

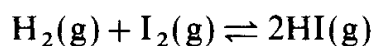
CHAPTER 2

FUNDAMENTAL THEORETICAL PRINCIPLES OF REACTIONS IN SOLUTION

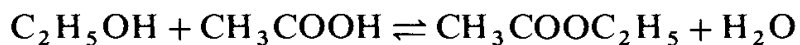
Many of the reactions of qualitative and quantitative chemical analysis take place in solution; the solvent is most commonly water but other liquids may also be used. It is, therefore, necessary to have a general knowledge of the conditions which exist in solutions, and also of the factors which influence chemical reactions.

2.1 CHEMICAL EQUILIBRIUM

If a mixture of hydrogen and iodine vapour is heated to a temperature of about 450 °C in a closed vessel, the two elements combine and hydrogen iodide is formed. It is found, however, that no matter how long the duration of the experiment, some hydrogen and iodine remain uncombined. If pure hydrogen iodide is heated in a closed vessel to a temperature of about 450 °C, the substance decomposes to form hydrogen and iodine, but again, no matter how prolonged the heating, some hydrogen iodide remains unchanged. This is an example of a **reversible reaction** in the gaseous phase.



An example of a reversible reaction in the liquid phase is afforded by the esterification reaction between ethanol and acetic (ethanoic) acid forming ethyl acetate and water. Since, however, ethyl acetate undergoes conversion to acetic acid and ethanol when heated with water, the esterification reaction never proceeds to completion.

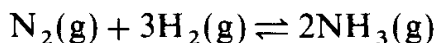


It is found that after the elapse of a sufficient time interval, all reversible reactions reach a state of **chemical equilibrium**. In this state the composition of the equilibrium mixture remains constant, provided that the temperature (and for some gaseous reactions, the pressure also) remains constant. Furthermore, provided that the conditions (temperature and pressure) are maintained constant, the same state of equilibrium may be obtained from either direction of a given reversible reaction. In the equilibrium state, the two opposing reactions are taking place at the same rate so that the system is in a state of **dynamic equilibrium**.

It must be emphasised that the composition of a given equilibrium system can be altered by changing the conditions under which the system is maintained and it is necessary to consider the effect of changes in (a) the temperature,

(b) the pressure and (c) the concentration of the components. According to the **Le Chatelier–Braun Principle**: ‘If a constraint is applied to a system in equilibrium, the system will adjust itself so as to nullify the effect of the constraint’, and the effect of the factors referred to can be considered in the light of this statement.

(a) Temperature. The formation of ammonia from its elements is a reversible process:



in which the forward reaction is accompanied by the evolution of heat (energy), and is said to be an exothermic reaction; the reverse reaction absorbs heat and is said to be endothermic. If the temperature of an equilibrium mixture of nitrogen, hydrogen and ammonia is increased, then the reaction which absorbs heat will be favoured, and so ammonia is decomposed.

(b) Pressure. Referring to the hydrogen iodide equilibrium system, the stoichiometric coefficients of the molecules on each side of the equation for the reaction are equal, and there is no change in volume when reaction occurs. Therefore, if the pressure of the system is doubled, thus halving the total volume, the two sides of the equation are equally affected, and so the composition of the equilibrium mixture remains unchanged.

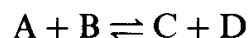
In the nitrogen, hydrogen, ammonia equilibrium system, there is a decrease in volume when ammonia is produced, and hence an increase in pressure will favour the formation of ammonia. Any gaseous equilibrium in which a change in volume takes place will be affected by a change in pressure. For equilibrium in the liquid phase, moderate changes in pressure have practically no effect on the volume owing to the small compressibility of liquids, and so moderate pressure changes do not affect the equilibrium.

(c) Concentration of reagents. If hydrogen is added to the equilibrium mixture resulting from the thermal decomposition of hydrogen iodide, it is found that more hydrogen iodide is present when equilibrium is restored. In accordance with the Le Chatelier–Braun Principle, the system has reacted to remove some of the added hydrogen.

2.2 THE LAW OF MASS ACTION

Guldberg and Waage (1867) clearly stated the Law of Mass Action (sometimes termed the Law of Chemical Equilibrium) in the form: ‘The velocity of a chemical reaction is proportional to the product of the active masses of the reacting substances’. ‘Active mass’ was interpreted as concentration and expressed in moles per litre. By applying the law to homogeneous systems, that is to systems in which all the reactants are present in one phase, for example in solution, we can arrive at a mathematical expression for the condition of equilibrium in a reversible reaction.

Consider first the simple reversible reaction at constant temperature:



The rate of conversion of A and B is proportional to their concentrations, or

$$r_1 = k_1 \times [\text{A}] \times [\text{B}]$$

where k_1 is a constant known as the rate constant or rate coefficient, and the square brackets (see footnote Section 2.21) denote the concentrations (mol L^{-1}) of the substances enclosed within the brackets.

Similarly, the rate of conversion of C and D is given by:

$$r_2 = k_2 \times [\text{C}] \times [\text{D}]$$

At equilibrium, the two rates of conversion will be equal:

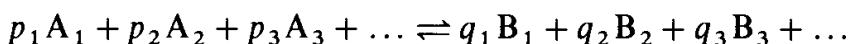
$$r_1 = r_2$$

$$\text{or} \quad k_1 \times [\text{A}] \times [\text{B}] = k_2 \times [\text{C}] \times [\text{D}]$$

$$\text{or} \quad \frac{[\text{C}] \times [\text{D}]}{[\text{A}] \times [\text{B}]} = \frac{k_1}{k_2} = K$$

K is the **equilibrium constant** of the reaction at the given temperature.

The expression may be generalised. For a reversible reaction represented by:



where p_1, p_2, p_3 and q_1, q_2, q_3 are the stoichiometric coefficients of the reacting species, the condition for equilibrium is given by the expression:

$$\frac{[\text{B}_1]^{q_1} \times [\text{B}_2]^{q_2} \times [\text{B}_3]^{q_3} \dots}{[\text{A}_1]^{p_1} \times [\text{A}_2]^{p_2} \times [\text{A}_3]^{p_3} \dots} = K$$

This result may be expressed in words: when equilibrium is reached in a reversible reaction, at constant temperature, the product of the concentrations of the resultants (the substances on the right-hand side of the equation) divided by the product of the concentrations of the reactants (the substances on the left-hand side of the equation), each concentration being raised to a power equal to the stoichiometric coefficient of the substance concerned in the equation for the reaction, is constant.

The equilibrium constant of a reaction can be related to the changes in Gibbs Free Energy (ΔG), enthalpy (ΔH) and entropy (ΔS) which occur during the reaction by the mathematical expressions:

$$\Delta G^\ominus = -RT \ln K^\ominus = -2.303 RT \log_{10} K^\ominus$$

$$\frac{d \ln K^\ominus}{dT} = \frac{\Delta H^\ominus}{RT^2}$$

$$\Delta G^\ominus = \Delta H^\ominus - T \Delta S^\ominus$$

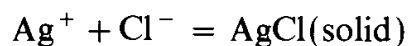
In these expressions, the superscript symbol (\ominus) indicates that the quantities concerned relate to a so-called 'standard state'. For the derivation and the significance of these expressions, a textbook of physical chemistry¹ should be consulted, but briefly a reaction will be spontaneous when ΔG is negative, it will be at equilibrium when ΔG is zero, and when ΔG is positive the reverse reaction will be spontaneous. It follows that a reaction is favoured when heat is produced, i.e. it is an exothermic reaction so that the enthalpy change ΔH is negative. It is also favoured by an increase in entropy, that is when ΔS is positive. A knowledge of the values of the equilibrium constants of certain selected systems can be of great value to the analyst; for example in dealing with acid-base interactions, with solubility equilibria, with systems involving complex ions,

with oxidation–reduction systems, and with many separation problems: note however that equilibrium constants do not give any indication of the *rate* of reaction. These matters are dealt with in detail in succeeding sections of this chapter, and in other pertinent chapters.

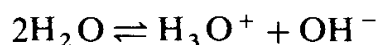
2.3 FACTORS AFFECTING CHEMICAL REACTIONS IN SOLUTION

There are three main factors whose influence on chemical reactions in solution need to be considered: (a) the nature of the solvent; (b) temperature; and (c) the presence of catalysts.

(a) **Nature of the solvent.** Reactions in aqueous solution generally proceed rapidly because they involve interaction between ions. Thus the precipitation of silver chloride from a chloride solution by the addition of silver nitrate solution can be formulated



Reactions between molecules in solution, for example the formation of ethyl acetate from acetic acid and ethanol, are generally comparatively slow. It is therefore convenient to classify solvents as **ionising solvents** if they tend to produce solutions in which the solute is ionised, and as **non-ionising solvents** if they give solutions in which the solute is not ionised. Common ionising solvents include water, acetic acid, hydrogen chloride, ammonia, amines, bromine trifluoride and sulphur dioxide. Of these solvents, the first four are characterised by a capability of giving rise to hydrogen ions, as for example with water:



and with ammonia:



These four solvents can thus be termed **protogenic solvents**, whilst bromine trifluoride and sulphur dioxide which do not contain hydrogen are **non-protogenic solvents**. Non-ionising solvents include hydrocarbons, ethers, esters and higher alcohols; the lower alcohols, especially methanol and ethanol, do show slight ionising properties with appropriate solutes.

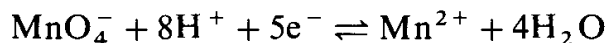
(b) **Temperature.** Reaction rates increase rapidly with rising temperature, and in some analytical procedures it is necessary to heat the solution to ensure that the required reaction takes place with sufficient rapidity.

An example of such behaviour is the titration of acidified oxalate solutions with potassium permanganate solution. When potassium permanganate solution is added to a solution of an oxalate containing sulphuric acid at room temperature, reaction proceeds very slowly, and the solution sometimes acquires a brown tinge due to the formation of manganese(IV) oxide. If, however, the solution is heated to about 70 °C before adding any permanganate solution, then the reaction becomes virtually instantaneous, and no manganese(IV) oxide is produced.

(c) **Catalysts.** The rates of some reactions can be greatly increased by the presence of a catalyst. This is a substance that alters the rate of a reaction

without itself undergoing any net change: it follows that a small amount of the catalyst can influence the conversion of large quantities of the reactants. If the reaction under consideration is reversible, then the catalyst affects both the forward and back reactions, and although the reaction is speeded up, the position of equilibrium is unchanged.

An example of catalytic action is provided by the titration of oxalates with potassium permanganate solution referred to above. It is found that even though the oxalate solution is heated, the first few drops of permanganate solution are only slowly decolorised, but as more permanganate solution is added the decoloration becomes instantaneous. This is because the reaction between oxalate ions and permanganate ions is catalysed by the Mn^{2+} ions formed by the reduction of permanganate ions:



Other examples are the use of osmium(VIII) oxide (osmium tetroxide) as catalyst in the titration of solutions of arsenic(III) oxide with cerium(IV) sulphate solution, and the use of molybdate(VI) ions to catalyse the formation of iodine by the reaction of iodide ions with hydrogen peroxide. Certain reactions of various organic compounds are catalysed by several naturally occurring proteins known as enzymes.

The determination of trace quantities of many substances can be accomplished by examining the rate of a chemical reaction for which the substance to be determined acts as a catalyst. By comparing the observed rate of reaction with rates determined for the same reaction, with known quantities of the same catalyst present, the unknown concentration can be calculated. Likewise a catalyst may be used to convert a substance for which no suitable analytical reaction exists for the conditions under which the substance is present, to a product which can be determined. Alternatively, the substance to be determined may be destroyed by adding a catalyst, and the resultant change in some measured property, for example the absorption of light, enables the amount of substance present to be evaluated. Thus, uric acid in blood can be determined by measurement of the absorption of ultraviolet radiation at a wavelength of 292 nm, but the absorption is not specific. The absorption meter reading is recorded, and then the uric acid is destroyed by addition of the enzyme uricase. The absorption reading is repeated, and from the difference between the two results, the amount of uric acid present can be calculated.

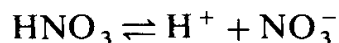
2.4 ELECTROLYTIC DISSOCIATION

Aqueous solutions of many salts, of the common 'strong acids' (hydrochloric, nitric and sulphuric), and of bases such as sodium hydroxide and potassium hydroxide are good conductors of electricity, whereas pure water shows only a very poor conducting capability. The above solutes are therefore termed electrolytes. On the other hand, certain solutes, for example ethane-1,2-diol (ethylene glycol) which is used as 'antifreeze', produce solutions which show a conducting capability only little different from that of water: such solutes are referred to as non-electrolytes. Most reactions of analytical importance occurring in aqueous solution involve electrolytes, and it is necessary to consider the nature of such solutions.

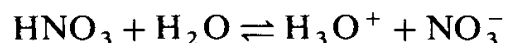
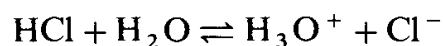
Salts. The structure of numerous salts in the solid state has been investigated by means of X-rays and by other methods, and it has been shown that they are composed of charged atoms or groups of atoms held together in a crystal lattice; they are said to be ionic compounds. When these salts are dissolved in a solvent of high dielectric constant such as water, or are heated to the melting point, the crystal forces are weakened and the substances dissociate into the pre-existing charged particles or ions, so that the resultant liquids are good conductors of electricity; they are referred to as **strong electrolytes**. Some salts, however, exemplified by cyanides, thiocyanates, the halides of mercury and cadmium, and by lead acetate, give solutions which show a significant electrical conductance, but which is not as great as that shown by solutions of strong electrolytes of comparable concentration. Solutes showing this behaviour are referred to as **weak electrolytes**: they are generally covalent compounds which undergo only limited ionisation when dissolved in water:



Acids and bases. An acid may be defined as a substance which, when dissolved in water, undergoes dissociation with the formation of hydrogen ions as the only positive ions:

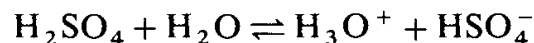


Actually the hydrogen ion H^+ (or proton) does not exist in the free state in aqueous solution; each hydrogen ion combines with one molecule of water to form the hydroxonium ion, H_3O^+ . The hydroxonium ion is a hydrated proton. The above equations are therefore more accurately written:



The ionisation may be attributed to the great tendency of the free hydrogen ions H^+ to combine with water molecules to form hydroxonium ions. Hydrochloric and nitric acids are almost completely dissociated in aqueous solution in accordance with the above equations; this is readily demonstrated by freezing-point measurements and by other methods.

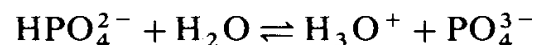
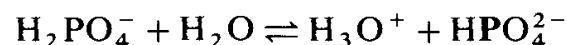
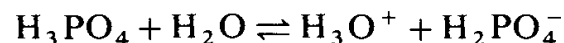
Polyprotic acids ionise in stages. In sulphuric acid, one hydrogen atom is almost completely ionised:



The second hydrogen atom is only partially ionised, except in very dilute solution:



Phosphoric(V) acid also ionises in stages:



The successive stages of ionisation are known as the primary, secondary, and

tertiary ionisations respectively. As already mentioned, these do not take place to the same degree. The primary ionisation is always greater than the secondary, and the secondary very much greater than the tertiary.

Acids of the type of acetic acid (CH_3COOH) give an almost normal freezing-point depression in aqueous solution; the extent of dissociation is accordingly small. It is usual, therefore, to distinguish between acids which are completely or almost completely ionised in solution and those which are only slightly ionised. The former are termed **strong acids** (examples: hydrochloric, hydrobromic, hydriodic, iodic(V), nitric and perchloric [chloric(VII)] acids, primary ionisation of sulphuric acid), and the latter are called **weak acids** (examples: nitrous acid, acetic acid, carbonic acid, boric acid, phosphorous (phosphoric(III)) acid, phosphoric(V) acid, hydrocyanic acid, and hydrogen sulphide). There is, however, no sharp division between the two classes.

A base was originally defined as a substance which, when dissolved in water, undergoes dissociation with the formation of hydroxide ions OH^- as the only negative ions. Thus sodium hydroxide, potassium hydroxide, and the hydroxides of certain bivalent metals are almost completely dissociated in aqueous solution:



These are **strong bases**. Aqueous ammonia solution, however, is a weak base. Only a small concentration of hydroxide ions is produced in aqueous solution:



General concept of acid and bases. The Brønsted–Lowry theory. The simple concept given in the preceding paragraphs suffices for many of the requirements of quantitative inorganic analysis in aqueous solution. It is, however, desirable to have some knowledge of the general theory of acids and bases proposed independently by J. N. Brønsted and by T. M. Lowry in 1923, since this is applicable to all solvents. According to this theory, an acid is a species having a tendency to lose a proton, and a base is a species having a tendency to add on a proton. This may be represented as:

Acid \rightleftharpoons Proton + Conjugate base



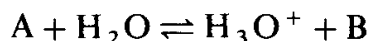
It must be emphasised that the symbol H^+ represents the proton and not the ‘hydrogen ion’ of variable nature existing in different solvents (OH_3^+ , NH_4^+ , $\text{CH}_3\text{CO}_2\text{H}_2^+$, $\text{C}_2\text{H}_5\text{OH}_2^+$, etc.); the definition is therefore independent of solvent. The above equation represents a hypothetical scheme for defining A and B and not a reaction which can actually occur. Acids need not be neutral molecules (e.g., HCl , H_2SO_4 , $\text{CH}_3\text{CO}_2\text{H}$), but may also be anions (e.g., HSO_4^- , H_2PO_4^- , $\text{HOOC}\cdot\text{COO}^-$) and cations (e.g., NH_4^+ , $\text{C}_6\text{H}_5\text{NH}_3^+$, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$). The same is true of bases where the three classes can be illustrated by NH_3 , $\text{C}_6\text{H}_5\text{NH}_2$, H_2O ; CH_3COO^- , OH^- , HPO_4^{2-} , OC_2H_5^- ; $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$.

Since the free proton cannot exist in solution in measurable concentration, reaction does not take place unless a base is added to accept the proton from the acid. By combining the equations $\text{A}_1 \rightleftharpoons \text{B}_1 + \text{H}^+$ and $\text{B}_2 + \text{H}^+ \rightleftharpoons \text{A}_2$, we obtain



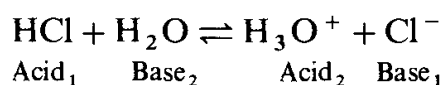
$A_1 - B_1$ and $A_2 - B_2$ are two conjugate acid–base pairs. This is the most important expression for reactions involving acids and bases; it represents the transfer of a proton from A_1 to B_2 or from A_2 to B_1 . The stronger the acid A_1 and the weaker A_2 , the more complete will be the reaction (*b*). The stronger acid loses its proton more readily than the weaker; similarly, the stronger base accepts a proton more readily than does the weaker base. It is evident that the base or acid conjugate to a strong acid or a strong base is always weak, whereas the base or acid conjugate to a weak acid or weak base is always strong.

In aqueous solution a Brønsted–Lowry acid A

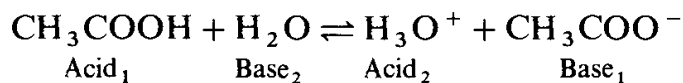


is strong when the above equilibrium is virtually complete to the right so that $[A]$ is almost zero. A strong base is one for which $[B]$, the equilibrium concentration of base other than hydroxide ion, is almost zero.

Acids may thus be arranged in series according to their relative combining tendencies with a base, which for aqueous solutions (in which we are largely interested) is water:



This process is essentially complete for all typical ‘strong’ (i.e. highly ionised) acids, such as HCl, HBr, HI, HNO_3 , and $HClO_4$. In contrast with the ‘strong’ acids, the reactions of a typical ‘weak’ or slightly ionised acid, such as acetic acid or propionic (propanoic) acid, proceeds only slightly to the right in the equation:



The typical strong acid of the water system is the hydrated proton H_3O^+ , and the role of the conjugate base is minor if it is a sufficiently weak base, e.g. Cl^- , Br^- , and ClO_4^- . The conjugate bases have strengths that vary inversely as the strengths of the respective acids. It can easily be shown that the basic ionisation constant of the conjugate base $K_{B,conj.}$ is equal to $K_w/K_{A,conj.}$, where K_w is the ionic product of water.

Scheme (*b*) includes reactions formerly described by a variety of names, such as dissociation, neutralisation, hydrolysis and buffer action (see below). One acid–base pair may involve the solvent (in water $H_3O^+ - H_2O$ or $H_2O - OH^-$), showing that ions such as H_3O^+ and OH^- are in principle only particular examples of an extended class of acids and bases though, of course, they do occupy a particularly important place in practice. It follows that the properties of an acid or base may be greatly influenced by the nature of the solvent employed.

Another definition of acids and bases is due to G. N. Lewis (1938). From the experimental point of view Lewis regarded all substances which exhibit ‘typical’ acid–base properties (neutralisation, replacement, effect on indicators, catalysis), irrespective of their chemical nature and mode of action, as acids or bases. He related the properties of acids to the acceptance of electron pairs, and bases as donors of electron pairs, to form covalent bonds regardless of whether protons are involved. On the experimental side Lewis’ definition brings together a wide range of qualitative phenomena, e.g. solutions of BF_3 , BCl_3 ,

AlCl_3 , or SO_2 in an inert solvent cause colour changes in indicators similar to those produced by hydrochloric acid, and these changes are reversed by bases so that titrations can be carried out. Compounds of the type of BF_3 are usually described as **Lewis acids** or **electron acceptors**. The Lewis bases (e.g. ammonia, pyridine) are virtually identical with the Brønsted–Lowry bases. The great disadvantage of the Lewis definition of acids is that, unlike proton-transfer reactions, it is incapable of general quantitative treatment.

The implications of the theory of the complete dissociation of strong electrolytes in aqueous solution were considered by Debye, Hückel and Onsager, and they succeeded in accounting quantitatively for the increasing molecular conductivity of a strong electrolyte producing singly charged ions with decreasing concentration of the solution over the concentration range 0–0.002M. For full details, textbooks of physical chemistry must be consulted.

It is important to realise that whilst complete dissociation occurs with strong electrolytes in aqueous solution, this does not mean that the effective concentrations of the ions are identical with their molar concentrations in any solution of the electrolyte: if this were the case the variation of the osmotic properties of the solution with dilution could not be accounted for. The variation of colligative, e.g. osmotic, properties with dilution is ascribed to changes in the activity of the ions; these are dependent upon the electrical forces between the ions. Expressions for the variations of the activity or of related quantities, applicable to dilute solutions, have also been deduced by the Debye–Hückel theory. Further consideration of the concept of activity follows in Section 2.5.

2.5 ACTIVITY AND ACTIVITY COEFFICIENT

In the deduction of the Law of Mass Action it was assumed that the effective concentrations or active masses of the components could be expressed by the stoichiometric concentrations. According to thermodynamics, this is not strictly true. The rigorous equilibrium equation for, say, a binary electrolyte:



is

$$\frac{(a_{\text{A}^+} \times a_{\text{B}^-})}{a_{\text{AB}}} = K_t$$

where a_{A^+} , a_{B^-} , and a_{AB} represent the **activities** of A^+ , B^- , and AB respectively, and K_t is the **true** or **thermodynamic, dissociation constant**. The concept of activity, a thermodynamic quantity, is due to G. N. Lewis. The quantity is related to the concentration by a factor termed the activity coefficient:

$$\text{Activity} = \text{Concentration} \times \text{Activity coefficient}$$

Thus at any concentration

$$a_{\text{A}^+} = y_{\text{A}^+} \cdot [\text{A}^+], a_{\text{B}^-} = y_{\text{B}^-} \cdot [\text{B}^-], \text{ and } a_{\text{AB}} = y_{\text{AB}} \cdot [\text{AB}]$$

where y refers to the activity coefficients,* and the square brackets to the

* The symbol used is dependent upon the method of expressing the concentration of the solution. The recommendations of the IUPAC Commission on Symbols, Terminology and Units (1969) are as follows: concentration in moles per litre (molarity), activity coefficient represented by y , concentration in mols per kilogram (molality), activity coefficient represented by γ , concentration expressed as mole fraction, activity coefficient represented by f .

concentrations. Substituting in the above equation, we obtain:

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

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 $I = 0.5 \sum c_i z_i^2$, 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 HNO₃ solution containing 0.2M Ba(NO₃)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:

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

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:

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

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

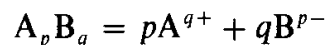
2.6 SOLUBILITY PRODUCT

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:



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

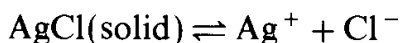
In general, for an electrolyte $A_p B_q$, which ionises into pA^{q+} and qB^{p-} ions:



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

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):



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:

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

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

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

or

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

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

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.

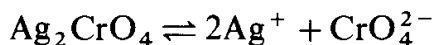
The following examples illustrate the method of calculating solubility products from solubility data and also the reverse procedure.

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 Ag^+ and Cl^- . Hence $[\text{Ag}^+] = 1.05 \times 10^{-5}$ and $[\text{Cl}^-] = 1.05 \times 10^{-5}$ mol L⁻¹.

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

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



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

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

$$\begin{aligned} K_{s(\text{Ag}_2\text{CrO}_4)} &= [\text{Ag}^+]^2 \times [\text{CrO}_4^{2-}] = (2 \times 7.5 \times 10^{-5})^2 \times (7.5 \times 10^{-5}) \\ &= 1.7 \times 10^{-12} \text{ mol}^3 \text{ L}^{-3} \end{aligned}$$

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



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

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 $x \text{ mol L}^{-1}$, $[\text{Mg}^{2+}] = x$ and $[\text{OH}^-] = 2x$. Substituting these values in the solubility product expression:

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

$$\text{or } x = 2.0 \times 10^{-4} \text{ mol L}^{-1}$$

$$= 2.0 \times 10^{-4} \times 58.3$$

$$= 1.2 \times 10^{-2} \text{ g L}^{-1}$$

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:

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

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

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) 0.001M and (b) 0.01M 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.

$$\begin{aligned} \text{For (a) } [Cl^-] &= 1 \times 10^{-3}, [Ag^+] = 1.1 \times 10^{-10}/1 \times 10^{-3} \\ &= 1.1 \times 10^{-7} \text{ mol L}^{-1} \end{aligned}$$

$$\begin{aligned} \text{For (b) } [Cl^-] &= 1 \times 10^{-2}, [Ag^+] = 1.1 \times 10^{-10}/1 \times 10^{-2} \\ &= 1.1 \times 10^{-8} \text{ mol L}^{-1} \end{aligned}$$

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

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

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

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

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

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

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

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

The solubility product equation gives:

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

$$\begin{aligned} \text{For } [CrO_4^{2-}] &= 0.001, [Ag^+] = \sqrt{1.7 \times 10^{-12}/1 \times 10^{-3}} \\ &= 4.1 \times 10^{-5} \text{ mol L}^{-1} \end{aligned}$$

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

$$\begin{aligned}\text{For } [\text{CrO}_4^{2-}] = 0.01, [\text{Ag}^+] &= \sqrt{1.7 \times 10^{-12} / 1 \times 10^{-2}} \\ &= 1.3 \times 10^{-5} \text{ mol L}^{-1}\end{aligned}$$

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 0.00075 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 $1.5 \times 10^{-5} \text{ g L}^{-1}$ (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 $1.2 \times 10^{-10} \text{ mol}^2 \text{ L}^{-2}$ and $1.7 \times 10^{-16} \text{ mol}^2 \text{ L}^{-2}$; i.e.

$$[\text{Ag}^+] \times [\text{Cl}^-] = 1.2 \times 10^{-10} \quad (1)$$

$$[\text{Ag}^+] \times [\text{I}^-] = 1.7 \times 10^{-16} \quad (2)$$

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 Ag^+ ion concentration is greater than

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

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

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

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

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

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

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).

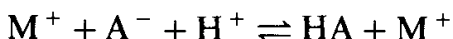
For a mixture of bromide and iodide:

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

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:



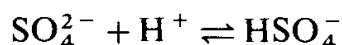
If the dissociation constant of the acid HA is very small, the anion A^- will be removed from the solution to form the undissociated acid HA. Consequently more of the salt will pass into solution to replace the anions removed in this way, and this process will continue until equilibrium is established (i.e. until $[\text{M}^+] \times [\text{A}^-]$ 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 ($K_1 = 7.5 \times 10^{-3} \text{ mol L}^{-1}$; $K_2 = 6.2 \times 10^{-8} \text{ mol L}^{-1}$; $K_3 = 5 \times 10^{-13} \text{ mol L}^{-1}$), oxalic acid ($K_1 = 5.9 \times 10^{-2} \text{ mol L}^{-1}$; $K_2 = 6.4 \times 10^{-5} \text{ mol L}^{-1}$), 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^- :



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 $\text{H}[\text{Ag}(\text{CN})_2]$), 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 ($K_2 = 1.2 \times 10^{-2} \text{ mol L}^{-1}$):



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

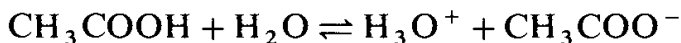
The solubility of the precipitates encountered in quantitative analysis increases with rise of temperature. With some substances the influence of temperature is small, but with others it is quite appreciable. Thus the solubility of silver chloride at 10 and 100 °C is 1.72 and 21.1 mg L^{-1} respectively, 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-1-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:



This will be written for simplicity in the conventional manner:



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

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

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:

$$K = \frac{\alpha^2 c}{(1 - \alpha)} \cdot \frac{y_{\text{H}^+} \cdot y_{\text{A}^-}}{y_{\text{HA}}}; \quad \text{A}^- = \text{CH}_3\text{COO}^-$$

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)



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

$$K = \frac{[\text{A}_2] [\text{B}_1]}{[\text{A}_1] [\text{B}_2]} \tag{5}$$

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:



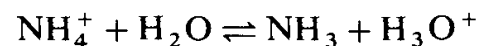
and the constant

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

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:

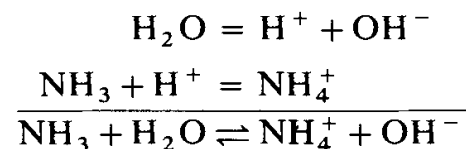
$$K_a = \frac{[B][H^+]}{[A]} \quad (7)$$

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



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.



The basic dissociation constant K_b is given by:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \quad (8)$$

Since $[\text{H}^+][\text{OH}^-] = K_w$ (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 $\text{p}K$ defined by

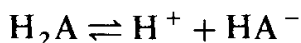
$$\text{p}K = \log_{10} 1/K = -\log_{10} K$$

The larger the $\text{p}K_a$ value is, the weaker is the acid and the stronger the base.

For very weak or slightly ionised electrolytes, 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 $\alpha_1 = \sqrt{K_1V}$ and $\alpha_2 = \sqrt{K_2V}$, 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:



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

$$[\text{H}^+][\text{HA}^-]/[\text{H}_2\text{A}] = K_1 \quad (9)$$

$$[\text{H}^+][\text{A}^{2-}]/[\text{HA}^-] = K_2 \quad (10)$$

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:

$$[\text{H}^+][\text{H}_2\text{A}^-]/[\text{H}_3\text{A}] = K_1 \quad (9')$$

$$[\text{H}^+][\text{HA}^{2-}]/[\text{H}_2\text{A}^-] = K_2 \quad (10')$$

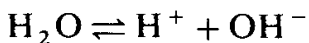
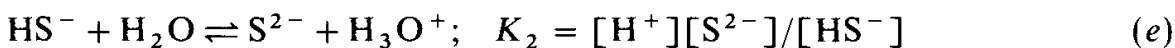
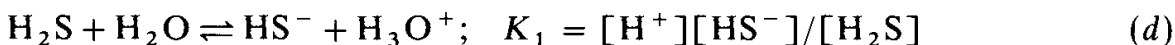
$$[\text{H}^+][\text{A}^{3-}]/[\text{HA}^{2-}] = K_3 \quad (11)$$

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 $1.0 \times 10^{-7} \text{ mol L}^{-1}$ and $1 \times 10^{-14} \text{ mol L}^{-1}$ respectively.

In the solution the following equilibria are involved:



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

$$[\text{H}^+] = [\text{HS}^-] + 2[\text{S}^{2-}] + [\text{OH}^-] \quad (f)$$

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

$$[\text{H}^+] = [\text{HS}^-] + 2[\text{S}^{2-}] \quad (g)$$

The $0.1 \text{ mol H}_2\text{S}$ is present partly as undissociated H_2S and partly as the ions HS^- and S^{2-} , and it follows that

$$[\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}] = 0.1 \quad (h)$$

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

$$[\text{H}^+] \approx [\text{HS}^-]$$

Since K_1 is also small, $[\text{H}^+] \ll [\text{H}_2\text{S}]$ and so equation (h) can be reduced to

$$[\text{H}_2\text{S}] \approx 0.1$$

Using these results in equation (d) we find

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

From equation (e) it then follows that

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

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

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 $1.75 \times 10^{-5} \text{ mol L}^{-1}$ 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,

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

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

The concentrations of sodium and acetate ions produced by the addition of the

completely dissociated sodium acetate are:

$$[\text{Na}^+] = 0.1, \text{ and } [\text{CH}_3\text{COO}^-] = 0.1 \text{ mol L}^{-1} \text{ respectively.}$$

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 $[\text{CH}_3\text{COO}^-] = 0.1$ for the solution, and if α' is the new degree of ionisation, $[\text{H}^+] = \alpha'c = 0.1\alpha'$, and $[\text{CH}_3\text{COOH}] = (1 - \alpha')c = 0.1$, since α' is negligibly small.

Substituting in the mass action equation:

$$\frac{[\text{H}^+] \times [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{0.1\alpha' \times 0.1}{0.1} = 1.75 \times 10^{-5}$$

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

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

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 NH₃ in water = 1.8 × 10⁻⁵ mol L⁻¹)

In 0.1 M ammonia solution $\alpha = \sqrt{1.8 \times 10^{-5}/0.1} = 0.0135$. Hence $[\text{OH}^-] = 0.00135$, $[\text{NH}_4^+] = 0.00135$, and $[\text{NH}_3] = 0.0986 \text{ mol L}^{-1}$. Let α' be the degree of ionisation in the presence of the added ammonium chloride. Then $[\text{OH}^-] = \alpha'c = 0.1\alpha'$, and $[\text{NH}_3] = (1 - \alpha')c = 0.1$, since α' may be taken as negligibly small. The addition of the completely ionised ammonium chloride will, of necessity, decrease the $[\text{NH}_4^+]$ derived from the base and increase $[\text{NH}_3]$, and as a first approximation $[\text{NH}_4^+] = 0.5$.

Substituting in the equation:

$$\frac{[\text{NH}_4^+] \times [\text{OH}^-]}{[\text{NH}_3]} = \frac{0.5 \times 0.1\alpha'}{0.1} = 1.8 \times 10^{-5}$$

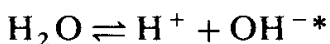
$$\alpha' = 3.6 \times 10^{-5} \text{ and } [\text{OH}^-] = 3.6 \times 10^{-6} \text{ mol L}^{-1}$$

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:



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

$$\frac{a_{\text{H}^+} \times a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}} = \frac{[\text{H}^+] \cdot [\text{OH}^-]}{[\text{H}_2\text{O}]} \times \frac{y_{\text{H}^+} \cdot y_{\text{OH}^-}}{y_{\text{H}_2\text{O}}} = \text{a constant}$$

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:

$$\frac{[\text{H}^+] \times [\text{OH}^-]}{[\text{H}_2\text{O}]} = \text{a constant}$$

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

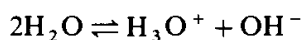
$$[\text{H}^+] \times [\text{OH}^-] = K_w$$

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 1×10^{-14} with concentrations expressed in mol L^{-1} . This is sensibly constant in dilute aqueous solutions. If the product of $[\text{H}^+]$ and $[\text{OH}^-]$ 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 $[\text{H}^+] = [\text{OH}^-] = \sqrt{K_w} = 10^{-7} \text{ mol L}^{-1}$ at about 25°C . A solution in which the hydrogen and hydroxide ion concentrations are equal is termed an **exactly neutral solution**. If $[\text{H}^+]$ 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 $[\text{OH}^-]$ 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:



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 $\text{pH} = 7$, an acid solution one in which $\text{pH} < 7$, and an alkaline solution one in which $\text{pH} > 7$. 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 $[H^+] = 4.0 \times 10^{-5} \text{ mol L}^{-1}$.

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

(ii) Find the hydrogen ion concentration corresponding to $\text{pH} = 5.643$.

$$\begin{aligned} \text{pH} &= \log_{10} 1/[\text{H}^+] = \log 1 - \log[\text{H}^+] = 5.643 \\ \therefore \log[\text{H}^+] &= -5.643 \end{aligned}$$

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

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

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

(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

$$= 1.25 \times 10^{-3} \text{ mol L}^{-1}$$

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

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

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

If we write the equation:

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

in the form:

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

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

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 $[\text{H}^+]$, pH, $[\text{OH}^-]$, 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 :

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

Similarly for any base with dissociation constant K_b :

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

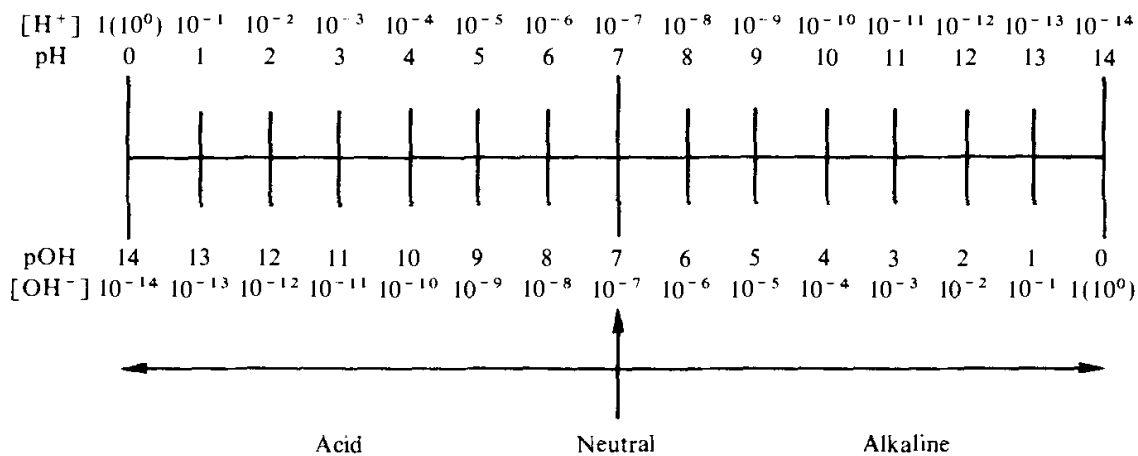


Fig. 2.1

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

$$pI = \log 1/[I] = -\log[I]$$

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

(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:



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:



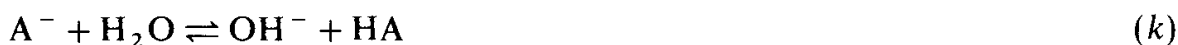
A very small concentration of hydrogen and hydroxide ions, originating from the small but finite ionisation of water, will be initially present. HA is a weak acid, i.e. it is dissociated only to a small degree; the concentration of A^- ions which can exist in equilibrium with H^+ ions is accordingly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



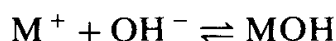
The hydrogen ions required for this reaction can be obtained only from the further dissociation of the water; this dissociation produces simultaneously an equivalent quantity of hydroxyl ions. The hydrogen ions are utilised in the formation of HA; consequently the hydroxide ion concentration of the solution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

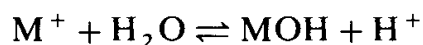


This equation can also be obtained by combining (i) and (j), since both equilibria must co-exist. This interaction between the ion (or ions) of a salt and water is called 'hydrolysis'.

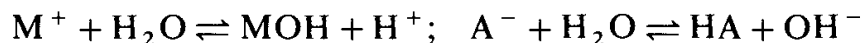
Consider now the salt of a strong acid and a weak base {class (3)}. Here the initial high concentration of cations M^+ will be reduced by combination with the hydroxide ions of water to form the little-dissociated base MOH until the equilibrium:



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:



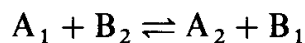
For salts of class (4), in which both the acid and the base are weak, two reactions will occur simultaneously



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

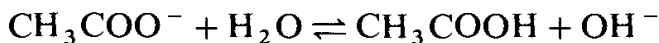


Thus the equation for the hydrolysis of ammonium salts



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



the hydrolysis constant is

$$[\text{CH}_3\text{COOH}][\text{OH}^-]/[\text{CH}_3\text{COO}^-] = K_h = K_w/K_a$$

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:



Applying the Law of Mass Action, we obtain:

$$\frac{a_{\text{OH}^-} \times a_{\text{HA}}}{a_{\text{A}^-}} = \frac{[\text{OH}^-] \cdot [\text{HA}]}{[\text{A}^-]} \times \frac{y_{\text{OH}^-} \cdot y_{\text{HA}}}{y_{\text{A}^-}} = K_h \quad (12)$$

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:

$$K_h = \frac{[\text{OH}^-] \times [\text{HA}]}{[\text{A}^-]} \quad (13)$$

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:

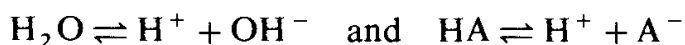
$$[\text{HA}] = [\text{OH}^-] = x/V; \quad [\text{A}^-] = (1-x)/V$$

Substituting these values in equation (13):

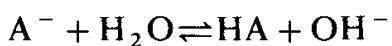
$$K_h = \frac{[\text{OH}^-] \times [\text{HA}]}{[\text{A}^-]} = \frac{x/V \times x/V}{(1-x)/V} = \frac{x^2}{(1-x)V}$$

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:



must co-exist with the hydrolytic equilibrium:



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:

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

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

$$\text{therefore } K_w/K_a = K_h$$

$$\text{or } pK_h = pK_w - pK_a$$

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 $c \text{ mol L}^{-1}$, then:

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

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

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

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

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

$$\text{pH} = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pc \quad (14)$$

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:

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

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

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 $2.38 \times 10^{-6} \text{ mol L}^{-1}$. This is also equal to the hydroxide ion concentration produced, i.e. $\text{pOH} = 5.62$.

$$\text{pH} = 14.0 - 5.62 = 8.38$$

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

$$\text{pH} = \frac{1}{2}\text{p}K_w + \frac{1}{2}\text{p}K_a - \frac{1}{2}\text{p}c = 7.0 + 2.38 - \frac{1}{2}(2) = 8.38$$

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



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

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

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

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

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

$$\text{or } \text{pH} = \frac{1}{2}\text{p}K_w - \frac{1}{2}\text{p}K_b + \frac{1}{2}\text{p}c \quad (15)$$

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:

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

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

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



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

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

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:

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

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

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

leading to the result

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

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

It may be readily shown that:

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

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

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:

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

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

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

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

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

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

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

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

* 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 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:



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

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

The expression may be approximated by writing concentrations for activities:

$$[\text{H}^+] = \frac{[\text{HA}]}{[\text{A}^-]} \times K_a \quad (18)$$

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 $(c_a - [\text{H}^+])$. The solution is electrically neutral, hence $[\text{A}^-] = c_s + [\text{H}^+]$ (the salt is completely dissociated). Substituting these values in the equilibrium equation (18), we have:

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

This is a quadratic equation in $[\text{H}^+]$ 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 $[\text{H}^+]$ may be taken as negligibly small by

comparison with c_a and c_s . Equation (19) then reduces to:

$$[\text{H}^+] = \frac{c_a}{c_s} K_a, \quad \text{or} \quad [\text{H}^+] = \frac{[\text{Acid}]}{[\text{Salt}]} \times K_a \quad (20)$$

$$\text{or} \quad \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad (21)$$

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:



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

$$\text{pH} = \text{p}K_a + \log \frac{[\text{B}]}{[\text{A}]}$$

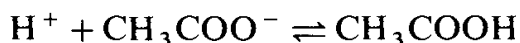
where $K_a = [\text{H}^+][\text{B}]/[\text{A}]$.

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

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

$$\text{or} \quad \text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \quad (23)$$

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 $\text{pH} = \text{p}K_a$. 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, $K_a = 1.75 \times 10^{-5} \text{ mol L}^{-1}$, $\text{p}K_a = 4.76$; a half-neutralised solution of, say 0.1 M 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:



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 1 M hydrochloric acid to 1 L of a solution which is 0.1 M in acetic (ethanoic) acid and 0.1 M in sodium acetate ($K_a = 1.75 \times 10^{-5} \text{ mol L}^{-1}$).

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

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

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

$$\text{CH}_3\text{COO}^- = 0.1 - 0.01 = 0.09$$

$$\text{CH}_3\text{COOH} = 0.1 + 0.01 = 0.11$$

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

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 (pH = 7) would lead to a solution with 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]:

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

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

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

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:

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

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:

$$a_{\text{H}^+} = \frac{a_{\text{HA}}}{a_{\text{A}^-}} \times K_a = \frac{c_a \cdot \gamma_a}{c_s \cdot \gamma_{\text{A}^-}} \times K_a \quad (24)$$

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:

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

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

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:



The ion H_2PO_4^- acts as a monoprotic acid:



for which K ($\equiv K_2$ for phosphoric acid) is $6.2 \times 10^{-8} \text{ mol L}^{-1}$. 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 ($\text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-}$) is small ($K_3 = 5 \times 10^{-13} \text{ mol L}^{-1}$). The mixture of NaH_2PO_4 and Na_2HPO_4 is therefore an effective buffer over the range $\text{pH } 7.2 \pm 1.0$ ($= \text{p}K \pm 1$). 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

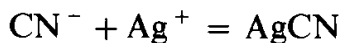
The increase in solubility of a precipitate upon the addition of excess of the precipitating agent is frequently due to the formation of a complex ion. A

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.

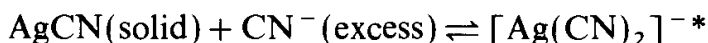
When potassium cyanide solution is added to a solution of silver nitrate, a white precipitate of silver cyanide is first formed because the solubility product of silver cyanide:

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

is exceeded. The reaction is expressed:

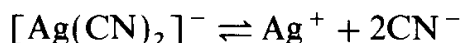


The precipitate dissolves upon the addition of excess of potassium cyanide, the complex ion $[\text{Ag}(\text{CN})_2]^-$ being produced:



(or $\text{AgCN} + \text{KCN} = \text{K}[\text{Ag}(\text{CN})_2]$ – 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 $1.6 \times 10^{-49} \text{ mol}^3 \text{ L}^{-3}$), and also silver is deposited from the complex cyanide solution upon electrolysis. The complex ion thus dissociates in accordance with the equation:



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

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

which has a value of $1.0 \times 10^{-21} \text{ mol}^2 \text{ L}^{-2}$ 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:

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

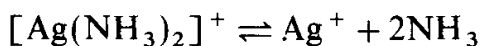
Consider now a somewhat different type of complex ion formation, viz. the production of a complex ion with constituents other than the common ion present in the solution. This is exemplified by the solubility of silver chloride in ammonia solution. The reaction is:



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

*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:



and the dissociation constant is given by:

$$K_{\text{diss.}} = \frac{[\text{Ag}^+] \times [\text{NH}_3]^2}{[\{\text{Ag}(\text{NH}_3)_2\}^+]} = 6.8 \times 10^{-8} \text{ mol}^2 \text{ L}^{-2}$$

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

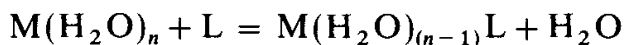
The magnitude of the dissociation constant clearly shows that only a very small silver ion concentration is produced by the dissociation of the complex ion.

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 $[\text{Fe}(\text{CN})_6]^{4-}$, 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 $[\text{Cd}(\text{CN})_4]^{2-}$ and $[\text{Cu}(\text{CN})_4]^{3-}$ 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:



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.

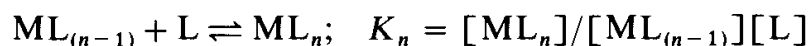
When, however, the ligand molecule or ion has two atoms, each of which has a lone pair of electrons, then the molecule has two donor atoms and it may be possible to form two coordinate bonds with the same metal ion; such a ligand is said to be **bidentate** and may be exemplified by consideration of the tris(ethylenediamine)cobalt(III) complex, $[\text{Co}(\text{en})_3]^{3+}$. 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. $[\text{Zn}_2\text{Cl}_6]^{2-}$, 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.

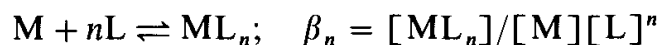
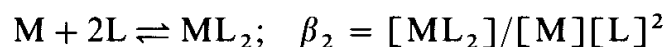
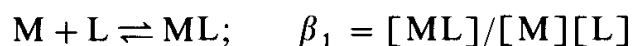
2.23 STABILITY OF COMPLEXES

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:



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

An alternative way of expressing the equilibria is as follows:



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

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

* Ethane-1,2-diamine.

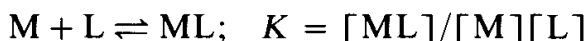
† 1,2-Bis[bis(carboxymethyl)amino]ethane.

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



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 multidentate 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' $\{(\text{H}_2\text{N}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}(\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2)_2\}$ 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.

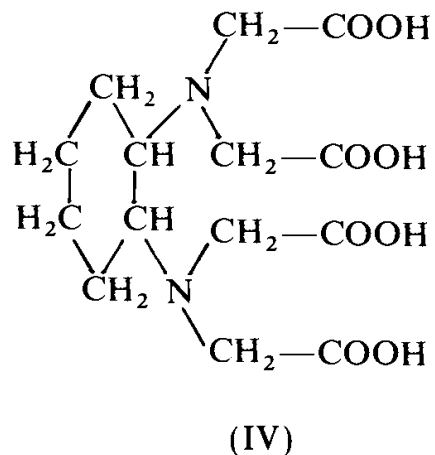
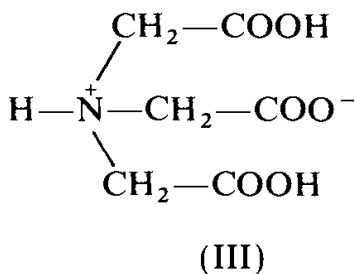
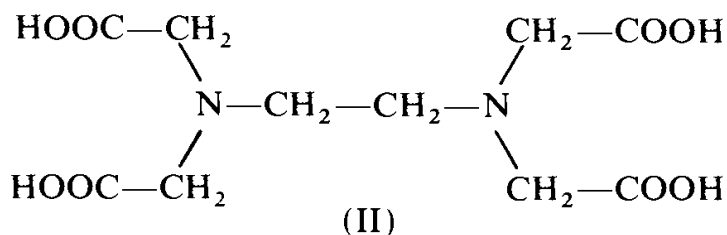
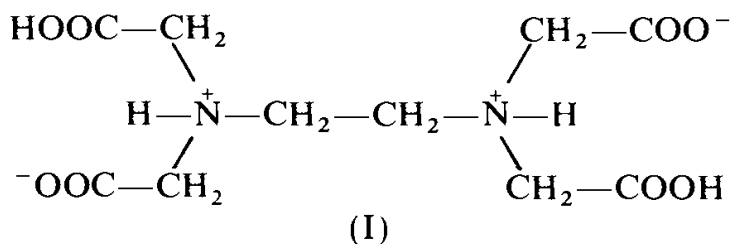
- (i) Main group elements usually form labile complexes.
- (ii) With the exception of Cr(III) and Co(III), most first-row transition elements form labile complexes.
- (iii) Second- and third-row transition elements tend to form inert complexes.

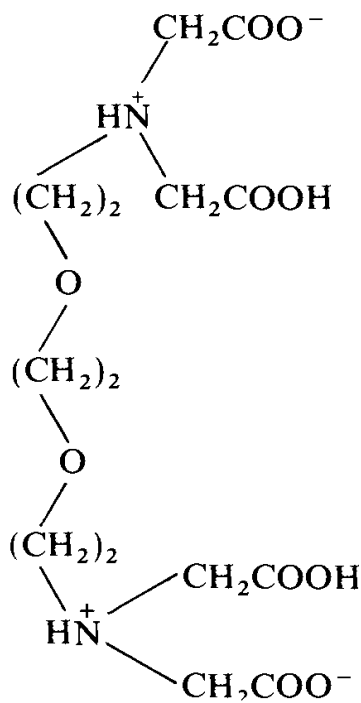
For a full discussion of the topics introduced in this section a textbook of inorganic chemistry (e.g. Ref. 4) or one dealing with complexes (e.g. Ref. 2), should be consulted.

2.26 COMPLEXONES

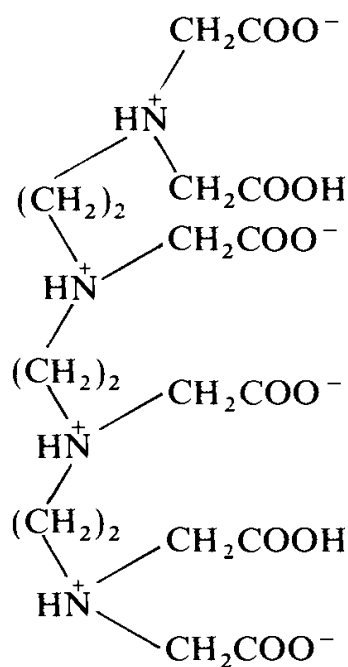
The formation of a single complex species rather than the stepwise production of such species will clearly simplify complexometric titrations and facilitate the detection of end points. Schwarzenbach² realised that the acetate ion is able to form acetato complexes of low stability with nearly all polyvalent 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 $pK_1 = 2.0$, $pK_2 = 2.7$,

$pK_3 = 6.2$, 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 ethylenediaminetetra-acetic 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.





(V) EGTA



(VI) TTHA

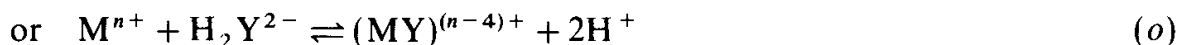
Other complexing agents (complexones) which are sometimes used include (a) nitrilotriacetic acid (III) (NITA or NTA or Complexone I; this has $pK_1 = 1.9$, $pK_2 = 2.5$, and $pK_3 = 9.7$), (b) *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid (IV): this should presumably be formulated as a 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'*-tetraacetic acid (EGTA), and (d) triethylenetetramine-*N,N,N',N'',N''',N''''*-hexaacetic 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:



For other cations, the reactions may be expressed as:



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 :



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

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

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

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 $\text{pH} = 1$ to $\log \alpha = 0$ at $\text{pH} = 12$: 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:

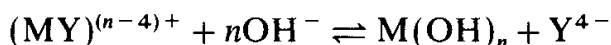
$$\log K_H = 18.0 - 7.0 = 11.0$$

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:

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

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:



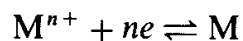
The extent of hydrolysis of $(MY)^{(n-4)+}$ depends upon the characteristics of the metal ion, and is largely controlled by the solubility product of the metallic hydroxide and, of course, the stability constant of the complex. Thus iron(III) is precipitated as hydroxide ($K_{sol} = 1 \times 10^{-36}$) 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:

$$\log K_{HZ} = \log K - \log \alpha - \log \beta. \quad (31)$$

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



is given by the expression:

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

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:

$$E = E^\ominus + \frac{0.0001984T}{n} \log a_{M^{n+}}$$

For a temperature of 25°C ($T = 298\text{K}$):

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

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):

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

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

If in equation (33), $a_{M^{n+}}$ 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 1.18 M 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

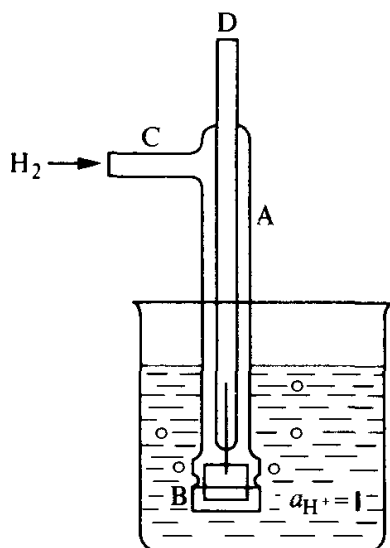
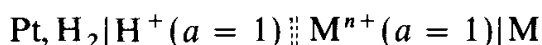
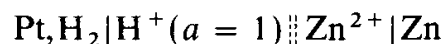


Fig. 2.2

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.

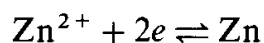
When reference is made to the electrode potential of a zinc electrode, it is the e.m.f. of the cell:



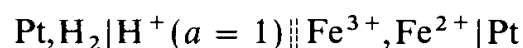
or the e.m.f. of the half-cell $\text{Zn}^{2+} | \text{Zn}$ which is meant. The cell reaction is:



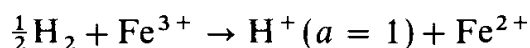
and the half-cell reaction is written as:



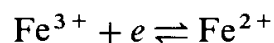
The electrode potential of the $\text{Fe}^{3+}, \text{Fe}^{2+} | \text{Pt}$ electrode is the e.m.f. of the cell:



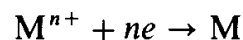
or the e.m.f. of the half-cell $\text{Fe}^{3+}, \text{Fe}^{2+} | \text{Pt}$. The cell reaction is:



and the half-cell reaction is written:



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



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

When the activity of the ion M^{n+} is equal to unity (approximately true for a 1 M 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)
$\text{Li}^+ + e = \text{Li}$	-3.045	$\text{Tl}^+ + e = \text{Tl}$	-0.336
$\text{K}^+ + e = \text{K}$	-2.925	$\text{Co}^{2+} + 2e = \text{Co}$	-0.277
$\text{Ba}^{2+} + 2e = \text{Ba}$	-2.90	$\text{Ni}^{2+} + 2e = \text{Ni}$	-0.25
$\text{Sr}^{2+} + 2e = \text{Sr}$	-2.89	$\text{Sn}^{2+} + 2e = \text{Sn}$	-0.136
$\text{Ca}^{2+} + 2e = \text{Ca}$	-2.87	$\text{Pb}^{2+} + 2e = \text{Pb}$	-0.126
$\text{Na}^+ + e = \text{Na}$	-2.714	$2\text{H}^+ + 2e = \text{H}_2$	0.000
$\text{Mg}^{2+} + 2e = \text{Mg}$	-2.37	$\text{Cu}^{2+} + 2e = \text{Cu}$	+0.337
$\text{Al}^{3+} + 3e = \text{Al}$	-1.66	$\text{Hg}^{2+} + 2e = \text{Hg}$	+0.789
$\text{Mn}^{2+} + 2e = \text{Mn}$	-1.18	$\text{Ag}^+ + e = \text{Ag}$	+0.799
$\text{Zn}^{2+} + 2e = \text{Zn}$	-0.763	$\text{Pd}^{2+} + 2e = \text{Pd}$	+0.987
$\text{Fe}^{2+} + 2e = \text{Fe}$	-0.440	$\text{Pt}^{2+} + 2e = \text{Pt}$	+1.2
$\text{Cd}^{2+} + 2e = \text{Cd}$	-0.403	$\text{Au}^{3+} + 3e = \text{Au}$	+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.

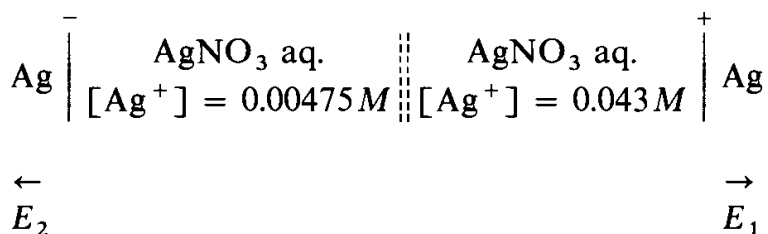
2.29 CONCENTRATION CELLS

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:

$$E = \frac{0.0591}{n} \log c_1 + E^\ominus - \left(\frac{0.0591}{n} \log c_2 + E^\ominus \right)$$

$$= \frac{0.0591}{n} \log \frac{c_1}{c_2}, \quad \text{where } c_1 > c_2$$

As an example consider the cell:



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

$$E = E_1 - E_2 = \frac{0.0591}{1} \log \frac{0.043}{0.00475} = 0.056 \text{ volt}$$

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

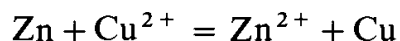
An interesting application of electrode potentials is to the calculation of the e.m.f. of a voltaic cell. One of the simplest of galvanic cells is the Daniell cell. It consists of a rod of zinc dipping into zinc sulphate solution and a strip of copper in copper sulphate solution; the two solutions are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



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: $\text{Zn} \rightleftharpoons \text{Zn}^{2+} + 2e$;
 (b) copper electrode: $\text{Cu}^{2+} + 2e \rightleftharpoons \text{Cu}$.

The net chemical reaction is:



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:

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

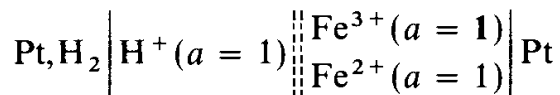
The small potential difference produced at the contact between the two solutions (the so-called liquid-junction potential) is neglected.

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 $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ and it will take electrons from the platinum, leaving the latter positively charged; if, however, the system has reducing properties ($\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$), 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 $\text{Fe}^{3+} - \text{Fe}^{2+}$ electrode, the redox cell would be:



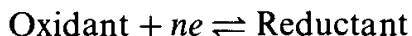
The potential measured in this way is called the **standard reduction potential**. A selection of standard reduction potentials is given in Table 2.6.

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 are those at the lower end. Thus permanganate ion can oxidise Cl^- , Br^- , I^- , Fe^{2+} and $[\text{Fe}(\text{CN})_6]^{4-}$; Fe^{3+} can oxidise H_3AsO_3 and I^- but not $\text{Cr}_2\text{O}_7^{2-}$ 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 $\text{MnO}_4^- - \text{Mn}^{2+}$ system; $\text{MnO}_4^- + 8\text{H}^+ + 5e = \text{Mn}^{2+} + 4\text{H}_2\text{O}$, 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 $\text{Cr}_2\text{O}_7^{2-} - \text{Cr}^{3+}$ system is $+1.33$ volts. This means that the $\text{MnO}_4^- - \text{Mn}^{2+}$ system is a better oxidising agent than the $\text{Cr}_2\text{O}_7^{2-} - \text{Cr}^{3+}$ system. Since the standard potentials for $\text{Cl}_2 - 2\text{Cl}^-$ and $\text{Fe}^{3+} - \text{Fe}^{2+}$ systems are $+1.36$ and 0.77 volt respectively, permanganate and dichromate will oxidise $\text{Fe}(\text{II})$ 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 $\text{Fe}(\text{II})$ 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.

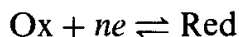
Standard potentials are determined with full consideration of activity effects, and are really limiting values. They are rarely, if ever, observed directly in a potentiometric measurement. In practice, measured potentials determined under defined concentration conditions (formal potentials) are very 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



or



(*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:

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

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

* 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:

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

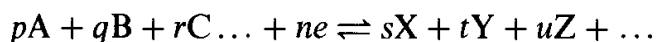
Substituting the known values of R and F , and changing from natural to common logarithms, at a temperature of 25°C ($T = 298\text{K}$):

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

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:



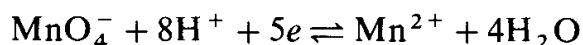
The potential is given by:

$$E = E^\ominus + \frac{RT}{nF} \ln \frac{a_A^p \cdot a_B^q \cdot a_C^r \dots}{a_X^s \cdot a_Y^t \cdot a_Z^u \dots}$$

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):

$$E = E^\ominus + \frac{0.0591}{n} \log \frac{c_A^p \cdot c_B^q \cdot c_C^r \dots}{c_X^s \cdot c_Y^t \cdot c_Z^u \dots}$$

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:



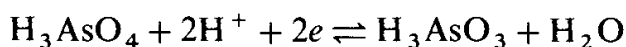
$$E = E^\ominus + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-] \times [\text{H}^+]^8}{[\text{Mn}^{2+}]} \quad (\text{at } 25^\circ\text{C})$$

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:

$$E = E^\ominus + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]} + \frac{0.0591}{5} \log [\text{H}^+]^8$$

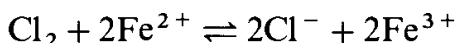
This enables us to calculate the effect of change in the ratio $[\text{MnO}_4^-]/[\text{Mn}^{2+}]$ at any hydrogen ion concentration, other factors being maintained constant. In this system, however, difficulties are experienced in the calculation owing to the fact that the reduction products of the 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:



$$E = E^\ominus + \frac{0.0591}{2} \log \frac{[\text{H}_3\text{AsO}_4] \times [\text{H}^+]^2}{[\text{H}_3\text{AsO}_3]} \quad (\text{at } 25^\circ\text{C})$$

$$\text{or } E = E^\ominus + \frac{0.0591}{2} \log \frac{[\text{H}_3\text{AsO}_4]}{[\text{H}_3\text{AsO}_3]} + \frac{0.0591}{2} \log [\text{H}^+]^2$$

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:



The equilibrium constant is given by:

$$\frac{[\text{Cl}^-]^2 \times [\text{Fe}^{3+}]^2}{[\text{Cl}_2] \times [\text{Fe}^{2+}]^2} = K$$

The reaction may be regarded as taking place in a voltaic cell, the two half-cells being a $\text{Cl}_2, 2\text{Cl}^-$ system and a $\text{Fe}^{3+}, \text{Fe}^{2+}$ 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:

$$E_{\text{Cl}_2, 2\text{Cl}^-}^\ominus + \frac{0.0591}{2} \log \frac{[\text{Cl}_2]}{[\text{Cl}^-]^2} = E_{\text{Fe}^{3+}, \text{Fe}^{2+}}^\ominus + \frac{0.0591}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

Now $E_{\text{Cl}_2, 2\text{Cl}^-}^\ominus = 1.36$ volts and $E_{\text{Fe}^{3+}, \text{Fe}^{2+}}^\ominus = 0.75$ volt, hence

$$\log \frac{[\text{Fe}^{3+}]^2 \times [\text{Cl}^-]^2}{[\text{Fe}^{2+}]^2 \times [\text{Cl}_2]} = \frac{0.61}{0.02965} = 20.67 = \log K$$

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

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:



The equilibrium constant K is given by:

$$K = \frac{[\text{Mn}^{2+}] \times [\text{Fe}^{3+}]^5}{[\text{MnO}_4^-] \times [\text{Fe}^{2+}]^5 \times [\text{H}^+]^8}$$

The term $4\text{H}_2\text{O}$ 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:



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

$$\begin{aligned} E &= E^\ominus + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-] \times [\text{H}^+]^8}{[\text{Mn}^{2+}]} \\ &= 1.52 + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-] \times [\text{H}^+]^8}{[\text{Mn}^{2+}]} \end{aligned}$$

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



For (37) as an oxidation–reduction electrode:

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

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

$$1.52 + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-] \times [\text{H}^+]^8}{[\text{Mn}^{2+}]} = 0.77 + \frac{0.0591}{5} \log \frac{[\text{Fe}^{3+}]^5}{[\text{Fe}^{2+}]^5}$$

$$\text{or } \log \frac{[\text{Mn}^{2+}] \times [\text{Fe}^{3+}]^5}{[\text{MnO}_4^-] \times [\text{Fe}^{2+}]^5 \times [\text{H}^+]^8} = \frac{5(1.52 - 0.77)}{0.0591} = 63.5$$

$$K = \frac{[\text{Mn}^{2+}] \times [\text{Fe}^{3+}]^5}{[\text{MnO}_4^-] \times [\text{Fe}^{2+}]^5 \times [\text{H}^+]^8} = 3 \times 10^{63}$$

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 $[\text{Fe}^{3+}] = 0.01 M$, since it is known that the reaction is practically complete, $[\text{Mn}^{2+}] = \frac{1}{5} \times [\text{Fe}^{3+}] = 0.002 M$, and $[\text{Fe}^{2+}] = x$. Let the excess of permanganate solution at the end-point be one drop or 0.05 mL; its concentration will be $0.05 \times 0.1/100 = 5 \times 10^{-5} M = [\text{MnO}_4^-]$. Substituting these values in the equation:

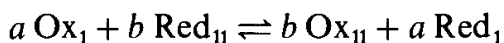
$$K = \frac{(2 \times 10^{-3}) \times (1 \times 10^{-2})^5}{10^{-5} \times x^5 \times 1^8} = 3 \times 10^{63}$$

$$\text{or } x = [\text{Fe}^{2+}] = 5.8 \times 10^{-15} \text{ mol L}^{-1}$$

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.:



The complete reaction may be regarded as composed of two oxidation–reduction electrodes. $a \text{Ox}_1$, $a \text{Red}_1$ and $b \text{Ox}_{11}$, $b \text{Red}_{11}$ combined together into a cell; at equilibrium, the potentials of both electrodes are the same:

$$E_1 = E_1^\ominus + \frac{0.0591}{n} \log \frac{[\text{Ox}_1]^a}{[\text{Red}_1]^a}$$

$$E_2 = E_2^\ominus + \frac{0.0591}{n} \log \frac{[\text{Ox}_{11}]^b}{[\text{Red}_{11}]^b}$$

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

$$E_1^\ominus + \frac{0.0591}{n} \log \frac{[\text{Ox}_1]^a}{[\text{Red}_1]^a} = E_2^\ominus + \frac{0.0591}{n} \log \frac{[\text{Ox}_{11}]^b}{[\text{Red}_{11}]^b}$$

$$\text{or } \log \frac{[\text{Ox}_{11}]^b \times [\text{Red}_1]^a}{[\text{Red}_{11}]^b \times [\text{Ox}_1]^a} = \log K = \frac{n}{0.0591} (E_1^\ominus - E_2^\ominus)$$

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_1 and Red_{11} are allowed to react, are given by:

$$\frac{[\text{Red}_1]}{[\text{Ox}_1]} = \frac{[\text{Ox}_{11}]}{[\text{Red}_{11}]} = \sqrt{(a+b)K}$$

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.