2]$), fluorides, acetates, and salts of other organic acids in strong acids.

The sparingly soluble sulphates (e.g. those of barium, strontium, and lead) also exhibit increased solubility in acids as a consequence of the weakness of the second-stage ionisation of sulphuric acid ($K_2 = 1.2 \times 10^{-2}$ mol L^{-1}):

$$SO_4^{2-} + H^+ \rightleftharpoons HSO_4^-$$

Since, however, K_2 is comparatively large, the solvent effect is relatively small; this is why in the quantitative separation of barium sulphate, precipitation may be carried out in slightly acid solution in order to obtain a more easily filterable precipitate and to reduce co-precipitation (Section 11.5).

The precipitation of substances within a controlled range of pH is discussed in Section 11.10.

2.10 EFFECT OF TEMPERATURE ON THE SOLUBILITY OF A PRECIPITATE

The solubility of the precipitates encountered in quantitative analysis increases with rise of temperature. With some substances the influence of temperature is small, but with others it is quite appreciable. Thus the solubility of silver chloride at 10 and 100 °C is 1.72 and 21.1 mg L^{-1} respectively, whilst that of barium sulphate at these two temperatures is 2.2 and 3.9 mg L^{-1} respectively. In many instances, the common ion effect reduces the solubility to so.small a value that the temperature effect, which is otherwise appreciable, becomes very small. Wherever possible it is advantageous to filter while the solution is hot; the rate of filtration is increased, as is also the solubility of foreign substances, thus rendering their removal from the precipitate more complete. The double phosphates of ammonium with magnesium, manganese or zinc, as well as lead sulphate and silver chloride, are usually filtered at the laboratory temperature to avoid solubility losses.

2.11 EFFECT OF THE SOLVENT ON THE SOLUBILITY OF A PRECIPITATE

The solubility of most inorganic compounds is reduced by the addition of organic solvents, such as methanol, ethanol, propan-l-ol, acetone, etc. For example, the addition of about 20 per cent by volume of ethanol renders the solubility of lead sulphate practically negligible, thus permitting quantitative separation. Similarly calcium sulphate separates quantitatively from 50 per cent ethanol. Other examples of the influence of solvents will be found in Chapter 11.

2.12 ACID–BASE EQUILIBRIA IN WATER

Consider the dissociation of a weak electrolyte, such as acetic acid, in dilute aqueous solution:

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

This will be written for simplicity in the conventional manner:

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

where H^+ represents the hydrated hydrogen ion. Applying the Law of Mass Action, we have:

$$[CH_3COO^-] \times [H^+]/[CH_3COOH] = K$$

K is the equilibrium constant at a particular temperature and is usually known as the **ionisation constant** or **dissociation constant**. If 1 mole of the electrolyte is dissolved in V litres of solution ($V = 1/c$, where c is the concentration in moles per litre), and if α is the degree of ionisation at equilibrium, then the amount of un-ionised electrolyte will be $(1 - \alpha)$ moles, and the amount of each of the ions will be α moles. The concentration of un-ionised acetic acid will therefore be $(1 - \alpha)/V$, and the concentration of each of the ions α/V. Substituting in the equilibrium equation, we obtain the expression:

$$\alpha^2/(1 - \alpha)V = K \quad \text{or} \quad \alpha^2 c/(1 - \alpha) = K$$

This is known as **Ostwald's Dilution Law**.

Interionic effects are, however, not negligible even for weak acids and the activity coefficient product must be introduced into the expression for the ionisation constant:

$$K = \frac{\alpha^2 c}{(1 - \alpha)} \cdot \frac{y_{H^+} \cdot y_{A^-}}{y_{HA}}; \quad A^- = CH_3COO^-$$

Reference must be made to textbooks of physical chemistry (see Bibliography, Section 3.39) for details of the methods used to evaluate true dissociation constants of acids.

From the point of view of quantitative analysis, sufficiently accurate values for the ionisation constants of weak monoprotic acids may be obtained by using the classical Ostwald Dilution Law expression: the resulting 'constant' is sometimes called the 'concentration dissociation constant'.

2.13 STRENGTHS OF ACIDS AND BASES

The Brønsted–Lowry expression for acid–base equilibria (see Section 2.4)

$$A_1 + B_2 \rightleftharpoons A_2 + B_1 \qquad (b)$$

leads, upon application of the Law of Mass Action, to the expression:

$$K = \frac{[A_2]\ [B_1]}{[A_1]\ [B_2]} \qquad (5)$$

where the constant K depends on the temperature and the nature of the solvent. This expression is strictly valid only for extremely dilute solutions: when ions are present the electrostatic forces between them have appreciable effects on the properties of their solutions, and deviations are apparent from ideal laws (which are assumed in the derivation of the Mass-Action Law by thermodynamic or kinetic methods); the deviations from the ideal laws are usually expressed in terms of activities or activity coefficients. For our purpose, the deviations due to interionic attractions and ionic activities will be regarded as small for small ionic concentrations and the equations will be regarded as holding in the same form at higher concentrations, provided that the total ionic concentration does not vary much in a given set of experiments.

To use the above expression for measuring the strength of an acid, a standard acid–base pair, say A_2–B_2, must be chosen, and it is usually convenient to refer acid–base strength to the solvent. In water the acid–base pair H_3O^+–H_2O is taken as the standard. The equilibrium defining acids is therefore:

$$A + H_2O \rightleftharpoons B + H_3O^+ \qquad (c)$$

and the constant

$$K' = \frac{[B][H_3O^+]}{[A][H_2O]} \qquad (6)$$

gives the strength of A, that of the ion H_3O^+ being taken as unity. Equation (*c*) represents what is usually described as the dissociation of the acid A in water, and the constant K' is closely related to the dissociation constant of A in water as usually defined and differing only in the inclusion of the term $[H_2O]$ in the denominator. The latter term represents the 'concentration' of water molecules in liquid water (55.5 moles per litre on the ordinary volume concentration scale). When dealing with dilute solutions, the value of $[H_2O]$ may be regarded as constant, and equation (6) may be expressed as:

$$K_a = \frac{[B][H^+]}{[A]} \qquad (7)$$

by writing H^+ for H_3O^+ and remembering that the hydrated proton is meant. This equation defines the strength of the acid A. If A is an uncharged molecule (e.g. a weak organic acid), B is the anion derived from it by the loss of a proton, and (7) is the usual expression for the ionisation constant. If A is an anion such as $H_2PO_4^-$, the dissociation constant $[HPO_4^{2-}][H^+]/[H_2PO_4^-]$ is usually referred to as the second dissociation constant of phosphoric(V) acid. If A is a cation acid, for example the ammonium ion, which interacts with water as shown by the equation

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

the acid strength is given by $[NH_3][H^+]/[NH_4^+]$.

On the above basis it is, in principle, unnecessary to treat the strength of bases separately from acids, since any protolytic reaction involving an acid must also involve its conjugate base. The basic properties of ammonia and various amines in water are readily understood on the Brønsted–Lowry concept.

$$\begin{array}{r}
H_2O = H^+ + OH^- \\
NH_3 + H^+ = NH_4^+ \\
\hline
NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-
\end{array}$$

The basic dissociation constant K_b is given by:

$$K_b = \frac{[\mathrm{NH_4^+}][\mathrm{OH^-}]}{[\mathrm{NH_3}]} \tag{8}$$

Since $[\mathrm{H^+}][\mathrm{OH^-}] = K_w$ (the ionic product of water), we have

$$K_b = K_w/K_a$$

The values of K_a and K_b for different acids and bases vary through many powers of ten. It is often convenient to use the dissociation constant exponent pK defined by

$$\mathrm{p}K = \log_{10} 1/K = -\log_{10} K$$

The larger the pK_a value is, the weaker is the acid and the stronger the base.

For very weak or slightly ionised electrolyes, the expression $\alpha^2/(1-\alpha)V = K$ reduces to $\alpha^2 = KV$ or $\alpha = \sqrt{KV}$, since α may be neglected in comparison with unity. Hence for any two weak acids or bases at a given dilution V (in L), we have $\alpha_1 = \sqrt{K_1 V}$ and $\alpha_2 = \sqrt{K_2 V}$, or $\alpha_1/\alpha_2 = \sqrt{K_1}/\sqrt{K_2}$. Expressed in words, for any two weak or slightly dissociated electrolytes at equal dilutions, the degrees of dissociation are proportional to the square roots of their ionisation constants. Some values for the dissociation constants at 25 °C for weak acids and bases are collected in Appendix 7.

2.14 DISSOCIATION OF POLYPROTIC ACIDS

When a polyprotic acid is dissolved in water, the various hydrogen atoms undergo ionisation to different extents. For a diprotic acid H_2A, the primary and secondary dissociations can be represented by the equations:

$$\mathrm{H_2A} \rightleftharpoons \mathrm{H^+} + \mathrm{HA^-}$$

$$\mathrm{HA^-} \rightleftharpoons \mathrm{H^+} + \mathrm{A^{2-}}$$

If the acid is a weak electrolyte, the Law of Mass Action may be applied, and the following expressions obtained:

$$[\mathrm{H^+}][\mathrm{HA^-}]/[\mathrm{H_2A}] = K_1 \tag{9}$$

$$[\mathrm{H^+}][\mathrm{A^{2-}}]/[\mathrm{HA^-}] = K_2 \tag{10}$$

K_1 and K_2 are known as the **primary** and **secondary dissociation constants** respectively. Each stage of the dissociation process has its own ionisation constant, and the magnitudes of these constants give a measure of the extent to which each ionisation has proceeded at any given concentration. The greater the value of K_1 relative to K_2, the smaller will be the secondary dissociation, and the greater must be the dilution before the latter becomes appreciable. It is therefore possible that a diprotic (or polyprotic) acid may behave, so far as dissociation is concerned, as a monoprotic acid. This is indeed characteristic of many polyprotic acids.

A triprotic acid H_3A (e.g. phosphoric(V) acid) will similarly yield three dissociation constants, K_1, K_2, and K_3, which may be derived in an analogous manner:

$$[\mathrm{H^+}][\mathrm{H_2A^-}]/[\mathrm{H_3A}] = K_1 \tag{9'}$$

$$[H^+][HA^{2-}]/[H_2A^-] = K_2 \tag{10'}$$

$$[H^+][A^{3-}]/[HA^{2-}] = K_3 \tag{11}$$

Application of these theoretical considerations to situations encountered in practice may be illustrated by numerical examples.

Example 6. Calculate the concentrations of HS^- and S^{2-} in a solution of hydrogen sulphide.

A saturated aqueous solution of hydrogen sulphide at 25 °C, at atmospheric pressure, is approximately $0.1M$, and for H_2S the primary and secondary dissociation constants may be taken as 1.0×10^{-7} mol L^{-1} and 1×10^{-14} mol L^{-1} respectively.

In the solution the following equilibria are involved:

$$H_2S + H_2O \rightleftharpoons HS^- + H_3O^+; \quad K_1 = [H^+][HS^-]/[H_2S] \tag{d}$$

$$HS^- + H_2O \rightleftharpoons S^{2-} + H_3O^+; \quad K_2 = [H^+][S^{2-}]/[HS^-] \tag{e}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

Electroneutrality requires that the total cation concentration must equal total anion concentration and hence, taking account of charge numbers,

$$[H^+] = [HS^-] + 2[S^{2-}] + [OH^-] \tag{f}$$

but since in fact we are dealing with an acid solution, $[H^+] > 10^{-7} > [OH^-]$ and we can simplify equation (*e*) to read

$$[H^+] = [HS^-] + 2[S^{2-}] \tag{g}$$

The 0.1 mol H_2S is present partly as undissociated H_2S and partly as the ions HS^- and S^{2-}, and it follows that

$$[H_2S] + [HS^-] + [S^{2-}] = 0.1 \tag{h}$$

The very small value of K_2 indicates that the secondary dissociation and therefore $[S^{2-}]$ are extremely minute, and ignoring $[S^{2-}]$ in equation (*g*) we are left with the result

$$[H^+] \approx [HS^-]$$

Since K_1 is also small, $[H^+] \ll [H_2S]$ and so equation (*h*) can be reduced to

$$[H_2S] \approx 0.1$$

Using these results in equation (*d*) we find

$$[H^+]^2/0.1 = 1 \times 10^{-7}; \quad [H^+] = [HS^-] = 1.0 \times 10^{-4}\ \text{mol L}^{-1}.$$

From equation (*e*) it then follows that

$$(1.0 \times 10^{-4})[S^{2-}]/(1.0 \times 10^{-4}) = 1 \times 10^{-14}$$

and $[S^{2-}] = 1 \times 10^{-14}$ mol L^{-1}.

2.15 COMMON ION EFFECT

The concentration of a particular ion in an ionic reaction can be increased by the addition of a compound which produces that ion upon dissociation. The particular ion is thus derived from the compound already in solution and also from the added reagent, hence the name 'common ion'. If the original compound is a weak electrolyte, the Law of Mass Action will be applicable. The result is that there is a higher concentration of this ion in solution than that derived from the original compound alone, and new equilibrium conditions will be produced. Examples of the calculation of the common ion effect are given below. In general, it may be stated that if the total concentration of the common ion is only slightly greater than that which the original compound alone would furnish, the effect is small; if, however, the concentration of the common ion is very much increased (e.g. by the addition of a completely dissociated salt), the effect is very great, and may be of considerable practical importance. Indeed, the common ion effect provides a valuable method for controlling the concentration of the ions furnished by a weak electrolyte.

Example 7. Calculate the sulphide ion concentration in a $0.25M$ hydrochloric acid solution saturated with hydrogen sulphide.

This concentration has been chosen since it is that at which the sulphides of certain heavy metals are precipitated. The total concentration of hydrogen sulphide may be assumed to be approximately the same as in aqueous solution, i.e. $0.1M$; the $[H^+]$ will be equal to that of the completely dissociated HCl, i.e. $0.25M$, but the $[S^{2-}]$ will be reduced below 1×10^{-14} (see *Example 6*).

Substituting in equations (*d*) and (*e*) (*Example 6*), we find:

$$[HS^-] = \frac{K_1 \times [H_2S]}{[H^+]} = \frac{1.0 \times 10^{-7} \times 0.1}{0.25} = 4.0 \times 10^{-8}\,\text{mol L}^{-1}$$

$$[S^{2-}] = \frac{K_2 \times [HS^-]}{[H^+]} = \frac{(1 \times 10^{-14}) \times (4 \times 10^{-8})}{0.25} = 1.6 \times 10^{-21}\,\text{mol L}^{-1}$$

Thus by changing the acidity from $1.0 \times 10^{-4}M$ (that present in saturated H_2S water) to $0.25M$, the sulphide ion concentration is reduced from 1×10^{-14} to 1.6×10^{-21}.

Example 8. What effect has the addition of 0.1 mol of anhydrous sodium acetate to 1 L of $0.1M$ acetic acid upon the degree of dissociation of the acid?

The dissociation constant of acetic acid at 25 °C is 1.75×10^{-5} mol L^{-1} and the degree of ionisation α in $0.1M$ solution may be computed by solving the quadratic equation:

$$\frac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]} = \frac{\alpha^2 c}{(1-\alpha)} = 1.75 \times 10^{-5}$$

For our purpose it is sufficiently accurate to neglect α in $(1-\alpha)$ since α is small:

$$\therefore \alpha = \sqrt{K/c} = \sqrt{1.75 \times 10^{-4}} = 0.0132$$

Hence in $0.1M$ acetic acid,

$[H^+] = 0.00132$, $[CH_3COO^-] = 0.00132$,

and $[CH_3COOH] = 0.0987$ mol L^{-1}

The concentrations of sodium and acetate ions produced by the addition of the completely dissociated sodium acetate are:

$[Na^+] = 0.1$, and $[CH_3COO^-] = 0.1\ mol\ L^{-1}$ respectively.

The acetate ions from the salt will tend to decrease the ionisation of the acetic acid, and consequently the acetate ion concentration derived from it. Hence we may write $[CH_3COO^-] = 0.1$ for the solution, and if α' is the new degree of ionisation, $[H^+] = \alpha' c = 0.1\alpha'$, and $[CH_3COOH] = (1 - \alpha')c = 0.1$, since α' is negligibly small.

Substituting in the mass action equation:

$$\frac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]} = \frac{0.1\alpha' \times 0.1}{0.1} = 1.75 \times 10^{-5}$$

or $\alpha' = 1.75 \times 10^{-4}$

$[H^+] = \alpha' c = 1.75 \times 10^{-5}\ mol\ L^{-1}$

The addition of a tenth of a mole of sodium acetate to a 0.1 *M* solution of acetic acid has decreased the degree of ionisation from 1.32 to 0.018 per cent, and the hydrogen ion concentration from 0.00132 to 0.000018 mol L^{-1}.

Example 9. What effect has the addition of 0.5 mol of ammonium chloride to 1 L of 0.1 *M* aqueous ammonia solution upon the degree of dissociation of the base?

(Dissociation constant of NH_3 in water $= 1.8 \times 10^{-5}\ mol\ L^{-1}$)

In 0.1 *M* ammonia solution $\alpha = \sqrt{1.8 \times 10^{-5}/0.1} = 0.0135$. Hence $[OH^-] = 0.00135$, $[NH_4^+] = 0.00135$, and $[NH_3] = 0.0986\ mol\ L^{-1}$. Let α' be the degree of ionisation in the presence of the added ammonium chloride. Then $[OH^-] = \alpha' c = 0.1\alpha'$, and $[NH_3] = (1 - \alpha')c = 0.1$, since α' may be taken as negligibly small. The addition of the completely ionised ammonium chloride will, of necessity, decrease the $[NH_4^+]$ derived from the base and increase $[NH_3]$, and as a first approximation $[NH_4^+] = 0.5$.

Substituting in the equation:

$$\frac{[NH_4^+] \times [OH^-]}{[NH_3]} = \frac{0.5 \times 0.1\alpha'}{0.1} = 1.8 \times 10^{-5}$$

$\alpha' = 3.6 \times 10^{-5}$ and $[OH^-] = 3.6 \times 10^{-6}\ mol\ L^{-1}$

The addition of half a mole of ammonium chloride to 1 litre of a 0.1 *M* solution of aqueous ammonia has decreased the degree of ionisation from 1.35 to 0.0036 per cent, and the hydroxide ion concentration from 0.00135 to 0.0000036 mol L^{-1}.

2.16 THE IONIC PRODUCT OF WATER

Kohlrausch and Heydweiller (1894) found that the most highly purified water that can be obtained possesses a small but definite conductivity. Water must therefore be slightly ionised in accordance with the equation:

$H_2O \rightleftharpoons H^+ + OH^-$*

Applying the Law of Mass Action to this equation, we obtain, for any given temperature:

$$\frac{a_{H^+} \times a_{OH^-}}{a_{H_2O}} = \frac{[H^+].[OH^-]}{[H_2O]} \times \frac{y_{H^+}.y_{OH^-}}{y_{H_2O}} = \text{a constant}$$

Since water is only slightly ionised, the ionic concentrations will be small, and their activity coefficients may be regarded as unity; the activity of the un-ionised molecules may also be taken as unity. The expression thus becomes:

$$\frac{[H^+] \times [OH^-]}{[H_2O]} = \text{a constant}$$

In pure water or in dilute aqueous solutions, the concentration of the undissociated water may be considered constant. Hence:

$$[H^+] \times [OH^-] = K_w$$

where K_w is the **ionic product of water**. It must be pointed out that the assumption that the activity coefficients of the ions are unity and that the activity coefficient of water is constant applies strictly to pure water and to very dilute solutions (ionic strength < 0.01); in more concentrated solutions, i.e. in solutions of appreciable ionic strength, the activity coefficients of the ions are affected (compare Section 2.5), as is also the activity of the un-ionised water. The ionic product of water will then not be constant, but will depend upon the ionic strength of the solution. It is, however, difficult to determine the activity coefficients, except under specially selected conditions, so that in practice the ionic product K_w, although not strictly constant, is employed.

The ionic product varies with the temperature, but under ordinary experimental conditions (at about 25 °C) its value may be taken as $\mathbf{1} \times 10^{-14}$ with concentrations expressed in mol L^{-1}. This is sensibly constant in dilute aqueous solutions. If the product of $[H^+]$ and $[OH^-]$ in aqueous solution momentarily exceeds this value, the excess ions will immediately combine to form water. Similarly, if the product of the two ionic concentrations is momentarily less than 10^{-14}, more water molecules will dissociate until the equilibrium value is attained.

The hydrogen and hydroxide ion concentrations are equal in pure water; therefore $[H^+] = [OH^-] = \sqrt{K_w} = 10^{-7}\,\text{mol L}^{-1}$ at about 25 °C. A solution in which the hydrogen and hydroxide ion concentrations are equal is termed an **exactly neutral solution**. If $[H^+]$ is greater than 10^{-7}, the solution is **acid**, and if less than 10^{-7}, the solution is **alkaline** (or basic). It follows that at ordinary temperatures $[OH^-]$ is greater than 10^{-7} in alkaline solution and less than this value in acid solution.

---

*Strictly speaking the hydrogen ion H^+ exists in water as the hydroxonium ion H_3O^+ (Section 2.4). The electrolytic dissociation of water should therefore be written:

$2H_2O \rightleftharpoons H_3O^+ + OH^-$

For the sake of simplicity, the more familiar symbol H^+ will be retained.

In all cases the reaction of the solution can be quantitatively expressed by the magnitude of the hydrogen ion (or hydroxonium ion) concentration, or, less frequently, of the hydroxide ion concentration, since the following simple relations between $[H^+]$ and $[OH^-]$ exist:

$$[H^+] = \frac{K_w}{[OH^-]}, \quad \text{and} \quad [OH^-] = \frac{K_w}{[H^+]}$$

The variation of K_w with temperature is shown in Table 2.1.

Table 2.1 Ionic product of water at various temperatures

Temp. (°C)	$K_w \times 10^{14}$	Temp. (°C)	$K_w \times 10^{14}$
0	0.12	35	2.09
5	0.19	40	2.92
10	0.29	45	4.02
15	0.45	50	5.47
20	0.68	55	7.30
25	1.01	60	9.61
30	1.47		

2.17 THE HYDROGEN ION EXPONENT

For many purposes, especially when dealing with small concentrations, it is cumbersome to express concentrations of hydrogen and hydroxyl ions in terms of moles per litre. A very convenient method was proposed by S. P. L. Sørensen (1909). He introduced the hydrogen ion exponent pH defined by the relationships:

$$\text{pH} = \log_{10} 1/[H^+] = -\log_{10}[H^+], \quad \text{or} \quad [H^+] = 10^{-\text{pH}}$$

The quantity pH is thus the logarithm (to the base 10) of the reciprocal of the hydrogen ion concentration, or is equal to the logarithm of the hydrogen ion concentration with negative sign. This method has the advantage that all states of acidity and alkalinity between those of solutions containing, on the one hand, 1 mol L^{-1} of hydrogen ions, and on the other hand, 1 mol L^{-1} of hydroxide ions, can be expressed by a series of positive numbers between 0 and 14. Thus a neutral solution with $[H^+] = 10^{-7}$ has a pH of 7; a solution with a hydrogen ion concentration of 1 mol L^{-1} has a pH of 0 ($[H^+] = 10^0$); and a solution with a hydroxide-ion concentration of 1 mol L^{-1} has $[H^+] = K_w/[OH^-] = 10^{-14}/10^0 = 10^{-14}$, and possesses a pH of 14. A neutral solution is therefore one in which pH = 7, an acid solution one in which pH < 7, and an alkaline solution one in which pH > 7. An alternative definition for a neutral solution, applicable to all temperatures, is one in which the hydrogen ion and hydroxide ion concentrations are equal. In an acid solution the hydrogen ion concentration exceeds the hydroxide ion concentration, whilst in an alkaline or basic solution, the hydroxide ion concentration is greater.

Example 10. (i) Find the pH of a solution in which $[H^+] = 4.0 \times 10^{-5}$ mol L^{-1}.

$$
\begin{aligned}
\mathrm{pH} = \log_{10} 1/[\mathrm{H}^+] &= \log 1 - \log[\mathrm{H}^+] \\
&= \log 1 - \log 4.0 \times 10^{-5} \\
&= 0 - \bar{5}.602 \\
&= \underline{4.398}
\end{aligned}
$$

(ii) Find the hydrogen ion concentration corresponding to pH = 5.643.

$$\mathrm{pH} = \log_{10} 1/[\mathrm{H}^+] = \log 1 - \log[\mathrm{H}^+] = 5.643$$

$$\therefore \log[\mathrm{H}^+] = -5.643$$

This must be written in the usual form containing a negative characteristic and a positive mantissa:

$$\log[\mathrm{H}^+] = -5.643 = \bar{6}.357$$

By reference to a calculator or to tables of antilogarithms we find $[\mathrm{H}^+] = \underline{2.28 \times 10^{-6}\ \mathrm{mol\ L^{-1}}}$.

(iii) Calculate the pH of a 0.01 M solution of acetic acid in which the degree of dissociation is 12.5 per cent.

The hydrogen ion concentration of the solution is 0.125×0.01

$$
\begin{aligned}
&= 1.25 \times 10^{-3}\ \mathrm{mol\ L^{-1}} \\
\mathrm{pH} = \log_{10} 1/[\mathrm{H}^+] &= \log 1 - \log[\mathrm{H}^+] \\
&= 0 - \bar{3}.097 \\
&= \underline{2.903}
\end{aligned}
$$

The hydroxide ion concentration may be expressed in a similar way:

$$\mathrm{pOH} = -\log_{10}[\mathrm{OH}^-] = \log_{10} 1/[\mathrm{OH}^-], \quad \text{or} \quad [\mathrm{OH}^-] = 10^{-\mathrm{pOH}}$$

If we write the equation:

$$[\mathrm{H}^+] \times [\mathrm{OH}^-] = K_w = 10^{-14}$$

in the form:

$$\log[\mathrm{H}^+] + \log[\mathrm{OH}^-] = \log K_w = -14$$

then $\mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_w = 14$

This relationship should hold for all dilute solutions at about 25 °C.

Figure 2.1 will serve as a useful mnemonic for the relation between $[\mathrm{H}^+]$, pH, $[\mathrm{OH}^-]$, and pOH in acid and alkaline solution.

The logarithmic or exponential form has also been found useful for expressing other small quantities which arise in quantitative analysis. These include: (i) dissociation constants (Section 2.13), (ii) other ionic concentrations, and (iii) solubility products (Section 2.6).

(i) For any acid with a dissociation constant of K_a:

$$\mathrm{p}K_a = \log 1/K_a = -\log K_a$$

Similarly for any base with dissociation constant K_b:

$$\mathrm{p}K_b = \log 1/K_b = -\log K_b$$

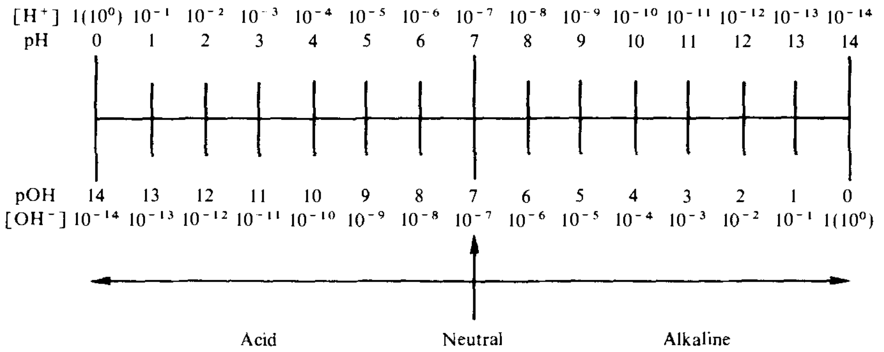


Fig. 2.1

(ii) For any ion I of concentration [I]:

$pI = \log 1/[\mathrm{I}] = -\log[\mathrm{I}]$

Thus, for $[\mathrm{Na}^+] = 8 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$, pNa = 4.1.

(iii) For a salt with a solubility product K_s:

$pK_s = \log 1/K_s = -\log K_s$.

2.18 THE HYDROLYSIS OF SALTS

Salts may be divided into four main classes:

(1) those derived from strong acids and strong bases, e.g. potassium chloride;
(2) those derived from weak acids and strong bases, e.g. sodium acetate;
(3) those derived from strong acids and weak bases, e.g. ammonium chloride; and
(4) those derived from weak acids and weak bases, e.g. ammonium formate or aluminium acetate.

When any of these from classes (2) to (4) is dissolved in water, the solution, as is well known, is not always neutral in reaction. Interaction may occur with the ions of water, and the resulting solution will be neutral, acid, or alkaline according to the nature of the salt.

With an aqueous solution of a salt of class (1), neither do the anions have any tendency to combine with the hydrogen ions nor do the cations with the hydroxide ions of water, since the related acids and bases are strong electrolytes. The equilibrium between the hydrogen and hydroxide ions in water:

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (i)$$

is therefore not disturbed and the solution remains neutral.

Consider, however, a salt MA derived from a weak acid HA and a strong base BOH {class (2)}. The salt is completely dissociated in aqueous solution:

$$MA \rightarrow M^+ + A^-$$

A very small concentration of hydrogen and hydroxide ions, originating from the small but finite ionisation of water, will be initially present. HA is a weak acid, i.e. it is dissociated only to a small degree; the concentration of A^- ions which can exist in equilibrium with H^+ ions is accordingly small. In order to maintain the equilibrium, the large initial concentration of A^- ions must be reduced by combination with H^+ ions to form undissociated HA:

$$H^+ + A^- \rightleftharpoons HA \qquad (j)$$

The hydrogen ions required for this reaction can be obtained only from the further dissociation of the water; this dissociation produces simultaneously an equivalent quantity of hydroxyl ions. The hydrogen ions are utilised in the formation of HA; consequently the hydroxide ion concentration of the solution will increase and the solution will react alkaline.

It is usual in writing equations involving equilibria between completely dissociated and slightly dissociated or sparingly soluble substances to employ the ions of the former and the molecules of the latter. The reaction is therefore written:

$$A^- + H_2O \rightleftharpoons OH^- + HA \qquad (k)$$

This equation can also be obtained by combining (*i*) and (*j*), since both equilibria must co-exist. This interaction between the ion (or ions) of a salt and water is called '**hydrolysis**'.

Consider now the salt of a strong acid and a weak base {class (3)}. Here the initial high concentration of cations M^+ will be reduced by combination with the hydroxide ions of water to form the little-dissociated base MOH until the equilibrium:

$$M^+ + OH^- \rightleftharpoons MOH$$

is attained. The hydrogen ion concentration of the solution will thus be increased, and the solution will react acid. The hydrolysis is here represented by:

$$M^+ + H_2O \rightleftharpoons MOH + H^+$$

For salts of class (4), in which both the acid and the base are weak, two reactions will occur simultaneously

$$M^+ + H_2O \rightleftharpoons MOH + H^+; \quad A^- + H_2O \rightleftharpoons HA + OH^-$$

The reaction of the solution will clearly depend upon the relative dissociation constants of the acid and the base. If they are equal in strength, the solution will be neutral; if $K_a > K_b$, it will be acid, and if $K_b > K_a$, it will be alkaline.

Having considered all the possible cases, we are now in a position to give a more general definition of hydrolysis. Hydrolysis is the interaction between an ion (or ions) of a salt and water with the production of (*a*) a weak acid or a weak base, or (*b*) of both a weak acid and a weak base.

The phenomenon of salt hydrolysis may be regarded as a simple application of the general Brønsted–Lowry equation

$$A_1 + B_2 \rightleftharpoons A_2 + B_1$$

Thus the equation for the hydrolysis of ammonium salts

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

is really identical with the expression used to define the strength of the ammonium ion as a Brønsted–Lowry acid (see Section 2.4) and the constant K_a for NH_4^+ is in fact what is usually termed the hydrolysis constant of an ammonium salt.

The hydrolysis of the sodium salt of a weak acid can be treated similarly. Thus for a solution of sodium acetate

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

the hydrolysis constant is

$$[CH_3COOH][OH^-]/[CH_3COO^-] = K_h = K_w/K_a$$

where K_a is the dissociation constant of acetic (ethanoic) acid.

2.19 HYDROLYSIS CONSTANT AND DEGREE OF HYDROLYSIS

Case 1. Salt of a weak acid and a strong base. The equilibrium in a solution of salt MA may be represented by:

$$A^- + H_2O \rightleftharpoons OH^- + HA$$

Applying the Law of Mass Action, we obtain:

$$\frac{a_{OH^-} \times a_{HA}}{a_{A^-}} = \frac{[OH^-].[HA]}{[A^-]} \times \frac{y_{OH^-}.y_{HA}}{y_{A^-}} = K_h \tag{12}$$

where K_h is the **hydrolysis constant**. The solution is assumed to be dilute so that the activity of the un-ionised water may be taken as constant, and the approximation that the activity coefficient of the un-ionised acid is unity and that both ions have the same activity coefficient may be introduced. Equation (12) then reduces to:

$$K_h = \frac{[OH^-] \times [HA]}{[A^-]} \tag{13}$$

This is often written in the form:

$$K_h = \frac{[\text{Base}] \times [\text{Acid}]}{[\text{Unhydrolysed salt}]}$$

The free strong base and the unhydrolysed salt are completely dissociated and the acid is very little dissociated.

The degree of hydrolysis is the fraction of each mole of anion A^- hydrolysed at equilibrium. Let 1 mole of salt be dissolved in V L of solution, and let x be the degree of hydrolysis. The concentrations in mol L^{-1} are:

$$[HA] = [OH^-] = x/V; \quad [A^-] = (1-x)/V$$

Substituting these values in equation (13):

$$K_h = \frac{[OH^-] \times [HA]}{[A^-]} = \frac{x/V \times x/V}{(1-x)/V} = \frac{x^2}{(1-x)V}$$

This expression enables us to calculate the degree of hydrolysis at the dilution V; it is evident that as V increases, the degree of hydrolysis x must increase.

The two equilibria:

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{and} \quad HA \rightleftharpoons H^+ + A^-$$

must co-exist with the hydrolytic equilibrium:

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

Hence the two relationships:

$$[H^+] \times [OH^-] = K_w \quad \text{and} \quad [H^+] \times [A^-]/[HA] = K_a$$

must hold in the same solution as:

$$[OH^-] \times [HA]/[A^-] = K_h$$

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

therefore $K_w/K_a = K_h$

or $pK_h = pK_w - pK_a$

The hydrolysis constant is thus related to the ionic product of water and the ionisation constant of the acid. Since K_a varies slightly and K_w varies considerably with temperature, K_h and consequently the degree of hydrolysis will be largely influenced by changes of temperature.

The hydrogen ion concentration of a solution of a hydrolysed salt can be readily calculated. The amounts of HA and of OH^- ions formed as a result of hydrolysis are equal; therefore, in a solution of the pure salt in water, $[HA] = [OH^-]$. If the concentration of the salt is c mol L^{-1}, then:

$$\frac{[HA] \times [OH^-]}{[A^-]} = \frac{[OH^-]^2}{c} = K_h = \frac{K_w}{K_a}$$

and $[OH^-] = \sqrt{c.K_w/K_a}$

or $[H^+] = \sqrt{K_w.K_a/c}$, since $[H^+] = K_w/[OH^-]$

and $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log c$

To be consistent we should use $pc = -\log c$ so that the equation becomes:

$$pH = \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_a - \tfrac{1}{2}pc \qquad (14)$$

Equation (14) can be employed for the calculation of the pH of a solution of a salt of a weak acid and a strong base. Thus the pH of a solution of sodium benzoate (0.05 mol L^{-1}) is given by:

$$pH = 7.0 + 2.10 - \tfrac{1}{2}(1.30) = 8.45$$

(Benzoic acid: $K_a = 6.37 \times 10^{-5}$ mol L^{-1}; $pK_a = 4.20$)

Such a calculation will provide useful information as to the indicator which should be employed in the titration of a weak acid and a strong base (see Section 10.13).

Example 11. Calculate: (i) the hydrolysis constant, (ii) the degree of hydrolysis, and (iii) the hydrogen ion concentration of a solution of sodium acetate (0.01 mol L^{-1}) at the laboratory temperature.

$$K_h = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

The degree of hydrolysis x is given by:

$$K_h = \frac{x^2}{(1-x)V}$$

Substituting for K_h and V ($=1/c$), we obtain:

$$5.7 \times 10^{-10} = \frac{x^2 \times 0.01}{(1-x)}$$

Solving this quadratic equation, $x = 0.000238$ or 0.0238 per cent.

If the solution were completely hydrolysed, the concentration of acetic (ethanoic) acid produced would be 0.01 mol L^{-1}. But the degree of hydrolysis is 0.0238 per cent, therefore the concentration of acetic acid is 2.38×10^{-6} mol L^{-1}. This is also equal to the hydroxide ion concentration produced, i.e. pOH = 5.62.

$$pH = 14.0 - 5.62 = 8.38$$

The pH may also be calculated from equation (14):

$$pH = \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_a - \tfrac{1}{2}pc = 7.0 + 2.38 - \tfrac{1}{2}(2) = 8.38$$

Case 2. Salt of a strong acid and a weak base. The hydrolytic equilibrium is represented by:

$$M^+ + H_2O \rightleftharpoons MOH + H^+$$

By applying the Law of Mass Action along the lines of Case 1, the following equations are obtained:

$$K_h = \frac{[H^+] \times [MOH]}{[M^+]} = \frac{[\text{Acid}] \times [\text{Base}]}{[\text{Unhydrolysed salt}]} = \frac{K_w}{K_b}$$
$$= \frac{x^2}{(1-x)V}$$

K_b is the dissociation constant of the base. Furthermore, since [MOH] and $[H^+]$ are equal:

$$K_h = \frac{[H^+] \times [MOH]}{[M^+]} = \frac{[H^+]^2}{c} = \frac{K_w}{K_b}$$

$$[H^+] = \sqrt{c.K_w/K_b},$$

or $pH = \tfrac{1}{2}pK_w - \tfrac{1}{2}pK_b + \tfrac{1}{2}pc$ (15)

Equation (15) may be applied to the calculation of the pH of solutions of salts of strong acids and weak bases. Thus the pH of a solution of ammonium chloride (0.2 mol L^{-1}) is:

$$pH = 7.0 - 2.37 + \tfrac{1}{2}(0.70) = 4.98$$

(Ammonia in water: $K_b = 1.8 \times 10^{-5}$ mol L^{-1}; $pK_b = 4.74$)

Case 3. Salt of a weak acid and a weak base. The hydrolytic equilibrium is expressed by the equation:

$$M^+ + A^- + H_2O \rightleftharpoons MOH + HA$$

Applying the Law of Mass Action and taking the activity of un-ionised water as unity, we have:

$$K_h = \frac{a_{\mathrm{MOH}} \times a_{\mathrm{HA}}}{a_{\mathrm{M^+}} \times a_{\mathrm{A^-}}} = \frac{[\mathrm{MOH}].[\mathrm{HA}]}{[\mathrm{M^+}].[\mathrm{A^-}]} \times \frac{y_{\mathrm{MOH}} \cdot y_{\mathrm{HA}}}{y_{\mathrm{M^+}} \cdot y_{\mathrm{A^-}}}$$

By the usual approximations, i.e. by assuming that the activity coefficients of the un-ionised molecules and, less justifiably, of the ions are unity, the following approximate equation is obtained:

$$K_h = \frac{[\mathrm{MOH}] \times [\mathrm{HA}]}{[\mathrm{M^+}] \times [\mathrm{A^-}]} = \frac{[\mathrm{Base}] \times [\mathrm{Acid}]}{[\mathrm{Unhydrolysed\ salt}]^2}$$

If x is the degree of hydrolysis of 1 mole of the salt dissolved in V litres of solution, then the individual concentrations are:

$$[\mathrm{MOH}] = [\mathrm{HA}] = x/V; \quad [\mathrm{M^+}] = [\mathrm{A^-}] = (1-x)/V$$

leading to the result

$$K_h = \frac{x/V.x/V}{(1-x)/V.(1-x)/V} = \frac{x^2}{(1-x)^2}$$

The degree of hydrolysis and consequently the pH is independent of the concentration of the solution.*

It may be readily shown that:

$$K_h = K_w/K_a \times K_b$$

$$\text{or} \quad \mathrm{p}K_h = \mathrm{p}K_w - \mathrm{p}K_a - \mathrm{p}K_b$$

This expression enables us to calculate the value of the degree of hydrolysis from the dissociation constants of the acid and the base.

The hydrogen ion concentration of the hydrolysed solution is calculated in the following manner:

$$[\mathrm{H^+}] = K_a \times \frac{[\mathrm{HA}]}{[\mathrm{A^-}]} = K_a \times \frac{x/V}{(1-x)/V} = K_a \times \frac{x}{(1-x)}$$

$$\text{But} \quad x/(1-x) = \sqrt{K_h}$$

$$\text{Hence} \quad [\mathrm{H^+}] = K_a\sqrt{K_h} = \sqrt{K_w \times K_a/K_b}$$

$$\text{or} \quad \mathrm{pH} = \tfrac{1}{2}\mathrm{p}K_w + \tfrac{1}{2}\mathrm{p}K_a - \tfrac{1}{2}\mathrm{p}K_b \qquad (16)$$

If the ionisation constants of the acid and the base are equal, that is $K_a = K_b$, $\mathrm{pH} = \frac{1}{2}\mathrm{p}K_w = 7.0$ and the solution is neutral, although hydrolysis may be considerable. If $K_a > K_b$, $\mathrm{pH} < 7$ and the solution is acid, but when $K_b > K_a$, $\mathrm{pH} > 7$ and the solution reacts alkaline.

The pH of a solution of ammonium acetate is given by:

$$\mathrm{pH} = 7.0 + 2.38 - 2.37 = 7.1$$

i.e. the solution is approximately neutral. On the other hand, for a dilute

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*This applies only if the original assumptions as to activity coefficients are justified. In solutions of appreciable ionic strength, the activity coefficients of the ions will vary with the total ionic strength.

solution of ammonium formate:

$\text{pH} = 7.0 + 1.88 - 2.37 = 6.51$

(Formic acid: $K_a = 1.77 \times 10^{-4}\,\text{mol L}^{-1}$; $\text{p}K_a = 3.75$)

i.e. the solution has a slightly acid reaction.

2.20 BUFFER SOLUTIONS

A solution of hydrochloric acid ($0.0001\,\text{mol L}^{-1}$) 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 ($0.0001\,\text{mol L}^{-1}$), 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 ($1\,\text{mol L}^{-1}$) 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 **buffer action**; a solution which possesses such properties is known as a **buffer solution**. 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, then, 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 K_a:

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

The expression may be approximated by writing concentrations for activities:

$$[H^+] = \frac{[HA]}{[A^-]} \times K_a \tag{18}$$

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 equilibrium equation (18), we have:

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

This is a quadratic equation in $[H^+]$ and may be solved in the usual manner. It can, however, 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 Brønsted–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-neutralised acid then $pH = pK_a$. Thus the pH of a half-neutralised 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-neutralised 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 be added, the latter 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 $1M$ hydrochloric acid to 1 L of a solution which is $0.1M$ in acetic (ethanoic) acid and $0.1M$ 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:

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

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

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

$$CH_3COOH = 0.1 + 0.01 = 0.11$$

and $\mathrm{pH} = 4.76 + \log 0.09/0.11 = 4.76 - 0.09 = \underline{4.67}$

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 ($\mathrm{pH} = 7$) would lead to a solution with $\mathrm{pH} = -\log(0.01) = 2$; a change of 5 pH units. This example serves to illustrate the regulation of pH exercised by buffer solutions.

A solution containing equal concentrations of acid and its salt, or a half-neutralised solution of the acid, has the maximum 'buffer capacity'. Other mixtures also possess considerable buffer capacity, but the pH will differ slightly from that of the half-neutralised acid. Thus in a quarter-neutralised solution of acid, [Acid] = 3 [Salt]:

$$\mathrm{pH} = \mathrm{p}K_a + \log \tfrac{1}{3} = \mathrm{p}K_a + \bar{1}.52 = \mathrm{p}K_a - 0.48$$

For a three-quarter-neutralised acid, [Salt] = 3 [Acid]:

$$\mathrm{pH} = \mathrm{p}K_a + \log 3 = \mathrm{p}K_a + 0.48$$

In general, we may state that the buffering capacity is maintained for mixtures within the range 1 acid:10 salt and 10 acid:1 salt and the approximate pH range of a weak acid buffer is:

$$\mathrm{pH} = \mathrm{p}K_a \pm 1$$

The concentration of the acid is usually of the order 0.05–0.2 mol L^{-1}. Similar remarks apply to weak bases. It is clear that the greater the concentrations of acid and conjugate base in a buffer solution, the greater will be the buffer capacity. A quantitative measure of buffer capacity is given by the number of moles of strong base required to change the pH of 1 litre of the solution by 1 pH unit.

The preparation of a buffer solution of a definite pH is a simple process once the acid (or base) of appropriate dissociation constant is found: small variations in pH are obtained by variations in the ratios of the acid to the salt concentration. One example is given in Table 2.2.

Before leaving the subject of buffer solutions, it is necessary to draw attention to a possible erroneous deduction from equation (21), namely that the hydrogen-ion concentration of a buffer solution is dependent only upon the ratio of the concentrations of acid and salt and upon K_a, and not upon the actual concentrations; otherwise expressed, that the pH of such a buffer mixture should not change upon dilution with water. This is approximately although not strictly true. In deducing equation (18), concentrations have been substituted for activities, a step which is not entirely justifiable except in dilute solutions. The exact expression controlling buffer action is:

$$a_{H^+} = \frac{a_{HA}}{a_{A^-}} \times K_a = \frac{c_a \cdot y_a}{c_s \cdot y_{A^-}} \times K_a \qquad (24)$$

Table 2.2 pH of acetic acid–sodium acetate buffer mixtures

10 mL mixtures of x mL of 0.2M acetic acid and y mL of 0.2M sodium acetate

Acetic acid (x mL)	Sodium acetate (y mL)	pH
9.5	0.5	3.48
9.0	1.0	3.80
8.0	2.0	4.16
7.0	3.0	4.39
6.0	4.0	4.58
5.0	5.0	4.76
4.0	6.0	4.93
3.0	7.0	5.13
2.0	8.0	5.36
1.0	9.0	5.71
0.5	9.5	6.04

The activity coefficient y_a of the undissociated acid is approximately unity in dilute aqueous solution. Expression (24) thus becomes:

$$a_{\mathrm{H}^+} = \frac{[\mathrm{Acid}]}{[\mathrm{Salt}] \times y_{\mathrm{A}^-}} \times K_a \qquad (25)$$

$$\text{or} \quad \mathrm{pH} = \mathrm{p}K_a + \log[\mathrm{Salt}]/[\mathrm{Acid}] + \log y_{\mathrm{A}^-} \qquad (26)$$

This is known as the Henderson–Hasselbalch equation.

If a buffer solution is diluted, the ionic concentrations are decreased and so, as shown in Section 2.5, the ionic activity coefficients are increased. It follows from equation (26) that the pH is increased.

Buffer mixtures are not confined to mixtures of monoprotic acids or monoacid bases and their salts. We may employ a mixture of salts of a polyprotic acid, e.g. NaH_2PO_4 and Na_2HPO_4. The salt NaH_2PO_4 is completely dissociated:

$$NaH_2PO_4 \rightleftharpoons Na^+ + H_2PO_4^-$$

The ion $H_2PO_4^-$ acts as a monoprotic acid:

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$$

for which K ($\equiv K_2$ for phosphoric acid) is 6.2×10^{-8} mol L^{-1}. The addition of the salt Na_2HPO_4 is analogous to the addition of, say, acetate ions to a solution of acetic acid, since the tertiary ionisation of phosphoric acid ($HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$) is small ($K_3 = 5 \times 10^{-13}$ mol L^{-1}). The mixture of NaH_2PO_4 and Na_2HPO_4 is therefore an effective buffer over the range pH 7.2 ± 1.0 ($= \mathrm{p}K \pm 1$). It will be noted that this is a mixture of a Brønsted–Lowry acid and its conjugate base.

Buffer solutions find many applications in quantitative analysis, e.g. many precipitations are quantitative only under carefully controlled conditions of pH, as are also many compleximetric titrations: numerous examples of their use will be found throughout the book.

2.21 COMPLEX IONS

The increase in solubility of a precipitate upon the addition of excess of the precipitating agent is frequently due to the formation of a complex ion. A

complex ion is formed by the union of a simple ion with either other ions of opposite charge or with neutral molecules as shown by the following examples.

When potassium cyanide solution is added to a solution of silver nitrate, a white precipitate of silver cyanide is first formed because the solubility product of silver cyanide:

$$[\mathrm{Ag}^+] \times [\mathrm{CN}^-] = K_{\mathrm{s(AgCN)}} \tag{27}$$

is exceeded. The reaction is expressed:

$$\mathrm{CN}^- + \mathrm{Ag}^+ = \mathrm{AgCN}$$

The precipitate dissolves upon the addition of excess of potassium cyanide, the complex ion $[\mathrm{Ag(CN)_2}]^-$ being produced:

$$\mathrm{AgCN(solid)} + \mathrm{CN}^-\mathrm{(excess)} \rightleftharpoons [\mathrm{Ag(CN)_2}]^-{*}$$

$$(\text{or } \mathrm{AgCN} + \mathrm{KCN} = \mathrm{K[Ag(CN)_2]} - \text{a soluble complex salt})$$

This complex ion dissociates to give silver ions, since the addition of sulphide ions yields a precipitate of silver sulphide (solubility product $1.6 \times 10^{-49}\ \mathrm{mol^3\,L^{-3}}$), and also silver is deposited from the complex cyanide solution upon electrolysis. The complex ion thus dissociates in accordance with the equation:

$$[\mathrm{Ag(CN)_2}]^- \rightleftharpoons \mathrm{Ag}^+ + 2\mathrm{CN}^-$$

Applying the Law of Mass Action, we obtain the dissociation constant of the complex ion:

$$\frac{[\mathrm{Ag}^+] \times [\mathrm{CN}^-]^2}{[\{\mathrm{Ag(CN)_2}\}^-]} = K_{\mathrm{diss.}} \tag{28}$$

which has a value of $1.0 \times 10^{-21}\ \mathrm{mol^2\,L^{-2}}$ at the ordinary temperature. By inspection of this expression, and bearing in mind that excess of cyanide ion is present, it is evident that the silver ion concentration must be very small, so small in fact that the solubility product of silver cyanide is not exceeded.

The inverse of equation (28) gives us the stability constant or formation constant of the complex ion:

$$K = \frac{[\{\mathrm{Ag(CN)_2}\}^-]}{[\mathrm{Ag}^+] \times [\mathrm{CN}^-]^2} = 10^{21}\ \mathrm{mol^{-2}\,L^2} \tag{29}$$

Consider now a somewhat different type of complex ion formation, viz. the production of a complex ion with constituents other than the common ion present in the solution. This is exemplified by the solubility of silver chloride in ammonia solution. The reaction is:

$$\mathrm{AgCl} + 2\mathrm{NH_3} \rightleftharpoons [\mathrm{Ag(NH_3)_2}]^+ + \mathrm{Cl}^-$$

Here again, electrolysis, or treatment with hydrogen sulphide, shows that silver

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*Square brackets are commonly used for two purposes: to denote concentrations and also to include the whole of a complex ion; for the latter purpose curly brackets (braces) are sometimes used. With careful scrutiny there should be no confusion regarding the sense in which the square brackets are used: with complexes there will be no charge signs *inside* the brackets.

ions are present in solution. The dissociation of the complex ion is represented by:

$$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3$$

and the dissociation constant is given by:

$$K_{\text{diss.}} = \frac{[Ag^+] \times [NH_3]^2}{[\{Ag(NH_3)_2\}^+]} = 6.8 \times 10^{-8}\,\text{mol}^2\,\text{L}^{-2}$$

The stability constant $K = 1/K_{\text{diss.}} = 1.5 \times 10^7\,\text{mol}^{-2}\,\text{L}^2$

The magnitude of the dissociation constant clearly shows that only a very small silver ion concentration is produced by the dissociation of the complex ion.

The stability of complex ions varies within very wide limits. It is quantitatively expressed by means of the **stability constant**. The more stable the complex, the greater is the stability constant, i.e. the smaller is the tendency of the complex ion to dissociate into its constituent ions. When the complex ion is very stable, e.g. the hexacyanoferrate(II) ion $[Fe(CN)_6]^{4-}$, the ordinary ionic reactions of the components are not shown.

The application of complex-ion formation in chemical separations depends upon the fact that one component may be transformed into a complex ion which no longer reacts with a given reagent, whereas another component does react. One example may be mentioned here. This is concerned with the separation of cadmium and copper. Excess of potassium cyanide solution is added to the solution containing the two salts when the complex ions $[Cd(CN)_4]^{2-}$ and $[Cu(CN)_4]^{3-}$ respectively are formed. Upon passing hydrogen sulphide into the solution containing excess of CN^- ions, a precipitate of cadmium sulphide is produced. Despite the higher solubility product of CdS ($1.4 \times 10^{-28}\,\text{mol}^2\,\text{L}^{-2}$ as against $6.5 \times 10^{-45}\,\text{mol}^2\,\text{L}^{-2}$ for copper(II) sulphide), the former is precipitated because the complex cyanocuprate(I) ion has a greater stability constant ($2 \times 10^{27}\,\text{mol}^{-4}\,\text{L}^4$ as compared with $7 \times 10^{10}\,\text{mol}^{-4}\,\text{L}^4$ for the cadmium compound).

2.22 COMPLEXATION

The processes of complex-ion formation referred to above can be described by the general term **complexation**. A complexation reaction with a metal ion involves the replacement of one or more of the coordinated solvent molecules by other nucleophilic groups. The groups bound to the central ion are called **ligands** and in aqueous solution the reaction can be represented by the equation:

$$M(H_2O)_n + L = M(H_2O)_{(n-1)}L + H_2O$$

Here the ligand (L) can be either a neutral molecule or a charged ion, and successive replacement of water molecules by other ligand groups can occur until the complex ML_n is formed; n is the coordination number of the metal ion and represents the maximum number of monodentate ligands that can be bound to it.

Ligands may be conveniently classified on the basis of the number of points of attachment to the metal ion. Thus simple ligands, such as halide ions or the molecules H_2O or NH_3, are **monodentate**, i.e. the ligand is bound to the metal ion at only one point by the donation of a lone pair of electrons to the metal.

When, however, the ligand molecule or ion has two atoms, each of which has a lone pair of electrons, then the molecule has two donor atoms and it may be possible to form two coordinate bonds with the same metal ion; such a ligand is said to be **bidentate** and may be exemplified by consideration of the tris(ethylenediamine)cobalt(III) complex, $[Co(en)_3]^{3+}$. In this six-coordinate octahedral complex of cobalt(III), each of the bidentate ethylenediamine* molecules is bound to the metal ion through the lone pair electrons of the two nitrogen atoms. This results in the formation of three five-membered rings, each including the metal ion; the process of ring formation is called **chelation.**

Multidentate ligands contain more than two coordinating atoms per molecule, e.g. 1,2-diaminoethanetetra-acetic acid (ethylenediaminetetra-acetic acid, EDTA),† which has two donor nitrogen atoms and four donor oxygen atoms in the molecule, can be hexadentate.

In the foregoing it has been assumed that the complex species does not contain more than one metal ion, but under appropriate conditions a binuclear complex, i.e. one containing two metal ions, or even a polynuclear complex, containing more than two metal ions may be formed. Thus interaction between Zn^{2+} and Cl^- ions may result in the formation of binuclear complexes, e.g. $[Zn_2Cl_6]^{2-}$, in addition to simple species such as $ZnCl_3^-$ and $ZnCl_4^{2-}$. The formation of bi- and poly-nuclear complexes will clearly be favoured by a high concentration of the metal ion; if the latter is present as a trace constituent of a solution, polynuclear complexes are unlikely to be formed.

2.23 STABILITY OF COMPLEXES

The thermodynamic stability of a species is a measure of the extent to which this species will be formed from other species under certain conditions, provided that the system is allowed to reach equilibrium. Consider a metal ion M in solution together with a monodentate ligand L, then the system may be described by the following stepwise equilibria, in which, for convenience, coordinated water molecules are not shown:

$$M + L \rightleftharpoons ML; \qquad K_1 = [ML]/[M][L]$$

$$ML + L \rightleftharpoons ML_2; \qquad K_2 = [ML_2]/[ML][L]$$

$$ML_{(n-1)} + L \rightleftharpoons ML_n; \quad K_n = [ML_n]/[ML_{(n-1)}][L]$$

The equilibrium constants $K_1, K_2, \ldots, K_n$ are referred to as **stepwise stability constants.**

An alternative way of expressing the equilibria is as follows:

$$M + L \rightleftharpoons ML; \quad \beta_1 = [ML]/[M][L]$$

$$M + 2L \rightleftharpoons ML_2; \quad \beta_2 = [ML_2]/[M][L]^2$$

$$M + nL \rightleftharpoons ML_n; \quad \beta_n = [ML_n]/[M][L]^n$$

The equilibrium constants $\beta_1, \beta_2, \ldots, \beta_n$ are called the **overall stability constants** and are related to the stepwise stability constants by the general expression

$$\beta_n = K_1 \times K_2 \times \ldots K_n$$

---

* Ethane-1,2-diamine.

† 1,2-Bis[bis(carboxymethyl)amino]ethane.

In the above equilibria it has been assumed that no insoluble products are formed nor any polynuclear species.

A knowledge of stability constant values is of considerable importance in analytical chemistry, since they provide information about the concentrations of the various complexes formed by a metal in specified equilibrium mixtures; this is invaluable in the study of complexometry, and of various analytical separation procedures such as solvent extraction, ion exchange, and chromatography.[2,3]

2.24 METAL ION BUFFERS

Consider the equation for complex formation

$$M + L \rightleftharpoons ML; \quad K = [ML]/[M][L]$$

and assume that ML is the only complex to be formed by the particular system. The equilibrium constant expression can be rearranged to give:

$$[M] = 1/K \times [ML]/[L]$$

$$\log[M] = \log 1/K + \log[ML]/[L]$$

$$pM = \log K - \log[ML]/[L]$$

This shows that the pM value of the solution is fixed by the value of K and the ratio of complex-ion concentration to that of the free ligand. If more of M is added to the solution, more complex will be formed and the value of pM will not change appreciably. Likewise, if M is removed from the solution by some reaction, some of the complex will dissociate to restore the value of pM. This recalls the behaviour of buffer solutions encountered with acids and bases (Section 2.20), and by analogy, the complex–ligand system may be termed a **metal ion buffer**.

2.25 FACTORS INFLUENCING THE STABILITY OF COMPLEXES

The stability of a complex will obviously be related to (*a*) the complexing ability of the metal ion involved, and (*b*) characteristics of the ligand, and it is important to examine these factors briefly.

(*a*) Complexing ability of metals. The relative complexing ability of metals is conveniently described in terms of the **Schwarzenbach classification**, which is broadly based upon the division of metals into Class A and Class B Lewis acids, i.e. electron acceptors. Class A metals are distinguished by an order of affinity (in aqueous solution) towards the halogens $F^- \gg Cl^- > Br^- > I^-$, and form their most stable complexes with the first member of each group of donor atoms in the Periodic Table (i.e. nitrogen, oxygen and fluorine). Class B metals coordinate much more readily with I^- than with F^- in aqueous solution, and form their most stable complexes with the second (or heavier) donor atom from each group (i.e. P, S, Cl). The Schwarzenbach classification defines three categories of metal ion acceptors:

1. Cations with noble gas configurations. The alkali metals, alkaline earths and aluminium belong to this group which exhibit Class A acceptor properties. Electrostatic forces predominate in complex formation, so interactions

between small ions of high charge are particularly strong and lead to stable complexes.

2. Cations with completely filled *d* sub-shells. Typical of this group are copper(I), silver(I) and gold(I) which exhibit Class B acceptor properties. These ions have high polarising power and the bonds formed in their complexes have appreciable covalent character.
3. Transition metal ions with incomplete *d* sub-shells. In this group both Class A and Class B tendencies can be distinguished. The elements with Class B characteristics form a roughly triangular group within the Periodic Table, with the apex at copper and the base extending from rhenium to bismuth. To the left of this group, elements in their higher oxidation states tend to exhibit Class A properties, while to the right of the group, the higher oxidation states of a given element have a greater Class B character.

The concept of **'hard' and 'soft' acids and bases** is useful in characterising the behaviour of Class A and Class B acceptors. A soft base may be defined as one in which the donor atom is of high polarisability and of low electronegativity, is easily oxidised, or is associated with vacant, low-lying orbitals. These terms describe, in different ways, a base in which the donor atom electrons are not tightly held, but are easily distorted or removed. Hard bases have the opposite properties, i.e. the donor atom is of low polarisability and high electronegativity, is difficult to reduce, and is associated with vacant orbitals of high energy which are inaccessible.

On this basis, it is seen that Class A acceptors prefer to bind to hard bases, e.g. with nitrogen, oxygen and fluorine donor atoms, whilst Class B acceptors prefer to bind to the softer bases, e.g. P, As, S, Se, Cl, Br, I donor atoms. Examination of the Class A acceptors shows them to have the following distinguishing features; small size, high positive oxidation state, and the absence of outer electrons which are easily excited to higher states. These are all factors which lead to low polarisability, and such acceptors are called hard acids. Class B acceptors, however, have one or more of the following properties: low positive or zero oxidation state, large size, and several easily excited outer electrons (for metals these are the *d* electrons). These are all factors which lead to high polarisability, and Class B acids may be called soft acids.

A general principle may now be stated which permits correlation of the complexing ability of metals: 'Hard acids tend to associate with hard bases and soft acids with soft bases'. This statement must not, however, be regarded as exclusive, i.e. under appropriate conditions soft acids may complex with hard bases or hard acids with soft bases.

(*b*) Characteristics of the ligand. Among the characteristics of the ligand which are generally recognised as influencing the stability of complexes in which it is involved are (i) the basic strength of the ligand, (ii) its chelating properties (if any), and (iii) steric effects. From the point of view of the analytical applications of complexes, the chelating effect is of paramount importance and therefore merits particular attention.

The term **chelate effect** refers to the fact that a chelated complex, i.e. one formed by a bidentate or a multidenate ligand, is more stable than the *corresponding* complex with monodentate ligands: the greater the number of points of attachment of ligand to the metal ion, the greater the stability of the complex. Thus the complexes formed by the nickel(II) ion with (*a*) the monodentate NH_3 molecule, (*b*) the bidentate ethylenediamine (1,2-diaminoethane), and (*c*) the hexadentate ligand 'penten' $\{(H_2N \cdot CH_2 \cdot CH_2)_2N \cdot CH_2 \cdot CH_2 \cdot N(CH_2 \cdot CH_2 \cdot NH_2)_2\}$ show an overall stability constant value for the ammonia complex of 3.1×10^8, which is increased by a factor of about 10^{10} for the complex of ligand (*b*), and is approximately ten times greater still for the third complex.

The most common steric effect is that of inhibition of complex formation owing to the presence of a large group either attached to, or in close proximity to, the donor atom.

A further factor which must also be taken into consideration from the point of view of the analytical applications of complexes and of complex-formation reactions is the rate of reaction: to be analytically useful it is usually required that the reaction be rapid. An important classification of complexes is based upon the rate at which they undergo substitution reactions, and leads to the two groups of **labile** and **inert** complexes. The term labile complex is applied to those cases where nucleophilic substitution is complete within the time required for mixing the reagents. Thus, for example, when excess of aqueous ammonia is added to an aqueous solution of copper(II) sulphate, the change in colour from pale to deep blue is instantaneous; the rapid replacement of water molecules by ammonia indicates that the Cu(II) ion forms kinetically labile complexes. The term inert is applied to those complexes which undergo slow substitution reactions, i.e. reactions with half-times of the order of hours or even days at room temperature. Thus the Cr(III) ion forms kinetically inert complexes, so that the replacement of water molecules coordinated to Cr(III) by other ligands is a very slow process at room temperature.

Kinetic inertness or lability is influenced by many factors, but the following general observations form a convenient guide to the behaviour of the complexes of various elements.

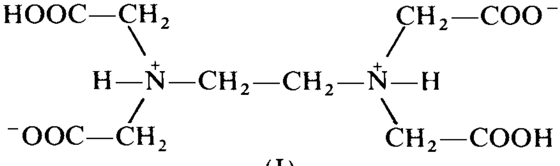
(i) Main group elements usually form labile complexes.
(ii) With the exception of Cr(III) and Co(III), most first-row transition elements form labile complexes.
(iii) Second- and third-row transition elements tend to form inert complexes.

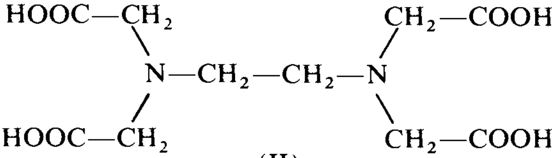
For a full discussion of the topics introduced in this section a textbook of inorganic chemistry (e.g. Ref. 4) or one dealing with complexes (e.g. Ref. 2), should be consulted.

2.26 COMPLEXONES

The formation of a single complex species rather than the stepwise production of such species will clearly simplify complexometric titrations and facilitate the detection of end points. Schwarzenbach[2] realised that the acetate ion is able to form acetato complexes of low stability with nearly all polyvalent cations, and that if this property could be reinforced by the chelate effect, then much stronger complexes would be formed by most metal cations. He found that the aminopolycarboxylic acids are excellent complexing agents: the most important of these is 1,2-diaminoethanetetra-acetic acid (ethylenediaminetetra-acetic acid). The formula (I) is preferred to (II), since it has been shown from measurements of the dissociation constants that two hydrogen atoms are probably held in the form of zwitterions. The values of pK are respectively p$K_1 = 2.0$, p$K_2 = 2.7$,

$pK_3 = 6.2$, and $pK_4 = 10.3$ at 20 °C; these values suggest that it behaves as a dicarboxylic acid with two strongly acidic groups and that there are two ammonium protons of which the first ionises in the pH region of about 6.3 and the second at a pH of about 11.5. Various trivial names are used for *e*thylene*d*iamine*t*etra-*a*cetic acid and its sodium salts, and these include Trilon B, Complexone III, Sequestrene, Versene, and Chelaton 3; the disodium salt is most widely employed in titrimetric analysis. To avoid the constant use of the long name, the abbreviation EDTA is utilised for the disodium salt.


(I)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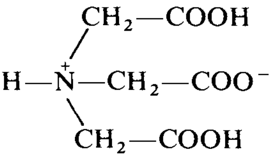
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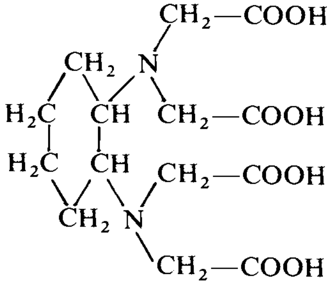
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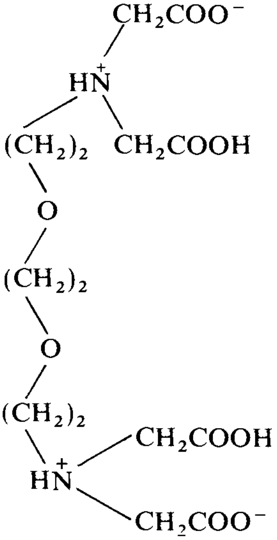
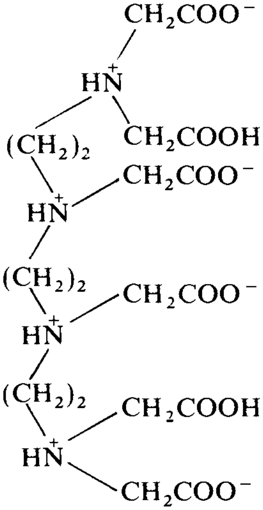


(V) EGTA



(VI) TTHA

Other complexing agents (complexones) which are sometimes used include (*a*) nitrilotriacetic acid (III) (NITA or NTA or Complexone I; this has $pK_1 = 1.9$, $pK_2 = 2.5$, and $pK_3 = 9.7$), (*b*) *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetra-acetic acid (IV): this should presumably be formulated as a zwitterion structure like (I); the abbreviated name is CDTA, DCyTA, DCTA or Complexone IV, (*c*) 2,2′-ethylenedioxybis{ethyliminodi(acetic acid)} (V) also known as ethylene glycolbis(2-aminoethyl ether)*N*,*N*,*N*′,*N*′-tetra-acetic acid (EGTA), and (*d*) triethylenetetramine-*N*,*N*,*N*′,*N*″,*N*‴,*N*‴-hexa-acetic acid (TTHA) (VI). CDTA often forms stronger metal complexes than does EDTA and thus finds applications in analysis, but the metal complexes are formed rather more slowly than with EDTA so that the end-point of the titration tends to be drawn out with the former reagent. EGTA finds analytical application mainly in the determination of calcium in a mixture of calcium and magnesium and is probably superior to EDTA in the calcium/magnesium water-hardness titration (Section 10.61) TTHA forms 1:2 complexes with many trivalent cations and with some divalent metals, and can be used for determining the components of mixtures of certain ions without the use of masking agents (see Section 10.47).

However, EDTA has the widest general application in analysis because of its powerful complexing action and commercial availability. The spatial structure of its anion, which has six donor atoms, enables it to satisfy the coordination number of six frequently encountered among the metal ions and to form strainless five-membered rings on chelation. The resulting complexes have similar structures but differ from one another in the charge they carry.

To simplify the following discussion EDTA is assigned the formula H_4Y: the disodium salt is therefore Na_2H_2Y and affords the complex-forming ion H_2Y^{2-} in aqueous solution; it reacts with all metals in a 1:1 ratio. The reactions with cations, e.g. M^{2+}, may be written as:

$$M^{2+} + H_2Y^{2-} \rightleftharpoons MY^{2-} + 2H^+ \qquad (l)$$

For other cations, the reactions may be expressed as:

$$M^{3+} + H_2Y^{2-} \rightleftharpoons MY^- + 2H^+ \tag{m}$$

$$M^{4+} + H_2Y^{2-} \rightleftharpoons MY + 2H^+ \tag{n}$$

or $$M^{n+} + H_2Y^{2-} \rightleftharpoons (MY)^{(n-4)+} + 2H^+ \tag{o}$$

One mole of the complex-forming H_2Y^{2-} reacts in all cases with one mole of the metal ion and in each case, also, two moles of hydrogen ion are formed. It is apparent from equation (*o*) that the dissociation of the complex will be governed by the pH of the solution; lowering the pH will decrease the stability of the metal–EDTA complex. The more stable the complex, the lower the pH at which an EDTA titration of the metal ion in question may be carried out. Table 2.3 indicates minimum pH values for the existence of EDTA complexes of some selected metals.

Table 2.3 Stability with respect to pH of some metal–EDTA complexes

Minimum pH at which complexes exist	Selected metals
1–3	Zr^{4+}; Hf^{4+}; Th^{4+}; Bi^{3+}; Fe^{3+}
4–6	Pb^{2+}; Cu^{2+}; Zn^{2+}; Co^{2+}; Ni^{2+}; Mn^{2+}; Fe^{2+}; Al^{3+}; Cd^{2+}; Sn^{2+}
8–10	Ca^{2+}; Sr^{2+}; Ba^{2+}; Mg^{2+}

It is thus seen that, in general, EDTA complexes with metal ions of the charge number 2 are stable in alkaline or slightly acidic solution, whilst complexes with ions of charge numbers 3 or 4 may exist in solutions of much higher acidity.

2.27 STABILITY CONSTANTS OF EDTA COMPLEXES

The stability of a complex is characterised by the stability constant (or formation constant) K:

$$M^{n+} + Y^{4-} \rightleftharpoons (MY)^{(n-4)+} \tag{p}$$

$$K = [(MY)^{(n-4)+}]/[M^{n+}][Y^{4-}] \tag{q}$$

Some values for the stability constants (expressed as $\log K$) of metal–EDTA complexes are collected in Table 2.4: these apply to a medium of ionic strength $I = 0.1$ at 20 °C.

Table 2.4 Stability constants (as log *K*) of metal–EDTA complexes

Mg^{2+}	8.7	Zn^{2+}	16.7	La^{3+}	15.7
Ca^{2+}	10.7	Cd^{2+}	16.6	Lu^{3+}	20.0
Sr^{2+}	8.6	Hg^{2+}	21.9	Sc^{3+}	23.1
Ba^{2+}	7.8	Pb^{2+}	18.0	Ga^{3+}	20.5
Mn^{2+}	13.8	Al^{3+}	16.3	In^{3+}	24.9
Fe^{2+}	14.3	Fe^{3+}	25.1	Th^{4+}	23.2
Co^{2+}	16.3	Y^{3+}	18.2	Ag^+	7.3
Ni^{2+}	18.6	Cr^{3+}	24.0	Li^+	2.8
Cu^{2+}	18.8	Ce^{3+}	15.9	Na^+	1.7

In equation (*q*) only the fully ionised form of EDTA, i.e. the ion Y^{4-}, has been taken into account, but at low pH values the species HY^{3-}, H_2Y^{2-}, H_3Y^- and even undissociated H_4Y may well be present; in other words, only a part of the EDTA uncombined with metal may be present as Y^{4-}. Further, in equation (*q*) the metal ion M^{n+} is assumed to be uncomplexed, i.e. in aqueous solution it is simply present as the hydrated ion. If, however, the solution also contains substances other than EDTA which can complex with the metal ion, then the whole of this ion uncombined with EDTA may no longer be present as the simple hydrated ion. Thus, in practice, the stability of metal–EDTA complexes may be altered (*a*) by variation in pH and (*b*) by the presence of other complexing agents. The stability constant of the EDTA complex will then be different from the value recorded for a specified pH in pure aqueous solution; the value recorded for the new conditions is termed the **'apparent'** or **'conditional' stability constant**. It is clearly necessary to examine the effect of these two factors in some detail.

(*a*) pH effect. The apparent stability constant at a given pH may be calculated from the ratio K/α, where α is the ratio of the total uncombined EDTA (in all forms) to the form Y^{4-}. Thus K_H, the apparent stability constant for the metal–EDTA complex at a given pH, can be calculated from the expression

$$\log K_H = \log K - \log \alpha \qquad (30)$$

The factor α can be calculated from the known dissociation constants of EDTA, and since the proportions of the various ionic species derived from EDTA will be dependent upon the pH of the solution, α will also vary with pH; a plot of $\log \alpha$ against pH shows a variation of $\log \alpha = 18$ at $\mathrm{pH} = 1$ to $\log \alpha = 0$ at $\mathrm{pH} = 12$: such a curve is very useful for dealing with calculations of apparent stability constants. Thus, for example, from Table 2.4, $\log K$ of the EDTA complex of the Pb^{2+} ion is 18.0 and from a graph of $\log \alpha$ against pH, it is found that at a pH of 5.0, $\log \alpha = 7$. Hence from equation (30), at a pH of 5.0 the lead–EDTA complex has an apparent stability constant given by:

$$\log K_H = 18.0 - 7.0 = 11.0$$

Carrying out a similar calculation for the EDTA complex of the Mg^{2+} ion ($\log K = 8.7$), for the same pH (5.0), it is found:

$$\log K_H(\mathrm{Mg(II)-EDTA}) = 8.7 - 7.0 = 1.7$$

These results imply that at the specified pH the magnesium complex is appreciably dissociated, whereas the lead complex is stable, and clearly titration of an Mg(II) solution with EDTA at this pH will be unsatisfactory, but titration of the lead solution under the same conditions will be quite feasible. In practice, for a metal ion to be titrated with EDTA at a stipulated pH the value of $\log K_H$ should be greater than 8 when a metallochromic indicator is used.

As indicated by the data quoted in the previous section, the value of $\log \alpha$ is small at high pH values, and it therefore follows that the larger values of $\log K_H$ are found with increasing pH. However, by increasing the pH of the solution the tendency to form slightly soluble metallic hydroxides is enhanced owing to the reaction:

$$(MY)^{(n-4)+} + nOH^- \rightleftharpoons M(OH)_n + Y^{4-}$$

The extent of hydrolysis of $(MY)^{(n-4)+}$ depends upon the characteristics of the metal ion, and is largely controlled by the solubility product of the metallic hydroxide and, of course, the stability constant of the complex. Thus iron(III) is precipitated as hydroxide ($K_{sol} = 1 \times 10^{-36}$) in basic solution, but nickel(II), for which the relevant solubility product is 6.5×10^{-18}, remains complexed. Clearly the use of excess EDTA will tend to reduce the effect of hydrolysis in basic solutions. It follows that for each metal ion there exists an optimum pH which will give rise to a maximum value for the apparent stability constant.

(*b*) The effect of other complexing agents. If another complexing agent (say NH_3) is also present in the solution, then in equation (q) $[M^{n+}]$ will be reduced owing to complexation of the metal ions with ammonia molecules. It is convenient to indicate this reduction in effective concentration by introducing a factor β, defined as the ratio of the sum of the concentrations of all forms of the metal ion not complexed with EDTA to the concentration of the simple (hydrated) ion. The apparent stability constant of the metal–EDTA complex, taking into account the effects of both pH and the presence of other complexing agents, is then given by:

$$\log K_{HZ} = \log K - \log \alpha - \log \beta. \tag{31}$$

2.28 ELECTRODE POTENTIALS

When a metal is immersed in a solution containing its own ions, say, zinc in zinc sulphate solution, a potential difference is established between the metal and the solution. The potential difference E for an electrode reaction

$$M^{n+} + ne \rightleftharpoons M$$

is given by the expression:

$$E = E^{\ominus} + \frac{RT}{nF} \ln a_{M^{n+}} \tag{32}$$

where R is the gas constant, T is the absolute temperature, F the Faraday constant, n the charge number of the ions, $a_{M^{n+}}$ the activity of the ions in the solution, and $E^{\ominus}$ is a constant dependent upon the metal. Equation (32) can be simplified by introducing the known values of R and F, and converting natural logarithms to base 10 by multiplying by 2.3026; it then becomes:

$$E = E^{\ominus} + \frac{0.000\,198\,4T}{n} \log a_{M^{n+}}$$

For a temperature of 25 °C ($T = 298$K):

$$E = E^{\ominus} + \frac{0.0591}{n} \log a_{M^{n+}} \tag{33}$$

For many purposes in quantitative analysis, it is sufficiently accurate to replace $a_{M^{n+}}$ by $c_{M^{n+}}$, the ion concentration (in moles per litre):

$$E = E^{\ominus} + \frac{0.0591}{n} \log c_{M^{n+}} \tag{34}$$

The latter is a form of the **Nernst equation**.

If in equation (33), $a_{\mathrm{M}^{n+}}$ is put equal to unity, E is equal to $E^{\ominus}$. $E^{\ominus}$ is called the **standard electrode potential** of the metal; both E and $E^{\ominus}$ are expressed in volts.

In order to determine the potential difference between an electrode and a solution, it is necessary to have another electrode and solution of accurately known potential difference. The two electrodes can then be combined to form a voltaic cell, the e.m.f. of which can be directly measured. The e.m.f. of the cell is the difference of the electrode potentials at zero current; the value of the unknown potential can then be calculated. The primary reference electrode is the **normal** or **standard hydrogen electrode** (see also Section 15.2). This consists of a piece of platinum foil, coated electrolytically with platinum black, and immersed in a solution of hydrochloric acid containing hydrogen ions at unit activity. (This corresponds to $1.18M$ hydrochloric acid at 25 °C.) Hydrogen gas at a pressure of one atmosphere is passed over the platinum foil through the side tube C (Fig. 2.2) and escapes through the small holes B in the surrounding glass tube A. Because of the periodic formation of bubbles, the level of the liquid inside the tube fluctuates, and a part of the foil is alternately exposed to the solution and to hydrogen. The lower end of the foil is continuously immersed in the solution to avoid interruption of the electric current. Connection between the platinum foil and an external circuit is made with mercury in D. The platinum black has the property of adsorbing large quantities of atomic hydrogen, and it permits the change from the gaseous to the ionic form and the reverse process to occur without hindrance; it therefore behaves as though it were composed entirely of hydrogen, that is, as a hydrogen electrode. Under fixed conditions, viz. hydrogen gas at atmospheric pressure and unit activity of hydrogen ions in the solution in contact with the electrode, the hydrogen electrode possesses a definite potential. By convention, the potential of the standard hydrogen electrode is equal to zero at all temperatures. Upon connecting the standard hydrogen electrode with a metal electrode consisting of a metal in contact with a solution of its ions of unit activity and measuring the cell e.m.f. the **standard electrode potential** of the metal may be determined. The cell is usually written as

$$\mathrm{Pt, H_2 | H^+}(a = 1) \vdots\vdots\, \mathrm{M}^{n+}(a = 1) | \mathrm{M}$$

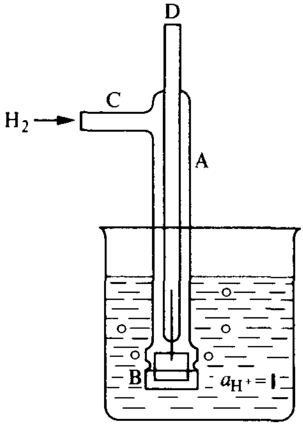


Fig. 2.2

In this scheme, a single vertical line represents a metal–electrolyte boundary at which a potential difference is taken into account: the double vertical broken lines represent a liquid junction at which the potential is to be disregarded or is considered to be eliminated by a salt bridge.

When reference is made to the electrode potential of a zinc electrode, it is the e.m.f. of the cell:

$$\mathrm{Pt,H_2|H^+}(a = 1)\vdots\vdots\mathrm{Zn^{2+}|Zn}$$

or the e.m.f. of the half-cell $\mathrm{Zn^{2+}|Zn}$ which is meant. The cell reaction is:

$$\mathrm{H_2 + Zn^{2+} \rightarrow 2H^+}(a = 1) + \mathrm{Zn}$$

and the half-cell reaction is written as:

$$\mathrm{Zn^{2+}} + 2e \rightleftharpoons \mathrm{Zn}$$

The electrode potential of the $\mathrm{Fe^{3+},Fe^{2+}|Pt}$ electrode is the e.m.f. of the cell:

$$\mathrm{Pt,H_2|H^+}(a = 1)\vdots\vdots\mathrm{Fe^{3+},Fe^{2+}|Pt}$$

or the e.m.f. of the half-cell $\mathrm{Fe^{3+},Fe^{2+}|Pt}$. The cell reaction is:

$$\tfrac{1}{2}\mathrm{H_2 + Fe^{3+} \rightarrow H^+}(a = 1) + \mathrm{Fe^{2+}}$$

and the half-cell reaction is written:

$$\mathrm{Fe^{3+}} + e \rightleftharpoons \mathrm{Fe^{2+}}$$

The convention is adopted of writing all half-cell reactions as reductions:

$$\mathrm{M}^{n+} + ne \rightarrow \mathrm{M}$$

e.g. $\mathrm{Zn^{2+}} + 2e \rightarrow \mathrm{Zn}$; $E^{\ominus} = -0.76$ volt

When the activity of the ion M^{n+} is equal to unity (approximately true for a $1M$ solution), the electrode potential E is equal to the standard potential $E^{\ominus}$. Some important standard electrode potentials referred to the standard hydrogen electrode at 25 °C (in aqueous solution) are collected in Table 2.5.[5]

Table 2.5 Standard electrode potentials at 25 °C

Electrode reaction	$E^{\ominus}$ (volts)	Electrode reaction	$E^{\ominus}$ (volts)
$\mathrm{Li^+} + e = \mathrm{Li}$	−3.045	$\mathrm{Tl^+} + e = \mathrm{Tl}$	−0.336
$\mathrm{K^+} + e = \mathrm{K}$	−2.925	$\mathrm{Co^{2+}} + 2e = \mathrm{Co}$	−0.277
$\mathrm{Ba^{2+}} + 2e = \mathrm{Ba}$	−2.90	$\mathrm{Ni^{2+}} + 2e = \mathrm{Ni}$	−0.25
$\mathrm{Sr^{2+}} + 2e = \mathrm{Sr}$	−2.89	$\mathrm{Sn^{2+}} + 2e = \mathrm{Sn}$	−0.136
$\mathrm{Ca^{2+}} + 2e = \mathrm{Ca}$	−2.87	$\mathrm{Pb^{2+}} + 2e = \mathrm{Pb}$	−0.126
$\mathrm{Na^+} + e = \mathrm{Na}$	−2.714	$\mathrm{2H^+} + 2e = \mathrm{H_2}$	0.000
$\mathrm{Mg^{2+}} + 2e = \mathrm{Mg}$	−2.37	$\mathrm{Cu^{2+}} + 2e = \mathrm{Cu}$	+0.337
$\mathrm{Al^{3+}} + 3e = \mathrm{Al}$	−1.66	$\mathrm{Hg^{2+}} + 2e = \mathrm{Hg}$	+0.789
$\mathrm{Mn^{2+}} + 2e = \mathrm{Mn}$	−1.18	$\mathrm{Ag^+} + e = \mathrm{Ag}$	+0.799
$\mathrm{Zn^{2+}} + 2e = \mathrm{Zn}$	−0.763	$\mathrm{Pd^{2+}} + 2e = \mathrm{Pd}$	+0.987
$\mathrm{Fe^{2+}} + 2e = \mathrm{Fe}$	−0.440	$\mathrm{Pt^{2+}} + 2e = \mathrm{Pt}$	+1.2
$\mathrm{Cd^{2+}} + 2e = \mathrm{Cd}$	−0.403	$\mathrm{Au^{3+}} + 3e = \mathrm{Au}$	+1.50

It may be noted that the standard hydrogen electrode is rather difficult to manipulate. In practice, electrode potentials on the hydrogen scale are usually determined indirectly by measuring the e.m.f. of a cell formed from the electrode in question and a convenient reference electrode whose potential with respect to the hydrogen electrode is accurately known. The reference electrodes generally used are the calomel electrode and the silver–silver chloride electrode (see Sections 15.3–4).

When metals are arranged in the order of their standard electrode potentials, the so-called **electrochemical series** of the metals is obtained. The greater the negative value of the potential, the greater is the tendency of the metal to pass into the ionic state. A metal will normally displace any other metal below it in the series from solutions of its salts. Thus magnesium, aluminium, zinc, or iron will displace copper from solutions of its salts; lead will displace copper, mercury, or silver; copper will displace silver.

The standard electrode potential is a quantitative measure of the readiness of the element to lose electrons. It is therefore a measure of the strength of the element as a reducing agent in aqueous solution; the more negative the potential of the element, the more powerful is its action as a reductant.

It must be emphasised that standard electrode potential values relate to an *equilibrium* condition between the metal electrode and the solution. Potentials determined under, or calculated for, such conditions are often referred to as 'reversible electrode potentials', and it must be remembered that the Nernst equation is only strictly applicable under such conditions.

2.29 CONCENTRATION CELLS

An electrode potential varies with the concentration of the ions in the solution. Hence two electrodes of the same metal, but immersed in solutions containing different concentrations of its ions, may form a cell. Such a cell is termed a **concentration cell**. The e.m.f. of the cell will be the algebraic difference of the two potentials, if a salt bridge be inserted to eliminate the liquid–liquid junction potential. It may be calculated as follows. At 25 °C:

$$\begin{aligned} E &= \frac{0.0591}{n}\log c_1 + E^{\ominus} - \left(\frac{0.0591}{n}\log c_2 + E^{\ominus}\right) \\ &= \frac{0.0591}{n}\log\frac{c_1}{c_2}, \quad \text{where } c_1 > c_2 \end{aligned}$$

As an example consider the cell:

$$\overset{-}{\mathrm{Ag}}\left|\begin{array}{c} \mathrm{AgNO_3\ aq.} \\ [\mathrm{Ag^+}] = 0.00475M \end{array}\right\|\begin{array}{c} \mathrm{AgNO_3\ aq.} \\ [\mathrm{Ag^+}] = 0.043M \end{array}\left|\overset{+}{\mathrm{Ag}}\right.$$

$$\overset{\leftarrow}{E_2} \qquad\qquad\qquad\qquad \overset{\rightarrow}{E_1}$$

Assuming that there is no potential difference at the liquid junction:

$$E = E_1 - E_2 = \frac{0.0591}{1}\log\frac{0.043}{0.004\,75} = 0.056 \text{ volt}$$

2.30 CALCULATION OF THE e.m.f. OF A VOLTAIC CELL

An interesting application of electrode potentials is to the calculation of the e.m.f. of a voltaic cell. One of the simplest of galvanic cells is the Daniell cell. It consists of a rod of zinc dipping into zinc sulphate solution and a strip of copper in copper sulphate solution; the two solutions are generally separated by placing one inside a porous pot and the other in the surrounding vessel. The cell may be represented as:

$\mathrm{Zn}|\mathrm{ZnSO_4aq.}\,\vdots\vdots\,\mathrm{CuSO_4aq.}|\mathrm{Cu}$

At the zinc electrode, zinc ions pass into solution, leaving an equivalent negative charge on the metal. Copper ions are deposited at the copper electrode, rendering it positively charged. By completing the external circuit, the current (electrons) passes from the zinc to the copper. The chemical reactions in the cell are as follows:

(*a*) zinc electrode: $\mathrm{Zn} \rightleftharpoons \mathrm{Zn^{2+}} + 2e$;
(*b*) copper electrode: $\mathrm{Cu^{2+}} + 2e \rightleftharpoons \mathrm{Cu}$.

The net chemical reaction is:

$\mathrm{Zn} + \mathrm{Cu^{2+}} = \mathrm{Zn^{2+}} + \mathrm{Cu}$

The potential difference at each electrode may be calculated by the formula given above, and the e.m.f. of the cell is the algebraic difference of the two potentials, the correct sign being applied to each.

As an example we may calculate the e.m.f. of the Daniell cell with molar concentrations of zinc ions and copper(II) ions:

$$E = E^{\ominus}_{(\mathrm{Cu})} - E^{\ominus}_{(\mathrm{Zn})} = +0.34 - (-0.76) = 1.10 \text{ volts}$$

The small potential difference produced at the contact between the two solutions (the so-called liquid–junction potential) is neglected.

2.31 OXIDATION–REDUCTION CELLS

Reduction is accompanied by a gain of electrons, and oxidation by a loss of electrons. In a system containing both an oxidising agent and its reduction product, there will be an equilibrium between them and electrons. If an inert electrode, such as platinum, is placed in a redox system, for example, one containing Fe(III) and Fe(II) ions, it will assume a definite potential indicative of the position of equilibrium. If the system tends to act as an oxidising agent, then $\mathrm{Fe^{3+}} \rightarrow \mathrm{Fe^{2+}}$ and it will take electrons from the platinum, leaving the latter positively charged; if, however, the system has reducing properties ($\mathrm{Fe^{2+}} \rightarrow \mathrm{Fe^{3+}}$), electrons will be given up to the metal, which will then acquire a negative charge. The magnitude of the potential will thus be a measure of the oxidising or reducing properties of the system.

To obtain comparative values of the 'strengths' of oxidising agents, it is necessary, as in the case of the electrode potentials of the metals, to measure under standard experimental conditions the potential difference between the platinum and the solution relative to a standard of reference. The primary standard is the standard or normal hydrogen electrode (Section 2.28) and its potential is taken as zero. The standard experimental conditions for the redox system are those in which the ratio of the activity of the oxidant to that of the reductant is unity. Thus for the $Fe^{3+} - Fe^{2+}$ electrode, the redox cell would be:

$$\mathrm{Pt,H_2}\left|\mathrm{H^+}(a = 1)\right\|\begin{array}{l}\mathrm{Fe^{3+}}(a = 1)\\ \mathrm{Fe^{2+}}(a = 1)\end{array}\Bigg|\mathrm{Pt}$$

The potential measured in this way is called the **standard reduction potential.** A selection of standard reduction potentials is given in Table 2.6.

The standard potentials enable us to predict which ions will oxidise or reduce other ions at unit activity (or molar concentration). The most powerful oxidising agents are those at the upper end of the table, and the most powerful reducing agents at the lower end. Thus permanganate ion can oxidise Cl^-, Br^-, I^-, Fe^{2+} and $[Fe(CN)_6]^{4-}$; Fe^{3+} can oxidise H_3AsO_3 and I^- but not $Cr_2O_7^{2-}$ or Cl^-. It must be emphasised that for many oxidants the pH of the medium is of great importance, since they are generally used in acidic media. Thus in measuring the standard potential of the $MnO_4^- - Mn^{2+}$ system; $MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$, it is necessary to state that the hydrogen-ion activity is unity; this leads to $E^{\ominus} = +1.52$ volts. Similarly, the value of $E^{\ominus}$ for the $Cr_2O_7^{2-} - Cr^{3+}$ system is $+1.33$ volts. This means that the $MnO_4^- - Mn^{2+}$ system is a better oxidising agent than the $Cr_2O_7^{2-} - Cr^{3+}$ system. Since the standard potentials for $Cl_2 - 2Cl^-$ and $Fe^{3+} - Fe^{2+}$ systems are $+1.36$ and 0.77 volt respectively, permanganate and dichromate will oxidise Fe(II) ions but only permanganate will oxidise chloride ions; this explains why dichromate but not permanganate (except under very special conditions) can be used for the titration of Fe(II) in hydrochloric acid solution. Standard potentials do not give any information as to the speed of the reaction: in some cases a catalyst is necessary in order that the reaction may proceed with reasonable velocity.

Standard potentials are determined with full consideration of activity effects, and are really limiting values. They are rarely, if ever, observed directly in a potentiometric measurement. In practice, measured potentials determined under defined concentration conditions (formal potentials) are very useful for predicting the possibilities of redox processes. Further details are given in Section 10.90.

2.32 CALCULATION OF THE STANDARD REDUCTION POTENTIAL

A reversible oxidation–reduction system may be written in the form

$$\text{Oxidant} + ne \rightleftharpoons \text{Reductant}$$

or

$$\text{Ox} + ne \rightleftharpoons \text{Red}$$

(*oxidant* = substance in oxidised state, *reductant* = substance in reduced state). The electrode potential which is established when an inert or unattackable electrode is immersed in a solution containing both oxidant and reductant is given by the expression:

$$E_T = E^{\ominus} + \frac{RT}{nF}\ln\frac{a_{\mathrm{Ox}}}{a_{\mathrm{Red}}}$$

where E_T is the observed potential of the redox electrode at temperature T

Table 2.6 Standard reduction potentials at 25 °C

Half-reaction	$E^{\ominus}$, volts
$F_2 + 2e \rightleftharpoons 2F^-$	+2.65
$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$	+2.01
$Co^{3+} + e \rightleftharpoons Co^{2+}$	+1.82
$Pb^{4+} + 2e \rightleftharpoons Pb^{2+}$	+1.70
$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O$	+1.69
$Ce^{4+} + e \rightleftharpoons Ce^{3+}$ (nitrate medium)	+1.61
$BrO_3^- + 6H^+ + 5e \rightleftharpoons \frac{1}{2}Br_2 + 3H_2O$	+1.52
$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52
$Ce^{4+} + e \rightleftharpoons Ce^{3+}$ (sulphate medium)	+1.44
$Cl_2 + 2e \rightleftharpoons 2Cl^-$	+1.36
$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$Tl^{3+} + 2e \rightleftharpoons Tl^+$	+1.25
$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O$	+1.23
$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$	+1.23
$IO_3^- + 6H^+ + 5e \rightleftharpoons \frac{1}{2}I_2 + 3H_2O$	+1.20
$Br_2 + 2e \rightleftharpoons 2Br^-$	+1.07
$HNO_2 + H^+ + e \rightleftharpoons NO + H_2O$	+1.00
$NO_3^- + 4H^+ + 3e \rightleftharpoons NO + 2H_2O$	+0.96
$2Hg^{2+} + 2e \rightleftharpoons Hg_2^{2+}$	+0.92
$ClO^- + H_2O + 2e \rightleftharpoons Cl^- + 2OH^-$	+0.89
$Cu^{2+} + I^- + e \rightleftharpoons CuI$	+0.86
$Hg_2^{2+} + 2e \rightleftharpoons 2Hg$	+0.79
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	+0.77
$BrO^- + H_2O + 2e \rightleftharpoons Br^- + 2OH^-$	+0.76
$BrO_3^- + 3H_2O + 6e \rightleftharpoons Br^- + 6OH^-$	+0.61
$MnO_4^{2-} + 2H_2O + 2e \rightleftharpoons MnO_2 + 4OH^-$	+0.60
$MnO_4^- + e \rightleftharpoons MnO_4^{2-}$	+0.56
$H_3AsO_4 + 2H^+ + 2e \rightleftharpoons H_3AsO_3 + H_2O$	+0.56
$Cu^{2+} + Cl^- + e \rightleftharpoons CuCl$	+0.54
$I_2 + 2e \rightleftharpoons 2I^-$	+0.54
$IO^- + H_2O + 2e \rightleftharpoons I^- + 2OH^-$	+0.49
$[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-}$	+0.36
$UO_2^{2+} + 4H^+ + 2e \rightleftharpoons U^{4+} + 2H_2O$	+0.33
$IO_3^- + 3H_2O + 6e \rightleftharpoons I^- + 6OH^-$	+0.26
$Cu^{2+} + e \rightleftharpoons Cu^+$	+0.15
$Sn^{4+} + 2e \rightleftharpoons Sn^{2+}$	+0.15
$TiO^{2+} + 2H^+ + e \rightleftharpoons Ti^{3+} + H_2O$	+0.10
$S_4O_6^{2-} + 2e \rightleftharpoons 2S_2O_3^{2-}$	+0.08
$2H^+ + 2e \rightleftharpoons H_2$	0.00
$V^{3+} + e \rightleftharpoons V^{2+}$	−0.26
$Cr^{3+} + e \rightleftharpoons Cr^{2+}$	−0.41
$Bi(OH)_3 + 3e \rightleftharpoons Bi + 3OH^-$	−0.44
$Fe(OH)_3 + e \rightleftharpoons Fe(OH)_2 + OH^-$	−0.56
$U^{4+} + e \rightleftharpoons U^{3+}$	−0.61
$AsO_4^{3-} + 3H_2O + 2e \rightleftharpoons H_2AsO_3^- + 4OH^-$	−0.67
$[Sn(OH)_6]^{2-} + 2e \rightleftharpoons [HSnO_2]^- + H_2O + 3OH^-$	−0.90
$[Zn(OH)_4]^{2-} + 2e \rightleftharpoons Zn + 4OH^-$	−1.22
$[H_2AlO_3]^- + H_2O + 3e \rightleftharpoons Al + 4OH^-$	−2.35

relative to the standard or normal hydrogen electrode taken as zero potential, $E^{\ominus}$ is the standard reduction potential,* n the number of electrons gained by

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* $E^{\ominus}$ is the value of E_T at unit activities of the oxidant and reductant. If both activities are variable, e.g. Fe^{3+} and Fe^{2+}, $E^{\ominus}$ corresponds to an activity ratio of unity.

the oxidant in being converted into the reductant, and a_{Ox} and a_{Red} are the activities of the oxidant and reductant respectively.

Since activities are often difficult to determine directly, they may be replaced by concentrations; the error thereby introduced is usually of no great importance. The equation therefore becomes:

$$E_T = E^{\ominus} + \frac{RT}{nF}\ln\frac{c_{\mathrm{Ox}}}{c_{\mathrm{Red}}}$$

Substituting the known values of R and F, and changing from natural to common logarithms, at a temperature of 25 °C ($T = 298\mathrm{K}$):

$$E_{25^\circ} = E^{\ominus} + \frac{0.0591}{n}\log\frac{[\mathrm{Ox}]}{[\mathrm{Red}]}$$

If the concentrations (or, more accurately, the activities) of the oxidant and reductant are equal, $E_{25^\circ} = E^{\ominus}$, i.e. the standard reduction potential. It follows from this expression that, for example, a ten-fold change in the ratio of the concentrations of the oxidant to the reductant will produce a change in the potential of the system of $0.0591/n$ volts.

2.33 EQUILIBRIUM CONSTANTS OF OXIDATION–REDUCTION REACTIONS

The general equation for the reaction at an oxidation–reduction electrode may be written:

$$p\mathrm{A} + q\mathrm{B} + r\mathrm{C}\ldots + ne \rightleftharpoons s\mathrm{X} + t\mathrm{Y} + u\mathrm{Z} + \ldots$$

The potential is given by:

$$E = E^{\ominus} + \frac{RT}{nF}\ln\frac{a_{\mathrm{A}}^{p}.a_{\mathrm{B}}^{q}.a_{\mathrm{C}}^{r}\ldots}{a_{\mathrm{X}}^{s}.a_{\mathrm{Y}}^{t}.a_{\mathrm{Z}}^{u}\ldots}$$

where a refers to activities, and n to the number of electrons involved in the oxidation–reduction reaction. This expression reduces to the following for a temperature of 25 °C (concentrations are substituted for activities to permit ease of application in practice):

$$E = E^{\ominus} + \frac{0.0591}{n}\log\frac{c_{\mathrm{A}}^{p}.c_{\mathrm{B}}^{q}.c_{\mathrm{C}}^{r}\ldots}{c_{\mathrm{X}}^{s}.c_{\mathrm{Y}}^{t}.c_{\mathrm{Z}}^{u}\ldots}$$

It is, of course, possible to calculate the influence of the change of concentration of certain constituents of the system by the use of the latter equation. Consider, for example, the permanganate reaction:

$$\mathrm{MnO_4^-} + 8\mathrm{H^+} + 5e \rightleftharpoons \mathrm{Mn^{2+}} + 4\mathrm{H_2O}$$

$$E = E^{\ominus} + \frac{0.0591}{5}\log\frac{[\mathrm{MnO_4^-}]\times[\mathrm{H^+}]^8}{[\mathrm{Mn^{2+}}]} \quad \text{(at 25 °C)}$$

The concentration (or activity) of the water is taken as constant, since it is assumed that the reaction takes place in dilute solution, and the concentration of the water does not change appreciably as the result of the reaction. The equation may be written in the form:

$$E = E^{\ominus} + \frac{0.0591}{5}\log\frac{[\mathrm{MnO_4^-}]}{[\mathrm{Mn^{2+}}]} + \frac{0.0591}{5}\log[\mathrm{H^+}]^8$$

This enables us to calculate the effect of change in the ratio $[\mathrm{MnO_4^-}]/[\mathrm{Mn^{2+}}]$ at any hydrogen ion concentration, other factors being maintained constant. In this system, however, difficulties are experienced in the calculation owing to the fact that the reduction products of the permanganate ion vary at different hydrogen ion concentrations. In other cases no such difficulties arise, and the calculation may be employed with confidence. Thus in the reaction:

$$\mathrm{H_3AsO_4 + 2H^+ + 2}e \rightleftharpoons \mathrm{H_3AsO_3 + H_2O}$$

$$E = E^{\ominus} + \frac{0.0591}{2}\log\frac{[\mathrm{H_3AsO_4}] \times [\mathrm{H^+}]^2}{[\mathrm{H_3AsO_3}]} \quad \text{(at 25 °C)}$$

$$\text{or} \quad E = E^{\ominus} + \frac{0.0591}{2}\log\frac{[\mathrm{H_3AsO_4}]}{[\mathrm{H_3AsO_3}]} + \frac{0.0591}{2}\log[\mathrm{H^+}]^2$$

It is now possible to calculate the equilibrium constants of oxidation–reduction reactions, and thus to determine whether such reactions can find application in quantitative analysis. Consider first the simple reaction:

$$\mathrm{Cl_2 + 2Fe^{2+} \rightleftharpoons 2Cl^- + 2Fe^{3+}}$$

The equilibrium constant is given by:

$$\frac{[\mathrm{Cl^-}]^2 \times [\mathrm{Fe^{3+}}]^2}{[\mathrm{Cl_2}] \times [\mathrm{Fe^{2+}}]^2} = K$$

The reaction may be regarded as taking place in a voltaic cell, the two half-cells being a $\mathrm{Cl_2,2Cl^-}$ system and a $\mathrm{Fe^{3+},Fe^{2+}}$ system. The reaction is allowed to proceed to equilibrium, and the total voltage or e.m.f. of the cell will then be zero, i.e. the potentials of the two electrodes will be equal:

$$E^{\ominus}_{\mathrm{Cl_2,2Cl^-}} + \frac{0.0591}{2}\log\frac{[\mathrm{Cl_2}]}{[\mathrm{Cl^-}]^2} = E^{\ominus}_{\mathrm{Fe^{3+},Fe^{2+}}} + \frac{0.0591}{1}\log\frac{[\mathrm{Fe^{3+}}]}{[\mathrm{Fe^{2+}}]}$$

Now $E^{\ominus}_{\mathrm{Cl_2,2Cl^-}} = 1.36$ volts and $E^{\ominus}_{\mathrm{Fe^{3+},Fe^{2+}}} = 0.75$ volt, hence

$$\log\frac{[\mathrm{Fe^{3+}}]^2 \times [\mathrm{Cl^-}]^2}{[\mathrm{Fe^{2+}}]^2 \times [\mathrm{Cl_2}]} = \frac{0.61}{0.02965} = 20.67 = \log K$$

$$\text{or} \quad K = 4.7 \times 10^{20}$$

The large value of the equilibrium constant signifies that the reaction will proceed from left to right almost to completion, i.e. an iron(II) salt is almost completely oxidised by chlorine.

Consider now the more complex reaction:

$$\mathrm{MnO_4^- + 5Fe^{2+} + 8H^+ \rightleftharpoons Mn^{2+} + 5Fe^{3+} + 4H_2O}$$

The equilibrium constant K is given by:

$$K = \frac{[\mathrm{Mn^{2+}}] \times [\mathrm{Fe^{3+}}]^5}{[\mathrm{MnO_4^-}] \times [\mathrm{Fe^{2+}}]^5 \times [\mathrm{H^+}]^8}$$

The term $4H_2O$ is omitted, since the reaction is carried out in dilute solution, and the water concentration may be assumed constant. The hydrogen ion concentration is taken as molar. The complete reaction may be divided into two half-cell reactions corresponding to the partial equations:

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O \tag{35}$$

and $$Fe^{2+} \rightleftharpoons Fe^{3+} + e \tag{36}$$

For (35) as an oxidation–reduction electrode, we have:

$$\begin{aligned} E &= E^{\ominus} + \frac{0.0591}{5}\log\frac{[MnO_4^-]\times[H^+]^8}{[Mn^{2+}]} \\ &= 1.52 + \frac{0.0591}{5}\log\frac{[MnO_4^-]\times[H^+]^8}{[Mn^{2+}]} \end{aligned}$$

The partial equation (36) may be multiplied by 5 in order to balance (35) electrically:

$$5Fe^{2+} \rightleftharpoons 5Fe^{3+} + 5e \tag{37}$$

For (37) as an oxidation–reduction electrode:

$$E = E^{\ominus} + \frac{0.0591}{5}\log\frac{[Fe^{3+}]^5}{[Fe^{2+}]^5} = 0.77 + \frac{0.0591}{5}\log\frac{[Fe^{3+}]^5}{[Fe^{2+}]^5}$$

Combining the two electrodes into a cell, the e.m.f. will be zero when equilibrium is attained, i.e.

$$1.52 + \frac{0.0591}{5}\log\frac{[MnO_4^-]\times[H^+]^8}{[Mn^{2+}]} = 0.77 + \frac{0.0591}{5}\log\frac{[Fe^{3+}]^5}{[Fe^{2+}]^5}$$

$$\text{or}\quad \log\frac{[Mn^{2+}]\times[Fe^{3+}]^5}{[MnO_4^-]\times[Fe^{2+}]^5\times[H^+]^8} = \frac{5(1.52-0.77)}{0.0591} = 63.5$$

$$K = \frac{[Mn^{2+}]\times[Fe^{3+}]^5}{[MnO_4^-]\times[Fe^{3+}]^5\times[H^+]^8} = 3\times10^{63}$$

This result clearly indicates that the reaction proceeds virtually to completion. It is a simple matter to calculate the residual Fe(II) concentration in any particular case. Thus consider the titration of 10 mL of a 0.1 *M* solution of iron(II) ions with 0.02 *M* potassium permanganate in the presence of hydrogen ions, concentration 1 *M*. Let the volume of the solution at the equivalence point be 100 mL. Then $[Fe^{3+}] = 0.01\,M$, since it is known that the reaction is practically complete, $[Mn^{2+}] = \frac{1}{5}\times[Fe^{3+}] = 0.002\,M$, and $[Fe^{2+}] = x$. Let the excess of permanganate solution at the end-point be one drop or 0.05 mL; its concentration will be $0.05\times0.1/100 = 5\times10^{-5}\,M = [MnO_4^-]$. Substituting these values in the equation:

$$K = \frac{(2\times10^{-3})\times(1\times10^{-2})^5}{10^{-5}\times x^5\times1^8} = 3\times10^{63}$$

$$\text{or}\quad x = [Fe^{2+}] = 5.8\times10^{-15}\,\text{mol L}^{-1}$$

It is clear from what has already been stated that standard reduction potentials may be employed to determine whether redox reactions are sufficiently complete for their possible use in quantitative analysis. It must be emphasised, however, that these calculations provide no information as to the speed of the reaction, upon which the application of that reaction in practice will ultimately depend. This question must form the basis of a separate experimental study, which may include the investigation of the influence of temperature, variation of pH and of the concentrations of the reactants, and the influence of catalysts. Thus, theoretically, potassium permanganate should quantitatively oxidise oxalic acid in aqueous solution. It is found, however, that the reaction is extremely slow at the ordinary temperature, but is more rapid at about 80 °C, and also increases in velocity when a little manganese(II) ion has been formed, the latter apparently acting as a catalyst.

It is of interest to consider the calculation of the equilibrium constant of the general redox reaction, viz.:

$$a\,\mathrm{Ox}_{\mathrm{I}} + b\,\mathrm{Red}_{\mathrm{II}} \rightleftharpoons b\,\mathrm{Ox}_{\mathrm{II}} + a\,\mathrm{Red}_{\mathrm{I}}$$

The complete reaction may be regarded as composed of two oxidation–reduction electrodes. $a\,\mathrm{Ox}_{\mathrm{I}}$, $a\,\mathrm{Red}_{\mathrm{I}}$ and $b\,\mathrm{Ox}_{\mathrm{II}}$, $b\,\mathrm{Red}_{\mathrm{II}}$ combined together into a cell; at equilibrium, the potentials of both electrodes are the same:

$$E_1 = E_1^\ominus + \frac{0.0591}{n}\log\frac{[\mathrm{Ox}_{\mathrm{I}}]^a}{[\mathrm{Red}_{\mathrm{I}}]^a}$$

$$E_2 = E_2^\ominus + \frac{0.0591}{n}\log\frac{[\mathrm{Ox}_{\mathrm{II}}]^b}{[\mathrm{Red}_{\mathrm{II}}]^b}$$

At equilibrium, $E_1 = E_2$, and hence:

$$E_1^\ominus + \frac{0.0591}{n}\log\frac{[\mathrm{Ox}_{\mathrm{I}}]^a}{[\mathrm{Red}_{\mathrm{I}}]^a} = E_2^\ominus + \frac{0.0591}{n}\log\frac{[\mathrm{Ox}_{\mathrm{II}}]^b}{[\mathrm{Red}_{\mathrm{II}}]^b}$$

$$\text{or}\quad \log\frac{[\mathrm{Ox}_{\mathrm{II}}]^b \times [\mathrm{Red}_{\mathrm{I}}]^a}{[\mathrm{Red}_{\mathrm{II}}]^b \times [\mathrm{Ox}_{\mathrm{I}}]^a} = \log K = \frac{n}{0.0591}(E_1^\ominus - E_2^\ominus)$$

This equation may be employed to calculate the equilibrium constant of any redox reaction, provided the two standard potentials $E_1^\ominus$ and $E_2^\ominus$ are known; from the value of K thus obtained, the feasibility of the reaction in analysis may be ascertained.

It can readily be shown that the concentrations at the equivalence point, when equivalent quantities of the two substances Ox_{I} and $\mathrm{Red}_{\mathrm{II}}$ are allowed to react, are given by:

$$\frac{[\mathrm{Red}_{\mathrm{I}}]}{[\mathrm{Ox}_{\mathrm{I}}]} = \frac{[\mathrm{Ox}_{\mathrm{II}}]}{[\mathrm{Red}_{\mathrm{II}}]} = \sqrt[(a+b)]{K}$$

This expression enables us to calculate the exact concentration at the equivalence point in any redox reaction of the general type given above, and therefore the feasibility of a titration in quantitative analysis.

For References and Bibliography see Sections 3.38 and 3.39.

potassium hydroxide solution with $0.5M$ 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 $0.5M$ hydrochloric acid (record as titration b mL).

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

COMPLEXATION TITRATIONS

10.43 INTRODUCTION

The nature of complexes, their stabilities and the chemical characteristics of complexones have been dealt with in some detail in Sections 2.21 to 2.27. This particular section is concerned with the way in which complexation reactions can be employed in titrimetry, especially for determining the proportions of individual cations in mixtures.

The vast majority of complexation titrations are carried out using multidentate ligands such as EDTA or similar substances as the complexone. However, there are other more simple processes which also involve complexation using monodentate or bidentate ligands and which also serve to exemplify the nature of this type of titration. This is demonstrated in the determination outlined in Section 10.44.

10.44 A SIMPLE COMPLEXATION TITRATION

A simple example of the application of a complexation reaction to a titration procedure is the titration of cyanides with silver nitrate solution. When a solution of silver nitrate is added to a solution containing cyanide ions (e.g. an alkali cyanide) a white precipitate is formed when the two liquids first come into contact with one another, but on stirring it re-dissolves owing to the formation of a stable complex cyanide, the alkali salt of which is soluble:

$$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$$

When the above reaction is complete, further addition of silver nitrate solution yields the insoluble silver cyanoargentate (sometimes termed insoluble silver cyanide); the end point of the reaction is therefore indicated by the formation of a permanent precipitate or turbidity.

The only difficulty in obtaining a sharp end point lies in the fact that silver cyanide, precipitated by local excess concentration of silver ion somewhat prior to the equivalence point, is very slow to re-dissolve and the titration is time-consuming. In the Dénigès modification, iodide ion (usually as KI, *ca* $0.01M$) is used as the indicator and aqueous ammonia (*ca* $0.2M$) is introduced to dissolve the silver cyanide.

The iodide ion and ammonia solution are added before the titration is commenced; the formation of silver iodide (as a turbidity) will indicate the end point:

$$[Ag(NH_3)_2]^+ + I^- \rightleftharpoons AgI + 2NH_3$$

During the titration any silver iodide which would tend to form will be kept in solution by the excess of cyanide ion always present until the equivalence point is reached:

$$AgI + 2CN^- \rightleftharpoons [Ag(CN)_2]^- + I^-$$

The method may also be applied to the analysis of silver halides by dissolution in excess of cyanide solution and back-titration with standard silver nitrate. It can also be utilised indirectly for the determination of several metals, notably nickel, cobalt, and zinc, which form stable stoichiometric complexes with cyanide ion. Thus if a Ni(II) salt in ammoniacal solution is heated with excess of cyanide ion, the $[Ni(CN)_4]^{2-}$ ion is formed quantitatively; since it is more stable than the $[Ag(CN)_2]^-$ ion, the excess of cyanide may be determined by the Liebig–Dénigès method. The metal ion determinations are, however, more conveniently made by titration with EDTA: see the following sections.

10.45 TITRATION CURVES

If, in the titration of a strong acid, pH is plotted against the volume of the solution of the strong base added, a point of inflexion occurs at the equivalence point (compare Section 10.12). Similarly, in the EDTA titration, if pM (negative logarithm of the 'free' metal ion concentration: $pM = -\log[M^{n+}]$) is plotted against the volume of EDTA solution added, a point of inflexion occurs at the equivalence point; in some instances this sudden increase may exceed 10 pM units. The general shape of titration curves obtained by titrating 10.0 mL of a 0.01 *M* solution of a metal ion M with a 0.01 *M* EDTA solution is shown in Fig. 10.11. The apparent stability constants (see Sections 2.21, 2.23 and 2.27) of various metal–EDTA complexes are indicated at the extreme right of the

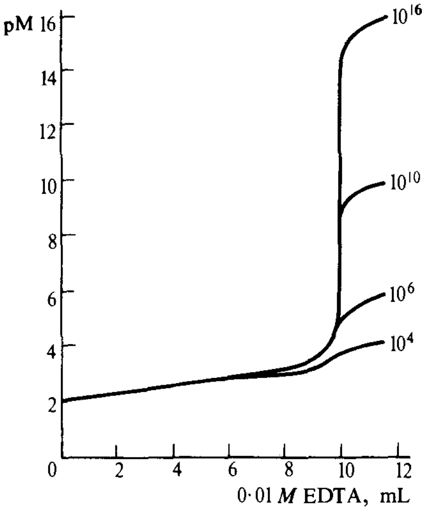

Fig. 10.11

curves. It is evident that the greater the stability constant, the sharper is the end point provided the pH is maintained constant.

In acid–base titrations the end point is generally detected by a pH-sensitive indicator. In the EDTA titration a metal ion-sensitive indicator (abbreviated, to **metal indicator** or **metal-ion indicator**) is often employed to detect changes of pM. Such indicators (which contain types of chelate groupings and generally possess resonance systems typical of dyestuffs) form complexes with specific metal ions, which differ in colour from the free indicator and produce a sudden colour change at the equivalence point. The end point of the titration can also be evaluated by other methods including potentiometric, amperometric, and spectrophotometric techniques.

10.46 TYPES OF EDTA TITRATIONS

The most important procedures for the titration of metal ions with EDTA are the following.

A. Direct titration. The solution containing the metal ion to be determined is buffered to the desired pH (e.g. to $\mathrm{pH} = 10$ with NH_4^+–aq. NH_3) and titrated directly with the standard EDTA solution. It may be necessary to prevent precipitation of the hydroxide of the metal (or a basic salt) by the addition of some auxiliary complexing agent, such as tartrate or citrate or triethanolamine. At the equivalence point the magnitude of the concentration of the metal ion being determined decreases abruptly. This is generally determined by the change in colour of a metal indicator or by amperometric, spectrophotometric, or potentiometric methods.

B. Back-titration. Many metals cannot, for various reasons, be titrated directly; thus they may precipitate from the solution in the pH range necessary for the titration, or they may form inert complexes, or a suitable metal indicator is not available. In such cases an excess of standard EDTA solution is added, the resulting solution is buffered to the desired pH, and the excess of the EDTA is back-titrated with a standard metal ion solution; a solution of zinc chloride or sulphate or of magnesium chloride or sulphate is often used for this purpose. The end point is detected with the aid of the metal indicator which responds to the zinc or magnesium ions introduced in the back-titration.

C. Replacement or substitution titration. Substitution titrations may be used for metal ions that do not react (or react unsatisfactorily) with a metal indicator, or for metal ions which form EDTA complexes that are more stable than those of other metals such as magnesium and calcium. The metal cation M^{n+} to be determined may be treated with the magnesium complex of EDTA, when the following reaction occurs:

$$M^{n+} + MgY^{2-} \rightleftharpoons (MY)^{(n-4)+} + Mg^{2+}$$

The amount of magnesium ion set free is equivalent to the cation present and can be titrated with a standard solution of EDTA and a suitable metal indicator.

An interesting application is the titration of calcium. In the direct titration of calcium ions, solochrome black gives a poor end point; if magnesium is present, it is displaced from its EDTA complex by calcium and an improved end point results (compare Section 10.51).

D. Alkalimetric titration. When a solution of disodium ethylenediaminetetraacetate, Na_2H_2Y, is added to a solution containing metallic ions, complexes are formed with the liberation of two equivalents of hydrogen ion:

$$M^{n+} + H_2Y^{2-} \rightleftharpoons (MY)^{(n-4)+} + 2H^+$$

The hydrogen ions thus set free can be titrated with a standard solution of sodium hydroxide using an acid–base indicator or a potentiometric end point; alternatively, an iodate–iodide mixture is added as well as the EDTA solution and the liberated iodine is titrated with a standard thiosulphate solution.

The solution of the metal to be determined must be accurately neutralised before titration; this is often a difficult matter on account of the hydrolysis of many salts, and constitutes a weak feature of alkalimetric titration.

E. Miscellaneous methods. Exchange reactions between the tetracyanonickelate(II) ion $[Ni(CN)_4]^{2-}$ (the potassium salt is readily prepared) and the element to be determined, whereby nickel ions are set free, have a limited application. Thus silver and gold, which themselves cannot be titrated complexometrically, can be determined in this way.

$$[Ni(CN)_4]^{2-} + 2Ag^+ \rightleftharpoons 2[Ag(CN)_2]^- + Ni^{2+}$$

These reactions take place with sparingly soluble silver salts, and hence provide a method for the determination of the halide ions Cl^-, Br^-, I^-, and the thiocyanate ion SCN^-. The anion is first precipitated as the silver salt, the latter dissolved in a solution of $[Ni(CN)_4]^{2-}$, and the equivalent amount of nickel thereby set free is determined by rapid titration with EDTA using an appropriate indicator (murexide, bromopyrogallol red).

Fluoride may be determined by precipitation as lead chlorofluoride, the precipitate being dissolved in dilute nitric acid and, after adjusting the pH to 5–6, the lead is titrated with EDTA using xylenol orange indicator.[10]

Sulphate may be determined by precipitation as barium sulphate or as lead sulphate. The precipitate is dissolved in an excess of standard EDTA solution, and the excess of EDTA is back-titrated with a standard magnesium or zinc solution using solochrome black as indicator.

Phosphate may be determined by precipitating as $Mg(NH_4)PO_4,6H_2O$, dissolving the precipitate in dilute hydrochloric acid, adding an excess of standard EDTA solution, buffering at pH = 10, and back-titrating with standard magnesium ion solution in the presence of solochrome black.

10.47 TITRATION OF MIXTURES, SELECTIVITY, MASKING AND DEMASKING AGENTS

EDTA is a very unselective reagent because it complexes with numerous doubly, triply and quadruply charged cations. When a solution containing two cations which complex with EDTA is titrated without the addition of a complex-forming indicator, and if a titration error of 0.1 per cent is permissible, then the ratio of the stability constants of the EDTA complexes of the two metals M and N must be such that $K_M/K_N \geqq 10^6$ if N is not to interfere with the titration of M. Strictly, of course, the constants K_M and K_N considered in the above expression should be the apparent stability constants of the complexes. If complex-forming indicators are used, then for a similar titration error $K_M/K_N \geqq 10^8$.

The following procedures will help to increase the selectivity:

(*a*) **Suitable control of the pH of the solution.** This, of course, makes use of the different stabilities of metal–EDTA complexes. Thus bismuth and thorium can be titrated in an acidic solution (pH = 2) with xylenol orange or methylthymol blue as indicator and most divalent cations do not interfere. A mixture of bismuth and lead ions can be successfully titrated by first titrating the bismuth at pH 2 with xylenol orange as indicator, and then adding hexamine to raise the pH to about 5, and titrating the lead (see Section 10.70).

(*b*) **Use of masking agents. Masking** may be defined as the process in which a substance, without physical separation of it or its reaction products, is so transformed that it does not enter into a particular reaction. **Demasking** is the process in which the masked substance regains its ability to enter into a particular reaction.

By the use of masking agents, some of the cations in a mixture can often be 'masked' so that they can no longer react with EDTA or with the indicator. An effective masking agent is the cyanide ion; this forms stable cyanide complexes with the cations of Cd, Zn, Hg(II), Cu, Co, Ni, Ag, and the platinum metals, but not with the alkaline earths, manganese, and lead:

$$M^{2+} + 4CN^- \rightarrow [M(CN)_4]^{2-}$$

It is therefore possible to determine cations such as Ca^{2+}, Mg^{2+}, Pb^{2+}, and Mn^{2+} in the presence of the above-mentioned metals by masking with an excess of potassium or sodium cyanide. A small amount of iron may be masked by cyanide if it is first reduced to the iron(II) state by the addition of ascorbic acid. Titanium(IV), iron(III), and aluminium can be masked with triethanolamine; mercury with iodide ions; and aluminium, iron(III), titanium(IV), and tin(II) with ammonium fluoride (the cations of the alkaline-earth metals yield slightly soluble fluorides).

Sometimes the metal may be transformed into a different oxidation state: thus copper(II) may be reduced in acid solution by hydroxylamine or ascorbic acid. After rendering ammoniacal, nickel or cobalt can be titrated using, for example, murexide as indicator without interference from the copper, which is now present as Cu(I). Iron(III) can often be similarly masked by reduction with ascorbic acid.

(*c*) **Selective demasking.** The cyanide complexes of zinc and cadmium may be demasked with formaldehyde–acetic acid solution or, better, with chloral hydrate:

$$[Zn(CN)_4]^{2-} + 4H^+ + 4HCHO \rightarrow Zn^{2+} + 4HO\cdot CH_2\cdot CN$$

The use of masking and selective demasking agents permits the successive titration of many metals. Thus a solution containing Mg, Zn, and Cu can be titrated as follows:

1. Add excess of standard EDTA and back-titrate with standard Mg solution using solochrome black as indicator. This gives the sum of all the metals present.
2. Treat an aliquot portion with excess of KCN (**CARE!**)* and titrate as before. This gives Mg only.

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*Considerable care must be taken at all times when using potassium cyanide to avoid any form of physical contact and chemical antidotes must be kept permanently and easily available.

3. Add excess of chloral hydrate (or of formaldehyde–acetic acid solution, 3:1) to the titrated solution in order to liberate the Zn from the cyanide complex, and titrate until the indicator turns blue. This gives the Zn only. The Cu content may then be found by difference.

(*d*) **Classical separation.** These may be applied if they are not tedious; thus the following precipitates may be used for separations in which, after being re-dissolved, the cations can be determined complexometrically: CaC_2O_4, nickel dimethylglyoximate, $Mg(NH_4)PO_4,6H_2O$, and CuSCN.

(*e*) **Solvent extraction.** This is occasionally of value. Thus zinc can be separated from copper and lead by adding excess of ammonium thiocyanate solution and extracting the resulting zinc thiocyanate with 4-methylpentan-2-one (isobutyl methyl ketone); the extract is diluted with water and the zinc content determined with EDTA solution.

(*f*) **Choice of indicators.** The indicator chosen should be one for which the formation of the metal–indicator complex is sufficiently rapid to permit establishment of the end point without undue waiting, and should preferably be reversible.

(*g*) **Removal of anions.** Anions, such as orthophosphate, which can interfere in complexometric titrations may be removed using ion exchange resins. For the use of ion exchange resins in the separation of cations and their subsequent EDTA titration, see Chapter 7.

(*h*) **'Kinetic masking'.** This is a special case in which a metal ion does not effectively enter into the complexation reaction because of its kinetic inertness (see Section 2.25). Thus the slow reaction of chromium(III) with EDTA makes it possible to titrate other metal ions which react rapidly, without interference from Cr(III); this is illustrated by the determination of iron(III) and chromium(III) in a mixture (Section 10.66).

10.48 METAL ION INDICATORS

General properties. The success of an EDTA titration depends upon the precise determination of the end point. The most common procedure utilises metal ion indicators. The requisites of a metal ion indicator for use in the visual detection of end points include:

(*a*) The colour reaction must be such that before the end point, when nearly all the metal ion is complexed with EDTA, the solution is strongly coloured.
(*b*) The colour reaction should be specific or at least selective.
(*c*) The metal–indicator complex must possess sufficient stability, otherwise, because of dissociation, a sharp colour change is not obtained. The metal–indicator complex must, however, be less stable than the metal–EDTA complex to ensure that, at the end point, EDTA removes metal ions from the metal indicator–complex. The change in equilibrium from the metal–indicator complex to the metal–EDTA complex should be sharp and rapid.
(*d*) The colour contrast between the free indicator and the metal–indicator complex should be such as to be readily observed.
(*e*) The indicator must be very sensitive to metal ions (i.e. to pM) so that the colour change occurs as near to the equivalence point as possible.

(*f*) The above requirements must be fulfilled within the pH range at which the titration is performed.

Dyestuffs which form complexes with specific metal cations can serve as indicators of pM values; 1:1-complexes (metal: dyestuff = 1:1) are common, but 1:2-complexes and 2:1-complexes also occur. The metal ion indicators, like EDTA itself, are chelating agents; this implies that the dyestuff molecule possesses several ligand atoms suitably disposed for coordination with a metal atom. They can, of course, equally take up protons, which also produces a colour change; metal ion indicators are therefore not only pM but also pH indicators.

Theory of the visual use of metal ion indicators. Discussion will be confined to the more common 1:1-complexes. The use of a metal ion indicator in an EDTA titration may be written as:

$$\text{M-In} + \text{EDTA} \rightarrow \text{M-EDTA} + \text{In}$$

This reaction will proceed if the metal–indicator complex M–In is less stable than the metal–EDTA complex M–EDTA. The former dissociates to a limited extent, and during the titration the free metal ions are progressively complexed by the EDTA until ultimately the metal is displaced from the complex M–In to leave the free indicator (In). The stability of the metal–indicator complex may be expressed in terms of the formation constant (or indicator constant) K_{In}:

$$K_{\text{In}} = [\text{M-In}]/[\text{M}][\text{In}]$$

The indicator colour change is affected by the hydrogen ion concentration of the solution, and no account of this has been taken in the above expression for the formation constant. Thus solochrome black, which may be written as H_2In^-, exhibits the following acid–base behaviour:

$$\underset{\text{Red}}{H_2In^-} \underset{5.3-7.3}{\overset{\text{pH}}{\rightleftharpoons}} \underset{\text{Blue}}{HIn^{2-}} \underset{10.5-12.5}{\overset{\text{pH}}{\rightleftharpoons}} \underset{\text{Yellow-orange}}{In^{3-}}$$

In the pH range 7–11, in which the dye itself exhibits a blue colour, many metal ions form red complexes; these colours are extremely sensitive, as is shown, for example, by the fact that $10^{-6} - 10^{-7}$ molar solutions of magnesium ion give a distinct red colour with the indicator. From the practical viewpoint, it is more convenient to define the apparent indicator constant K'_{In}, which varies with pH, as:

$$K'_{\text{In}} = [\text{MIn}^-]/[\text{M}^{n+}][\text{In}]$$

where

$[\text{MIn}^-]$ = concentration of metal–indicator complex,
$[\text{M}^{n+}]$ = concentration of metallic ion, and
$[\text{In}]$ = concentration of indicator not complexed with metallic ion.

(This, for the above indicator, is equal to $[H_2In^-] + [HIn^{2-}] + [In^{3-}]$.)

The equation may be expressed as:

$$\log K'_{\text{In}} = \text{pM} + \log[\text{MIn}^-]/[\text{In}];$$

The simplest method for decomposing an organic sample is to heat it in an open crucible until all carbonaceous matter has been oxidised leaving a residue of inorganic components, usually as oxide. The residue can then be dissolved in dilute acid giving a solution which can be analysed by appropriate procedures. This technique is referred to as **dry ashing**; it is obviously inapplicable when the inorganic component is volatile. Under these conditions the wet ashing procedure described under perchloric acid must be used. A full discussion of the destruction of organic matrices is given in Ref. 20.

3.32 PRECIPITATION

The conditions for precipitation of inorganic substances are given in Section 11.6. Precipitations are usually carried out in resistance-glass beakers, and the solution of the precipitant is added slowly (for example, by means of a pipette, burette, or tap funnel) and with efficient stirring of the suitably diluted solution. The addition must always be made without splashing; this is best achieved by allowing the solution of the reagent to flow down the side of the beaker or precipitating vessel. Only a moderate excess of the reagent is generally required; a very large excess may lead to increasing solubility (compare Section 2.6) or contamination of the precipitate. After the precipitate has settled, a few drops of the precipitant should always be added to determine whether further precipitation occurs. As a general rule, precipitates are not filtered off immediately after they have been formed; most precipitates, with the exception of those which are definitely colloidal, such as iron(III) hydroxide, require more or less digestion (Section 11.5) to complete the precipitation and make all particles of filterable size. In some cases digestion is carried out by setting the beaker aside and leaving the precipitate in contact with the mother liquor at room temperature for 12–24 hours; in others, where a higher temperature is permissible, digestion is usually effected near the boiling point of the solution. Hot plates, water baths, or even a low flame if no bumping occurs, are employed for the latter purpose; in all cases the beaker should be covered with a clockglass with the convex side turned down. If the solubility of the precipitate is appreciable, it may be necessary to allow the solution to attain room temperature before filtration.

3.33 FILTRATION

This operation is the separation of the precipitate from the mother liquor, the object being to get the precipitate and the filtering medium quantitatively free from the solution. The media employed for filtration are: (**1**) filter paper; (2) porous fritted plates of resistance glass, e.g. Pyrex (sintered-glass filtering crucibles), of silica (Vitreosil filtering crucibles), or of porcelain (porcelain filtering crucibles): see Section 3.24.

The choice of the filtering medium will be controlled by the nature of the precipitate (filter paper is especially suitable for gelatinous precipitates) and also by the question of cost. The limitations of the various filtering media are given in the account which follows.

3.34 FILTER PAPERS

Quantitative filter papers must have a very small ash content; this is achieved during manufacture by washing with hydrochloric and hydrofluoric acids. The sizes generally used are circles of 7.0, 9.0, 11.0, and 12.5 cm diameter, those of 9.0 and 11.0 cm being most widely employed. The ash of a 11 cm circle should not exceed 0.0001 g; if the ash exceeds this value, it should be deducted from the weight of the ignited residue. Manufacturers give values for the average ash per paper: the value may also be determined, if desired, by igniting several filter papers in a crucible. Quantitative filter paper is made of various degrees of porosity. The filter paper used must be of such texture as to retain the smallest particles of precipitate and yet permit of rapid filtration. Three textures are generally made, one for very fine precipitates, a second for the average precipitate which contains medium-sized particles, and a third for gelatinous precipitates and coarse particles. The speed of filtration is slow for the first, fast for the third, and medium for the second. 'Hardened' filter papers are made by further treatment of quantitative filter papers with acid; these have an extremely small ash, a much greater mechanical strength when wet, and are more resistant to acids and alkalis: they should be used in all quantitative work. The characteristics of the Whatman series of hardened ashless filter papers are shown in Table 3.7.

Table 3.7 'Whatman' quantitative filter papers

Filter paper	Hardened ashless		
Number	540	541	542
Speed	Medium	Fast	Slow
Particle size retention	Medium	Coarse	Fine
Ash (%)	0.008	0.008	0.008

The size of the filter paper selected for a particular operation is determined by the bulk of the precipitate, and not by the volume of the liquid to be filtered. The entire precipitate should occupy about a third of the capacity of the filter at the end of the filtration. The funnel should match the filter paper in size; the folded paper should extend to within 1–2 cm of the top of the funnel, but never closer than 1 cm.

A funnel with an angle as nearly 60° as possible should be employed; the stem should have a length of about 15 cm in order to promote rapid filtration. The filter paper must be carefully fitted into the funnel so that the upper portion beds tightly against the glass. To prepare the filter paper for use, the dry paper is usually folded exactly in half and exactly again in quarters. The folded paper is then opened so that a 60° cone is formed with three thicknesses of paper on the one side and a single thickness on the other; the paper is then adjusted to fit the funnel. The paper is placed in the funnel, moistened thoroughly with water, pressed down tightly to the sides of the funnel, and then filled with water. If the paper fits properly, the stem of the funnel will remain filled with liquid during the filtration.

To carry out a filtration, the funnel containing the properly fitted paper is placed in a funnel stand (or is supported vertically in some other way) and a clean beaker placed so that the stem of the funnel just touches the side; this will prevent splashing. The liquid to be filtered is then poured down a glass rod into the filter, directing the liquid against the side of the filter and not into the apex; the lower end of the stirring rod should be very close to, but should not quite touch, the filter paper on the side having three thicknesses of paper. The paper is never filled completely with the solution; the level of the liquid should not rise closer than to within 5–10 mm of the top of the paper. A precipitate which tends to remain in the bottom of the beaker should be removed by holding the glass rod across the beaker, tilting the beaker, and directing a jet of water from a wash bottle so that the precipitate is rinsed into the filter funnel. This procedure may also be adopted to transfer the last traces of the precipitate in the beaker to the filter. Any precipitate which adheres firmly to the side of the beaker or to the stirring rod may be removed with a rubber tipped rod or 'policeman' (Section 3.23).

Filtration by suction is rarely necessary: with gelatinous and some finely divided precipitates, the suction will draw the particles into the pores of the paper, and the speed of filtration will actually be reduced rather than increased.

3.35 CRUCIBLES WITH PERMANENT POROUS PLATES

Reference has already been made in Section 3.24 to these crucibles and to crucibles with a porous base. In use, the crucible is supported in a special holder, known as a crucible adapter, by means of a wide rubber tube (Fig. 3.12); the bottom of the crucible should be quite free from the side of the funnel and from the rubber gasket, the latter in order to be sure that the filtrate does not come into contact with the rubber. The adapter passes through a one-holed rubber bung into a large filter flask of about 750 mL capacity. The tip of the funnel must project below the side arm of the filter flask so that there is no risk that the liquid may be sucked out of the filter flask. The filter flask should be coupled with another flask of similar capacity, and the latter connected to a water filter pump; if the water in the pump should 'suck back', it will first enter the empty flask and the filtrate will not be contaminated. It is advisable also to have some sort of pressure regulator to limit the maximum pressure under which filtration is conducted. A simple method is to insert a glass tap in the second filter flask, as in the figure; alternatively, a glass **T**-piece may be introduced between the receiver and the pump, and one arm closed either by a glass tap or by a piece of heavy rubber tubing ('pressure' tubing) carrying a screw clip.

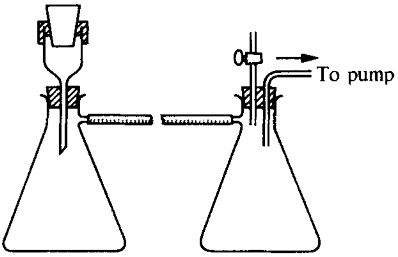

Fig. 3.12

When the apparatus is assembled, the crucible is half-filled with distilled water, then gentle suction is applied to draw the water through the crucible. When the water has passed through, suction is maintained for 1–2 minutes to remove as much water as possible from the filter plate. The crucible is then placed on a small ignition dish or saucer or upon a shallow-form Vitreosil capsule and dried to constant weight at the same temperature as that which will be subsequently used in drying the precipitate. For temperatures up to about 250 °C a thermostatically controlled electric oven should be used. For higher temperatures, the crucible may be heated in an electrically heated muffle furnace. In all cases the crucible is allowed to cool in a desiccator before weighing.

When transferring a precipitate into the crucible, the same procedure is employed as described in Section 3.34 referring to the use of filter papers: care must be taken that the liquid level in the crucible is never less than 1 cm from the top of the crucible.

Care must be taken with both sintered glass and porous base crucibles to avoid attempting the filtration of materials that may clog the filter plate. A new crucible should be washed with concentrated hydrochloric acid and then with distilled water. The crucibles are chemically inert and are resistant to all solutions which do not attack silica; they are attacked by hydrofluoric acid, fluorides, and strongly alkaline solutions.

Crucibles fitted with permanent porous plates are cleaned by shaking out as much of the solid as possible, and then dissolving out the remainder of the solid with a suitable solvent. A hot $0.1M$ solution of the tetrasodium salt of the ethylenediaminetetra-acetic acid is an excellent solvent for many of the precipitates [except metallic sulphides and hexacyanoferrates(III)] encountered in analysis. These include barium sulphate, calcium oxalate, calcium phosphate, calcium oxide, lead carbonate, lead iodate, lead oxalate, and ammonium magnesium phosphate. The crucible may either be completely immersed in the hot reagent or the latter may be drawn by suction through the crucible.

3.36 WASHING PRECIPITATES

Most precipitates are produced in the presence of one or more soluble compounds. Since the latter are frequently not volatile at the temperature at which the precipitate is ultimately dried, it is necessary to wash the precipitate to remove such material as completely as possible. The minimum volume of the washing liquid required to remove the objectionable matter should be used, since no precipitate is absolutely insoluble. Qualitative tests for the removal of the impurities should be made on small volumes of the filtered washing solution. Furthermore, it is better to wash with a number of small portions of the washing liquid, which are well drained between each washing, than with one or two large portions, or by adding fresh portions of the washing liquid while solution still remains on the filter (see Section 11.8).

The ideal washing liquid should comply as far as possible with the following conditions.

1. It should have no solvent action upon the precipitate, but dissolve foreign substances easily.
2. It should have no dispersive action on the precipitate.
3. It should form no volatile or insoluble product with the precipitate.
4. It should be easily volatile at the temperature of drying of the precipitate.
5. It should contain no substance which is likely to interfere with subsequent determinations in the filtrate.

In general, pure water should not be used unless it is certain that it will not dissolve appreciable amounts of the precipitate or peptise it. If the precipitate is appreciably soluble in water, a common ion is usually added, since any electrolyte is less soluble in a dilute solution containing one of its ions than it is in pure water (Section 2.7); as an example the washing of calcium oxalate with dilute ammonium oxalate solution may be cited. If the precipitate tends to become colloidal and pass through the filter paper (this is frequently observed with gelatinous or flocculent precipitates), a wash solution containing an electrolyte must be employed (compare Section 11.3). The nature of the electrolyte is immaterial, provided it has no action upon the precipitate during washing and is volatilised during the final heating. Ammonium salts are usually selected for this purpose: thus ammonium nitrate solution is employed for washing iron(III) hydroxide. In some cases it is possible to select a solution which will both reduce the solubility of the precipitate and prevent peptisation; for example, the use of dilute nitric acid with silver chloride. Some precipitates tend to oxidise during washing; in such instances the precipitate cannot be allowed to run dry, and a special washing solution which re-converts the oxidised compounds into the original condition must be employed, e.g. acidified hydrogen sulphide water for copper sulphide. Gelatinous precipitates, like aluminium hydroxide, require more washing than crystalline ones, such as calcium oxalate.

In most cases, particularly if the precipitate settles rapidly or is gelatinous, **washing by decantation** may be carried out. As much as possible of the liquid above the precipitate is transferred to the prepared filter (either filter paper or filter crucible), observing the usual precautions, and taking care to avoid, as far as possible, disturbing the precipitate. Twenty to fifty millilitres of a suitable wash liquid is added to the residue in the beaker, the solid stirred up and allowed to settle. If the solubility of the precipitate allows, the solution should be heated, since the rate of filtration will thus be increased. When the supernatant liquid is clear, as much as possible of the liquid is decanted through the filtering medium. This process is repeated three to five times (or as many times as is necessary) before the precipitate is transferred to the filter. The main bulk of the precipitate is first transferred by mixing with the wash solution and pouring off the suspension, the process being repeated until most of the solid has been removed from the beaker. Precipitate adhering to the sides and bottom of the beaker is then transferred to the filter with the aid of a wash bottle as described in Section 3.34, using a 'policeman' if necessary to transfer the last traces of precipitate. Finally, a wash bottle is used to wash the precipitate down to the bottom of the filter paper or to the plate of the filter crucible.

In all cases, tests for the completeness of washing must be made by collecting a small sample of the washing solution after it is estimated that most of the impurities have been removed, and applying an appropriate qualitative test. Where filtration is carried out under suction, a small test-tube is placed under the crucible adapter.

3.37 DRYING AND IGNITING PRECIPITATES

After a precipitate has been filtered and washed, it must be brought to a constant composition before it can be weighed. The further treatment will depend both upon the nature of the precipitate and upon that of the filtering medium; this treatment consists in drying or igniting the precipitate. Which of the latter two terms is employed depends upon the temperature at which the precipitate is heated. There is, however, no definite temperature below or above which the precipitate is said to be dried or ignited respectively. The meaning will be adequately conveyed for our purpose if we designate *drying* when the temperature is below 250 °C (the maximum temperature which is readily reached in the usual thermostatically controlled, electric drying-oven), and *ignition* above 250 °C up to, say 1200 °C. Precipitates that are to be dried should be collected on filter paper, or in sintered-glass or porcelain filtering crucibles. Precipitates that are to be ignited are collected on filter paper, porcelain filtering crucibles, or silica filtering crucibles. Ignition is simply effected by placing in a special ignition dish and heating with the appropriate burner; alternatively, these crucibles (and, indeed, any type of crucible) may be placed in an electrically heated muffle furnace, which is equipped with a pyrometer and a means for controlling the temperature.

Attention is directed to the information provided by thermogravimetric analysis[21,22] concerning the range of temperature to which a precipitate should be heated for a particular composition. In general, thermal gravimetric curves seem to suggest that in the past precipitates were heated for too long a period and at too high a temperature. It must, however, be borne in mind that in some cases the thermal gravimetric curve is influenced by the experimental conditions of precipitation, and even if a horizontal curve is not obtained, it is possible that a suitable weighing form may be available over a certain temperature range. Nevertheless, thermograms do provide valuable data concerning the range of temperature over which a precipitate has a constant composition under the conditions that the thermogravimetric analysis was made; these, at the very least, provide a guide for the temperature at which a precipitate should be dried and heated for quantitative work, but due regard must be paid to the general chemical properties of the weighing form.

Although precipitates which require ignition will usually be collected in porcelain or silica filtering crucibles, there may be some occasions where filter paper has been used, and it is therefore necessary to describe the method to be adopted in such cases. The exact technique will depend upon whether the precipitate may be safely ignited in contact with the filter paper or not. It must be remembered that some precipitates, such as barium sulphate, may be reduced or changed in contact with filter paper or its decomposition products.

A. Incineration of the filter paper in the presence of the precipitate. A silica crucible is first ignited to constant weight (i.e. to within 0.0002 g) at the same temperature as that to which the precipitate is ultimately heated. The well-drained filter paper and precipitate are carefully detached from the funnel; the filter paper is folded so as to enclose the precipitate completely, care being taken not to tear the paper. The packet is placed point-down in the weighed crucible, which is supported on a pipe-clay, or better, a silica triangle resting on a ring stand. The crucible is slightly inclined, and partially covered with the lid, which should rest partly on the triangle. A *very small flame* is then placed under the crucible lid; drying thus proceeds quickly and without undue risk. When the moisture has been expelled, the flame is increased slightly so as to carbonise the paper *slowly*. The paper should not be allowed to inflame, as this may cause a mechanical expulsion of fine particles of the precipitate owing to the rapid escape of the products of combustion: if, by chance, it does catch fire, the flame should be extinguished by momentarily placing the cover on the mouth of the crucible with the aid of a pair of crucible tongs. When the paper has completely carbonised and vapours are no longer evolved, the flame is moved to the back (bottom) of the crucible and the carbon slowly burned off while the flame is gradually increased.* After all the carbon has been burned away, the crucible is covered completely (if desired, the crucible may be placed in a vertical position for this purpose) and heated to the required temperature by means of a Bunsen burner. Usually it takes about 20 minutes to char the paper, and 30–60 minutes to complete the ignition

When the ignition is ended, the flame is removed and, after 1–2 minutes, the crucible and lid are placed in a desiccator containing a suitable desiccant (Section 3.22), and allowed to cool for 25–30 minutes. The crucible and lid are then weighed. The crucible and contents are then ignited at the same temperature for 10–20 minutes, allowed to cool in a desiccator as before, and weighed again. The ignition is repeated until constant weight is attained. Crucibles should always be handled with clean crucible tongs and preferably with platinum-tipped tongs.

It is important to note that 'heating to constant weight' has no real significance unless the periods of heating, cooling of the *covered* crucible, and weighing are duplicated.

B. Incineration of the filter paper apart from the precipitate. This method is employed in all those cases where the ignited substance is reduced by the burning paper; for example, barium sulphate, lead sulphate, bismuth oxide, copper oxide, etc. The funnel containing the precipitate is covered by a piece of qualitative filter paper upon which is written the formula of the precipitate and the name of the owner; the paper is made secure by crumpling its edges over the rim of the funnel so that they will engage the outer conical portion of the funnel. The funnel is placed in a drying oven maintained at 100–105 °C, for 1–2 hours or until completely dry. A sheet of glazed paper about 25 cm square (white or black, to contrast with the colour of the precipitate) is placed on the bench away from all draughts. The dried filter is removed from the funnel, and as much as possible of the precipitate is removed from the paper and allowed to drop on a clockglass resting upon the glazed paper. This is readily done by very gently rubbing the sides of the filter paper together, when the bulk of the precipitate becomes detached and drops upon the clockglass. Any small particles of the precipitate which may have fallen upon the glazed paper are brushed into the clockglass with a small camel-hair brush. The clockglass containing the precipitate is then covered with a larger clockglass or with a beaker. The filter paper is now carefully folded and placed inside a weighed porcelain or silica crucible. The crucible is placed on a triangle and the filter paper incinerated as detailed above. The crucible is allowed to cool, and the filter ash subjected to a suitable chemical treatment in order to convert any reduced or changed material into the form finally desired. The cold crucible is then placed upon the glazed paper and the main part of the precipitate carefully transferred from the clockglass to the crucible. A small camel-hair brush will assist in the transfer. Finally, the precipitate is brought to constant weight by heating to the necessary temperature as detailed under A.

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* If the carbon on the lid is oxidised only slowly, the cover may be heated separately in a flame. It is, of course, held in clean crucible tongs.

Ref.

Vogel's Textbook of Quantitative Chemical Analysis

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