CHAPTER 20

IONIC EQUILIBRIA

Chemical equilibria involving dissociation of chemical compounds, both solid and gaseous, and phase equilibria involving various phase transitions such as solid $\rightleftharpoons$ liquid, liquid $\rightleftharpoons$ vapour, solid $\rightleftharpoons$ vapour, one allotropic form $\rightleftharpoons$ another allotropic form, etc., have been discussed in previous chapters. In this chapter, we shall discuss ionic equilibria involving dissociation of weak acids and weak bases in aqueous solutions, dissociation of sparingly soluble salts in aqueous solutions, dissociation of water and hydrolytic dissociation of salts, etc., in some details.

ACIDS AND BASES

Different concepts have been put forth by different investigators to characterise acids and bases. While some of the concepts are quite narrow in their approach, others are fairly comprehensive. Some important concepts of acids and bases are discussed below.

Arrhenius Concept

According to Arrhenius concept, an acid is a substance that dissociates to give hydrogen ions when dissolved in water. Thus, hydrogen chloride gas is an acid because when dissolved in water, it gives hydrogen ions.

$$HCl(g) + \text{water} \rightleftharpoons H^+(aq) + Cl^-(aq)$$

The symbol *aq* indicates that the ions are hydrated, *i.e.*, associated with one or more molecules of water. The dissociation of acetic acid when dissolved in water is represented as

$$CH_3COOH + \text{water} \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

Similarly, a base is a substance which dissociates into hydroxyl ions when dissolved in water. The dissociation of a base like calcium hydroxide may be represented by the equation

$$Ca(OH)_2 + \text{water} \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$$

The high dielectric constant of water lowers the force of attraction between the oppositely charged ions and thus causes the dissociation of the electrolyte. The greater the number of H^+ or OH^- ions given by an acid or a base in water, the greater is the strength of the acid or the base.

Although the H^+ ion in aqueous solution is largely hydrated, with H_3O^+ **(hydronium ion)** as its probable structure, it is customary to represent it as $H^+(aq)$ for the sake of convenience.

Since almost all ions are hydrated to more or less extent, therefore, it is customary to put (*aq*) after each ion.

The Swedish chemist S. Arrhenius (1859–1927) was awarded the 1903 Chemistry Nobel Prize for his theory of electrolytic dissociation.

Bronsted-Lowry Concept

In 1923, Lowry and Bronsted suggested a more general definition of acids and bases. According to their concept, an **acid** is defined *as a substance which has a tendency to donate a proton to any other substance* and a **base** *as a substance which has a tendency to accept a proton from any other substance.* In other words, *an* **acid** *is a proton-donor and a* **base** *is a proton-acceptor.*

When an acid loses a proton, *i.e.*, an H^+ ion, the residual part of it has a tendency to regain the proton. Therefore, it behaves as a base. An acid and a base may, therefore, be defined by the general equation

$$\text{Acid} \rightleftharpoons \underset{\text{(Proton)}}{H^+} + \text{Base} \qquad ...(1)$$

Conjugate Acids and Bases. Consider the dissociation of acetic acid in water which may be represented as

$$\underset{\text{Acid}}{CH_3COOH} + \underset{\substack{\text{Base}\\ \text{(Solvent)}}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{CH_3COO^-} \qquad ...(2)$$

It is evident that acetic acid *donates* a proton to water and thus acts as an *acid*. Water *accepts* a proton and, therefore, acts as a *base*. In the reverse reaction, hydronium ion (H_3O^+) *donates* a proton to the acetate ion and, therefore, acts as an *acid*. The acetate ion *accepts* a proton and, therefore, behaves as a *base*. *Such pairs of substances which can be formed from one another by the gain or loss of a proton are known as* **conjugate acid-base pairs.** Thus, acetic acid is the conjugate acid of acetate ion and acetate ion is the conjugate base of acetic acid. Similarly, water is the conjugate base of hydronium ion and hydronium ion is the conjugate acid of water.

The dissociation of hydrochloric acid in water may be represented as

$$\underset{\text{Acid}}{HCl} + \underset{\substack{\text{Base}\\ \text{(Solvent)}}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{Cl^-} \qquad ...(3)$$

Evidently, hydrochloric acid is the conjugate acid of chloride ion and chloride ion is the conjugate base of hydrochloric acid.

The following points emerge out of the above discussion :

1. Firstly, it is evident that a substance is able to show its acidic character only if another substance capable of accepting a proton is present. For example, acetic acid or hydrogen chloride solution in benzene is not acidic because benzene is not in a position to take up protons. But, a solvent like water can take up protons and, therefore, acetic acid or hydrochloric acid can dissociate in water, as shown in the above examples.

2. Secondly, hydrogen ion in aqueous solution does not exist as H^+ ion but as hydrated ion, H_3O^+. It is called **hydronium ion** because of its resemblance with ammonium ion, NH_4^+.

3. Thirdly, not only molecules but even ions may act as acids or bases. Thus, in the above examples, acetate ion (or chloride ion) acts as a base as it can accept a proton to form acetic acid (or hydrochloric acid). In fact, anion of any acid is the conjugate base of the acid.

As will be seen from the dissociation of acetic acid or hydrochloric acid represented above, there is one acid and one base on each side of the equation. Suppose, acetic acid is designated as Acid_1, then the acetate ion, its conjugate base, may be designated as Base_1. Similarly, if water is referred to as Base_2, then the hydronium ion, its conjugate acid, may be designated as Acid_2. The dissociation of acetic acid in water may then be represented as

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1 \qquad ...(4)$$

Acid_1 and Base_1 is a *conjugate acid-base pair* and so is Acid_2 and Base_2.

In general, the dissociation of an acid HA in water may be represented as

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

Just as an acid requires a solvent that can take up a proton (*i.e.*, can act as a base) for its dissociation, similarly, a base requires a solvent that can give up a proton (*i.e.*, that can act as an acid) for its dissociation. Water possesses both basic and acidic properties. Therefore, acids as well as bases can dissociate in water. Thus, water acts as an acid (a proton-donor) towards ammonia and as a base (a proton-acceptor) towards acetic acid. Such substances are said to be **amphiprotic** or **amphoteric.**

Consider dissociation of ammonia in water which may be represented as

$$\underset{\text{Base}_1}{NH_3} + \underset{\text{Acid}_2}{H_2O} \rightleftharpoons \underset{\text{Acid}_1}{NH_4^+} + \underset{\text{Base}_2}{OH^-}$$

Ammonium ion (NH_4^+) is the conjugate acid (say, Acid$_1$) to the base NH_3 (Base$_1$) and hydroxyl (OH^-) ion is the conjugate base (Base$_2$) to the acid H_2O (Acid$_2$). Thus, this equilibrium also conforms to the usual pattern.

Example 1. Determine the trend in the relative basic strengths of anions in the series : $ClO_4^-, ClO_3^-, ClO_2^-$.

Solution : ClO_4^-, ClO_3^-, ClO_2^- are, respectively, the conjugate bases of $HClO_4$, $HClO_3$, $HClO_2$. A conjugate acid-base pair stands in complementary relation to each other. The stronger the acid, the weaker is its conjugate base. Since the strength of the acids varies in the order :

$$HClO_4 > HClO_3 > HClO_2,$$

the strength of their conjugate bases varies in the order :

$$ClO_4^- < ClO_3^- < ClO_2^-$$

Let us elucidate it by considering the generalized acid-base reaction

$$HA + B \rightleftharpoons A^- + BH^+$$

wherein HA-A^- and BH^+-B constitute conjugate acid-base pairs. In this reaction, the greater the tendency of HA to react with B, the farther will lie the equilibrium to the right and, the farther the equilibrium lies to the right, the less effective is A^-, the conjugate base of HA, in acting as a base by accepting a proton.

Some common cases of equilibria between acids and bases involving proton transfer are given in Table 1.

TABLE 1

Conjugate Acids and Bases

Acid$_1$	+	Base$_2$	$\rightleftharpoons$	Acid$_2$	+	Base$_1$
HCl	+	H_2O	$\rightleftharpoons$	H_3O^+	+	Cl^-
HNO_3	+	H_2O	$\rightleftharpoons$	H_3O^+	+	NO_3^-
H_2SO_4	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HSO_4^-
H_3PO_4	+	H_2O	$\rightleftharpoons$	H_3O^+	+	$H_2PO_4^-$
HSO_4^-	+	H_2O	$\rightleftharpoons$	H_3O^+	+	SO_4^{2-}
CH_3COOH	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CH_3COO^-
HSO_3^-	+	H_2O	$\rightleftharpoons$	H_3O^+	+	SO_3^{2-}
H_2CO_3	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HCO_3^-
HCN	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CN^-
NH_4^+	+	H_2O	$\rightleftharpoons$	H_3O^+	+	NH_3
HCO_3^-	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CO_3^{2-}
HS^-	+	H_2O	$\rightleftharpoons$	H_3O^+	+	S^{2-}
H_2O	+	H_2O	$\rightleftharpoons$	H_3O^+	+	OH^-

Relative Strengths of Acid-Base Pairs. According to the concept of Lowry and Bronsted, the strength of an acid depends upon its tendency to lose protons and the strength of a base depends upon its tendency to gain protons. If an acid, such as hydrochloric acid, is a strong acid, it will have a strong tendency to donate protons. Thus, the equilibrium,

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

lies very much to the right and the reverse reaction, representing the gain of proton by the chloride ion leading to the reformation of HCl, will take place to a very small extent. Thus, chloride ion is a *weak base.*

If an acid, such as acetic acid, is a *weak acid,* it would have only a weak tendency to lose protons. Thus, the equilibrium

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

lies mostly towards the left and the reverse reaction, representing the gain of protons by the CH_3COO^- ion leading to the formation of CH_3COOH, will take place to a very large extent. Thus, CH_3COO^- ion is a strong base.

As a general rule, the stronger an acid, the weaker must be its conjugate base and vice versa. If an acid (*e.g.*, HCl) is strong, its conjugate base (Cl^-) is weak. If a base (*e.g.*, CH_3COO^-) is strong, its conjugate acid (CH_3COOH) is weak.

Water is a very weak base because its conjugate acid, hydronium ion (H_3O^+), is a very strong acid. At the same time, water is a very weak acid because its conjugate base, hydroxide ion (OH^-), is a very strong base.

It may be pointed out that while strong acids like HCl, HNO_3, H_2SO_4, etc., being *covalent* compounds, get dissociated only in a solvent like water which can take up protons, strong bases such as NaOH, KOH, $Ba(OH)_2$, etc., being *electrovalent* compounds exist as ions even in the solid state. The basic character of these compounds is exclusively due to the presence of hydroxyl ions which are always there (even without a solvent) and, therefore, no interaction with a solvent is necessary in such cases. They are frequently referred to as *hydroxide bases* to distinguish them from other bases such as C_3COO^-, CO_3^{2-}, S^{2-} and NH_3 which furnish hydroxyl ions only on interaction with a solvent such as water.

Influence of Solvent on Acid Strength. As mentioned before, the term *acid strength* is a relative one. It depends also on the substance which acts as a base. Consider the general equation

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1$$

The capacity of the acid to dissociate (*i.e.*, to donate protons) also depends upon the basic strength of acids (*i.e.*, the capacity to accept protons) of the solvent which acts as a base. For the order of the relative strengths of acids given in Table 1, the base (solvent) is water. If some other solvent is used, the order of relative strengths may be quite different. To illustrate this point, three solvents, namely, glacial acetic acid, water and liquid ammonia of increasing basic character may be considered.

Dissociation in acetic acid. Although acetic acid is normally an acid, it is also able, to some extent, to accept a proton and thus to act as a base as well. The dissociation of a strong acid HA in this medium may be represented as

$$\underset{\text{Acid}}{HA} + \underset{\substack{\text{Base}\\\text{(solvent)}}}{CH_3COOH} \rightleftharpoons \underset{\text{Acid}}{CH_3COOH_2^+} + \underset{\text{Base}}{A^-}$$

But, the equilibrium cannot lie very much to the right since acetic acid has only very small tendency to accept protons. Therefore, even strong acids are only feebly dissociated in acetic acid.

The degrees of dissociation of a number of acids when dissolved in glacial acetic acid have been determined from conductance measurements (Chapter 22). Taking them as a measure of their relative strengths, some of the common acids have been arranged in the following order of their strengths :

$$HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$$

This is the correct order of decreasing strengths of these acids.

Dissociation in water. Water is a much stronger base, *i.e.*, it has a much greater tendency to accept protons than acetic acid. Therefore, the ionic equilibrium of a strong acid in water, represented as

$$\underset{\text{Acid}}{HA} + \underset{\substack{\text{Base}\\\text{(solvent)}}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{A^-}$$

lies very much to the right. All the five acids mentioned in the above series, therefore, react almost completely with water to form, in every case, hydronium ion, H_3O^+. Therefore, all the strong acids in aqueous solutions appear almost equally strong. Obviously, their relative strengths in aqueous solutions cannot be compared. This phenomenon is called **the levelling effect.**

However, the ionic equilibria in water do not proceed so far in the case of weak acids like formic, acetic, propionic, lactic, tartaric and phosphoric acids. It is, therefore, possible to distinguish between the relative strengths of these acids in aqueous medium.

Dissociation in liquid ammonia. Liquid ammonia has such a strong basic character, *i.e.*, it has such a strong tendency to take up protons, that even a weak acid, like acetic acid, dissociates to a considerable extent and behaves as a strong acid. The ionic equilibrium, represented below, lies very much to the right :

$$\underset{\text{Acid}}{CH_3COOH} + \underset{\substack{\text{Base}\\\text{(solvent)}}}{NH_3} \rightleftharpoons \underset{\text{Acid}}{NH_4^+} + \underset{\text{Base}}{CH_3COO^-}$$

By conductance measurements it has been found that all acids, which in aqueous solution behave stronger than acetic acid, appear to be of about the same strength when dissolved in liquid ammonia. Thus, such strong acids as hydrochloric and nitric and such weak acids as acetic and propionic, appear to be of almost equal strength when dissolved in liquid ammonia.

Dissociation in hydrogen fluoride. Hydrogen fluoride offers an example on the other extreme. It has strong acidic properties and no basic, *i.e.*, proton-accepting properties at all. Consequently, even the strongest acid is incapable of dissociating as an acid when dissolved in hydrogen fluoride. As a matter of fact, many substances, which are normally acids but have some tendency to accept protons as well under certain conditions, dissociate as bases when dissolved in hydrogen fluoride. Thus, nitric acid dissociates slightly as a base in hydrogen fluoride solution :

$$\underset{\text{Base}}{HNO_3} + \underset{\substack{\text{Acid}\\\text{(solvent)}}}{HF} \rightleftharpoons \underset{\text{Acid}}{H_2NO_3^+} + \underset{\text{Base}}{F^-}$$

It is thus interesting to note that even a strong acid like HNO_3 behaves as a base (a very weak base though) when dissolved in HF.

Influence of Solvent on Base Strength. The nature of the solvent plays an equally important role in the dissociation and relative strengths of bases as well. If the solvent is a weak acid, such as water, it will be possible to compare the strengths of different bases as they will dissociate to different extents. But if the solvent is even a slightly stronger acid, *e.g.*, acetic acid, it will not be possible to distinguish between the strengths of different bases.

For example, aniline, a very weak base and sodium hydroxide, a very strong base, in water, appear to be equally strong when acetic acid is used as the solvent. Sometimes advantage is taken of this fact in volumetric estimations of those bases which are too weak in aqueous solution to be titrated against acids.

Lewis Concept

In 1923, G.N. Lewis put forth a more general concept of acids and bases. According to him, *an acid is a species that is capable of accepting a pair of electrons to form a covalent bond and a* base *is a species that is capable of donating a pair of electrons to form a covalent bond.*

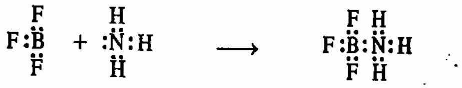
(i) $\underset{\text{(Acid)}}{BF_3} + \underset{\text{(Base)}}{NH_3} \longrightarrow F_3BNH_3$

(ii) $\underset{\text{(Acid)}}{BF_3} + \underset{\text{(Base)}}{F^-} \longrightarrow BF_4^-$

(iii) $\underset{\text{(Acid)}}{BCl_3} + \underset{\text{(Base)}}{(CH_3)_3N} \longrightarrow (CH_3)_3NBCl_3$

(iv) $\underset{\text{(Acid)}}{Cu^{2+}} + \underset{\text{(Base)}}{4CN^-} \longrightarrow [(Cu(CN)_4]^{2-}$

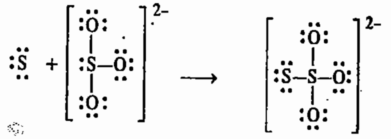
We see that the Lewis definition does not attribute acidity to any particular element but rather to unique electronic arrangement. Thus, rewriting reaction *(i)*, for instance, as



it is easy to say that NH_3 acts as a base by virtue of its tendency to donate the lone pair of electrons on the N atom to BF_3 which acts as an acid.

Example 2. How does the Lewis acid concept account for the formation of thiosulphate ion from sulphite ion and sulphur ?

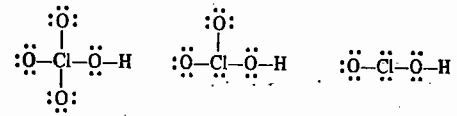
Solution : The sulphur atom, S, being electron-deficient, can be considered as a Lewis acid while the SO_3^{2-} ion having an octet structure can be regarded as the Lewis base. Their combination to form $S_2O_3^{2-}$ ion is represented below :



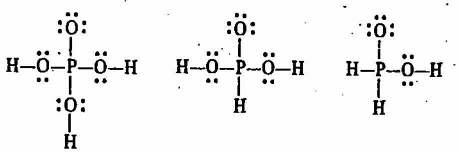
Example 3. Using the Lewis acid-base concept, determine the trend in the acid strengths in the series : *(a)* $HClO_4$, $HClO_3$, $HClO_2$ and *(b)* H_3PO_4, H_3PO_3, H_3PO_2.

Solution : In general, the greater the number of terminal oxygens in the Lewis structure of an oxyacid, the greater is its acidity. The Lewis structures of the given acids are :

(a)



(b)



Since oxygen atom is more electronegative than chlorine, each terminal oxygen atom tends to withdraw electrons from the chlorine atom and thereby also from the O—H bond, with the result that the proton acquires a greater tendency to get dissociated. Clearly, if there are more terminal oxygens in the oxyacid, the proton will get dissociated to a greater extent. This accounts for the decreasing acid strength in the series *(a)*, *i.e.*,

$$HClO_4 > HClO_3 > HClO_2$$

In the series *(b)*, on the other hand, an examination of the Lewis structures shows that the number of terminal oxygens is the same (*i.e.*, equal to one) in the three acids. Also, the hydrogens in the three acids are not all bonded to oxygens. The electronegativities of P and H, too, are almost the same. Thus, we do not expect very large differences in the strengths of the three acids.

DISSOCIATION OF WEAK ACIDS AND BASES

Dissociation of a Weak Acid. Consider the dissociation of a weak monobasic acid HA in water, represented by the equation

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

Applying the law of chemical equilibrium, the equilibrium constant K_c is given by the expression

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \qquad ...(5)$$

The square brackets, as usual, represent concentrations in moles per litre of the entities enclosed therein.

Since water is present in large excess in dilute solutions, its concentration may be taken as constant, say, k. Further, since the symbol H_3O^+ simply indicates that hydrogen ion is hydrated, it may be replaced by H^+, for simplicity. The above equation may then be put as

$$K_c = \frac{[H^+][A^-]}{[HA] \times k} \qquad ...(6)$$

assuming that the activity coefficients of the species involved are equal to unity each.

Since the product of the two constants K_c and k is equal to another constant, say, K_a, Eq. 6 may be written as

$$K_a = [H^+][A^-]/[HA] \qquad ...(7)$$

The significance of Eq. 7 is that the product of the concentrations of the hydrogen ion and the anion, irrespective of their source (*i.e.*, whether furnished by the acid itself or by any other substance present in the solution) divided by the concentration of the undissociated acid, is equal to a constant. This constant (K_a) is characteristic of the acid concerned and is known as the **dissociation constant of the acid.** This varies only with temperature, like other equilibrium constants.

If the dissociation of the acid is represented in accordance with Arrhenius concept, *i.e.*, as

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

the same expression as above for the dissociation constant of the acid will be obtained. Therefore, for simplicity, Arrhenius concept may be adopted.

Relative Strengths of Weak Acids. Eq. 7 for the dissociation constant of a weak acid can also be expressed in terms of the degree of dissociation (α) and the total molar concentration (c) of the acid. Consider, for example, the dissociation of acetic acid, represented below :

	CH_3COOH	$\rightleftharpoons$	H^+	+	CH_3COO^-
Original concs. :	c		0		0
Eqbm. concs. :	$c(1-\alpha)$		$c\alpha$		$c\alpha$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} \qquad ...(8)$$

Since for weak acids, α is very small, $1-\alpha$ in the denominator may be taken as 1. The above expression, therefore, reduces to

$$K_a = c\alpha^2 \quad \text{or} \quad \alpha = \sqrt{K_a/c} \qquad ...(9)$$

For two weak acids of dissociation constants K_{a_1} and K_{a_2}, at the same concentration c, it follows from Eq. 9 that

$$\alpha_1/\alpha_2 = \sqrt{K_{a_1}/K_{a_2}} \qquad ...(10)$$

where α_1 and α_2 are the respective degrees of dissociation of the two acids.

But, degree of dissociation of an acid is a measure of its capacity to furnish hydrogen ions and hence a measure of its strength.

$$\therefore \quad \frac{\text{Strength of one acid, } HA_1}{\text{Strength of another acid, } HA_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}} \qquad ...(11)$$

Example 4. The dissociation constants of formic and acetic acids are $1{\cdot}77\times10^{-4}$ and $1{\cdot}75\times10^{-5}$, respectively. Calculate the relative strengths of the two acids.

Solution : According to Eq. 11,

$$\frac{\text{Strength of formic acid}}{\text{Strength of acetic acid}} = \sqrt{\frac{K_a \text{ formic acid}}{K_a \text{ acetic acid}}} = \sqrt{\frac{1{\cdot}77\times10^{-4}}{1{\cdot}75\times10^{-5}}} = 3{\cdot}18$$

Thus, formic acid is **3·18** times stronger than acetic acid.

The dissociation constants of weak acids can be determined by using Eq. 9 since α, the degree of dissociation, can be obtained from conductance measurements, as shown in Chapter 22, by using the expression : $\alpha = \Lambda_m / \Lambda^\circ_m$.

Eq. 9 can also be used for calculating hydrogen ion concentrations of aqueous solutions of acids whose dissociation constants are known. Accordingly,

$$[H^+] = c\alpha = c\sqrt{K_a/c} = \sqrt{cK_a} \qquad ...(12)$$

Example 5. A solution of 0·100 M acetic acid is found to be dissociated to the extent of 1·33 per cent at the room temperature. Calculate the dissociation constant of the acid at this temperature.

Solution : Percentage dissociation of acetic acid = 1·33

$\therefore$ Degree of dissociation of acetic acid, $\alpha = 0{\cdot}0133$

Dissociation constant of acetic acid, $K_a = c\alpha^2/(1-\alpha)$

Since α is very small, hence $K_a = c\alpha^2 = 0{\cdot}1\times(0{\cdot}0133)^2 = \mathbf{1{\cdot}77\times10^{-5}}$

Example 6. A monobasic acid has a dissociation constant equal to $1{\cdot}8\times10^{-5}$ at 25°C. Calculate its degree of dissociation at a concentration of 0·20 M at the same temperature. What will be the concentration of hydrogen ions furnished by it ?

Solution : Assuming that degree of dissociation is very small,

$$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1{\cdot}8\times10^{-5}}{0{\cdot}2}} = 0{\cdot}009486$$

Thus, degree of dissociation of 0·20 M acid = **0·009486**

Further, $\quad [H^+] = \sqrt{cK_a} \qquad$ (Eq. 12)

$$= \sqrt{0{\cdot}2\text{M}\times1{\cdot}8\times10^{-5}} = \mathbf{0{\cdot}001897 \text{ mol dm}^{-3}}$$

Dissociation Constants of Polybasic Acids. Polybasic acids contain two or more hydrogens which can get dissociated. They always dissociate in stages. Consider, for example, the dissociation of carbonic acid :

$$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^- \qquad \textit{(First stage)}$$

$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-} \qquad \textit{(Second stage)}$$

The equilibrium constants K_{a_1} and K_{a_2}, corresponding to the first and second dissociations, are given by the expressions :

$$K_{a_1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \quad \text{and} \quad K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

K_{a_1} and K_{a_2}, at 25°C are known to be $4\cdot5\times10^{-7}$ and $4\cdot7\times10^{-11}$, respectively. The second dissociation constant is found to be 1/10000th of the first dissociation constant. K_{a_2} is always smaller than K_{a_1} which shows that second dissociation takes place to a much smaller extent than the first dissociation. Phosphoric acid is a tribasic acid. It dissociates in three stages, as shown below :

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^- \qquad \textit{(First stage)}$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-} \qquad \textit{(Second stage)}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-} \qquad \textit{(Third stage)}$$

The dissociation constants K_{a_1}, K_{a_2} and K_{a_3}, for the three successive stages are $7\cdot52\times10^{-3}$, $6\cdot23\times10^{-8}$ and $4\cdot80\times10^{-13}$, respectively.

The reason for the decrease in the dissociation constant of successive stages is that in the first dissociation, the positively charged proton comes from a neutral molecule while in the second stage of dissociation, the proton is detached from a negatively charged molecule and in the third dissociation, it is detached from a doubly negatively charged molecule.

The dissociation constants of some of the common acids at 25°C are given in Table 2.

TABLE 2

Dissociation Constants of Some Common Acids at 25°C

Acid	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Acetic acid	CH_3COOH	$1\cdot75\times10^{-5}$		
Arsenic acid	H_3AsO_4	$5\cdot00\times10^{-5}$	$8\cdot30\times10^{-8}$	6×10
Benzoic acid	C_6H_5COOH	$6\cdot29\times10^{-5}$		
Boric acid	H_3BO_3	$5\cdot80\times10^{-10}$		
Carbonic acid	H_2CO_3	$4\cdot52\times10^{-7}$	$4\cdot69\times10^{-10}$	
Chloracetic acid	$CH_2ClCOOH$	$1\cdot38\times10^{-3}$		
Dichloracetic acid	$CHCl_2COOH$	$5\cdot00\times10^{-2}$		
Formic acid	$HCOOH$	$1\cdot77\times10^{-4}$		
Hydrocyanic acid	HCN	$7\cdot20\times10^{-10}$		
Hydrogen sulphide	H_2S	$5\cdot70\times10^{-8}$	$1\cdot20\times10^{-15}$	
Iodic acid	HIO_3	$1\cdot67\times10^{-8}$		
Oxalic acid	$(COOH)_2$	$5\cdot02\times10^{-2}$	$5\cdot18\times10^{-5}$	
Phosphoric acid	H_3PO_4	$7\cdot52\times10^{-3}$	$6\cdot23\times10^{-8}$	$4\cdot8\times10^{-13}$
Phosphorous acid	H_3PO_3	$1\cdot60\times10^{-2}$	$7\cdot0\times10^{-7}$	
Propionic acid	C_2H_5COOH	$1\cdot34\times10^{-5}$		
Sulphuric acid	H_2SO_4	strong	$1\cdot01\times10^{-2}$	
Sulphurous acid	H_2SO_3	$1\cdot72\times10^{-2}$	$6\cdot24\times10^{-6}$	

Dissociation of a Weak Base. Representing the formula of a weak monoacid base as BOH, its dissociation, in accordance with Arrhenius concept, may by represented by the equation

$$BOH \rightleftharpoons B^+ + OH^-$$

Applying the equilibrium law equation, the **dissociation constant, K_b**, of the base, will be given by

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad \text{...(13)}$$

assuming that the activity coefficients of various species involved are equal to unity each.

If the initial concentration of the base is c moles per litre and if α is the degree of dissociation, then,

	BOH	⇌	B^+	+	OH^-
Original concs. :	c		0		0
Equilibrium concs. :	$c(1-\alpha)$		$c\alpha$		$c\alpha$

$$\therefore \qquad K_b = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)} \qquad \text{...(14)}$$

Since, for a weak base, α is very small as compared to 1, Eq. 14, as before, is reduced to

$$K_b = c\alpha^2 \qquad \text{or} \qquad \alpha = \sqrt{K_b/c}$$

$$\therefore \qquad [OH^-] = c\alpha = c\sqrt{K_b/c} = \sqrt{cK_b} \qquad \text{...(15)}$$

The dissociation constants of some common weak bases are given in Table 3.

TABLE 3

Dissociation Constants of Some Common Bases at 25°C

Base	Formula	K_b
Ammonia	NH_4OH	$1\cdot81\times10^{-5}$
Aniline	$C_6H_5NH_2$	$3\cdot83\times10^{-10}$
Dimethyl amine	$(CH_3)_2NH$	$5\cdot12\times10^{-4}$
Ethyl amine	$C_2H_5NH_2$	$5\cdot60\times10^{-4}$
Hydrazine	NH_2NH_2	$3\cdot00\times10^{-6}$
Methyl amine	CH_3NH_2	$4\cdot38\times10^{-4}$
Pyridine	C_5H_5N	$1\cdot30\times10^{-9}$
Quinoline	C_9N_7N	$6\cdot30\times10^{-10}$
Silver hydroxide	$AgOH$	$1\cdot10\times10^{-4}$
Trimethyl amine	$(CH_3)_3N$	$5\cdot21\times10^{-4}$
Urea	$CO(NH_2)_2$	$1\cdot50\times10^{-14}$

Dissociation of Water. Water is dissociated to a very small extent into hydrogen and hydroxyl ions, as represented by the equation

$$H_2O\,(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

More accurately,

$$2H_2O\,(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Applying the law of chemical equilibrium, its dissociation constant, K, is given by

$$K = \frac{[H^+][OH^-]}{[H_2O]} \qquad \text{...(16)}$$

Since dissociation takes place to a very small extent, the concentration of the undissociated water molecules, $[H_2O]$, may be regarded as constant, say k.

$$\therefore \qquad K \times k = [H^+][OH^-] \qquad \text{...(17)}$$

The product of the two constants K and k gives another constant which is designated by K_w.

Hence, Eq. 17 is written as

$$K_w = [H^+][OH^-] = 1\cdot0 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6} \text{ at } 25°\text{C} \qquad \text{...(18)}$$

where K_w, the dissociation constant, is called the **ionic product of water.**

Since in pure water, the concentration of hydrogen and hydroxyl ions must be equal to one another, hence

$$[H^+] = [OH^-] = \sqrt{K_w} = \sqrt{1\times10^{-14}\ \text{mol}^2\ \text{dm}^{-6}} = 1\times10^{-7}\ \text{mol dm}^{-3}$$

If a strong acid, like hydrochloric acid, is added to water, the concentration of H^+ ions will become very high and, therefore, the concentration of OH^- ions will correspondingly decrease so that the product of their concentrations remains constant. Similarly, if a strong base, like sodium hydroxide, is added to water, the concentration of OH^- ions will become very large and, therefore, that of H^+ ions will correspondingly become very small.

*p*H Scale

It should be clear from the above discussion that every aqueous solution, whether acidic, alkaline or neutral, contains both H^+ and OH^- ions. The product of their concentrations is always constant, equal to 1×10^{-14} at 25°C. Whether the solution is acidic or alkaline depends upon which of the two ions is present in greater concentration than the other. But, since knowing the concentration of one of these ions, that of the other can be calculated, it is convenient to express acidity or alkalinity of a solution by referring to the concentration of hydrogen ions only. Now, H^+ ion concentration can vary within wide limits, usually from about 1 mole per litre (as in 1 M HCl) to about 10^{-14} mole per litre (as in 1 M NaOH). The *p*H scale was introduced by the Danish biochemist S.P. Sörensen (1868-1939) in 1909. As defined by him, **the *p*H of a solution** is the negative logarithm (to the base 10) of the concentration (in moles per litre) of hydrogen ions which it contains.

Thus,
$$pH = -\log[H^+] = -\log[H_3O^+] \qquad \text{...(19)}$$

The *p*H of 1 M HCl solution in which $[H^+] = 1\text{ mol dm}^{-3}$, will be zero. In 1M NaOH solution, the $[OH^-] = 1\text{ mol dm}^{-3}$ and hence $[H^+]$ will be $10^{-14}\text{ mol dm}^{-3}$. The *p*H of 1 M NaOH solution will thus be 14. Obviously, the scale of *p*H would be from 0 to 14.

Example 7. Calculate the *p*H of *(a)* 0·0001 M HCl solution *(b)* 0·04 M HNO_3 solution, assuming complete dissociation in each case.

Solution : *(a)* Concentration of HCl = 0·0001 M

Since HCl is completely dissociated, hence

$$[H^+] = 0{\cdot}0001\text{ mol dm}^{-3}$$
$$\therefore \quad pH = -\log[H^+] = -\log[0{\cdot}0001] = 4$$

(b) Concentration of HNO_3 = 0·04 M

Since HNO_3 is completely dissociated, hence

$$[H^+] = 0{\cdot}04\text{ mol dm}^{-3}$$
$$\therefore \quad pH = -\log[H^+] = -\log[0{\cdot}04] = 1{\cdot}398$$

Example 8. Calculate the hydrogen ion concentration in moles per litre of a solution whose *p*H is 5·4.

Solution : *p*H of the solution = 5·4

$$pH = -\log[H^+]$$
$$\text{or} \quad \log[H^+] = -5{\cdot}4 = \bar{6}{\cdot}600$$
$$\therefore \quad [H^+] = 3{\cdot}98\times10^{-6}\text{ mol dm}^{-3}$$

Example 9. Calculate the *p*H of an aqueous solution obtained by mixing 50 ml of 0·2 M HCl with 50 ml 0·1 M NaOH.

Solution : Knowing that the product of volume in millilitres and molarity gives the number of millimoles of the acid or the base, we have

Number of millimoles of the acid in the solution = 50×0·2 = 10
Number of millimoles of the alkali in the solution = 50×0·1 = 5
Number of millimoles of the acid left in the solution after the addition of alkali = 10 − 5 = 5
Total volume of the solution = 50+50 = 100 ml

Thus, we have 5 millimoles of the acid in 100 ml of the solution or 0·05 mole of the acid per litre of the solution.

$$\therefore \quad \text{Concentration of } H^+ \text{ ions} = 0{\cdot}05\text{ mol dm}^{-3}$$
$$\therefore \quad pH \text{ of the solution} = -\log[H^+] = -\log(0{\cdot}05) = 1{\cdot}30$$

Example 10. Calculate the *p*H of an aqueous solution obtained by mixing 25 ml of 0·2 M HCl with 50 ml of 0·25 M NaOH. Take $K_w = 10^{-14}\text{ mol}^2\text{ dm}^{-6}$ at 25°C

Solution : Knowing that the product of volume in millilitres and molarity gives the number of millimoles of the acid or the base, we have

Number of millimoles of the acid in the solution = 25×0·2 = 5
Number of millimoles of the alkali in the solution = 50×0·25 = 12·5
Number of millimoles of the alkali left in the solution after the addition of the acid = 12·5 − 5 = 7·5
Total volume of the solution = 50+25 = 75 ml

$$\text{Concentration of } OH^- \text{ ions} = \frac{7{\cdot}5\times1000}{75\times1000} = 0{\cdot}10\text{ mol dm}^{-3}$$
$$[H^+][OH^-] = 10^{-14}\text{ mol}^2\text{ dm}^{-6}\text{ at }25°C$$
$$[OH^-] = 0{\cdot}10\text{ mol dm}^{-3}$$
$$[H^+] = 10^{-14}\text{ mol}^2\text{ dm}^{-6}/0{\cdot}10\text{ mol dm}^{-3} = 10^{-13}\text{ mol dm}^{-3}$$
$$pH = -\log[H^+] = -\log(10^{-13}) = 13$$

Example 11. Calculate the *p*H of 1×10^{-7} M aqueous solution of HCl at 25°C. Take $K_w = 10^{-14}\text{ mol}^2\text{ dm}^{-6}$.

Solution : The student may be tempted to write down the answer as

$$pH = -\log[H^+] = -\log(10^{-7}) = -(-7) = 7$$

But this value is not acceptable since this is also the *p*H of pure water ! The solution of HCl, howsoever small may be its concentration, must have a *p*H lower than 7. We must, therefore, approach the problem differently.

The dissociation of water may be represented as

$$\begin{array}{llccc} & H_2O & \rightleftharpoons H^+ & + & OH^- \\ \text{Concs. if no dissociation :} & c & 10^{-7} & & 0 \\ & & \text{(from HCl)} & & \\ \text{Concs. after dissociation :} & c-x & (10^{-7}+x) & & x \end{array}$$

where x is the molar amount of H_2O per litre of the solution which dissociates.

If we consider that there is no dissociation of water, then, $[H^+]$ contribution comes only from HCl. If we recognize that a small amount (x mole) of water *does dissociate*, then the $[H^+]$ contribution would be $(10^{-7}+x)\text{ mol dm}^{-3}$. Now, at 25°C,

$$K_w = [H^+][OH^-] = 10^{-14}\text{ mol}^2\text{ dm}^{-6} = (10^{-7}+x)\text{ mol dm}^{-3}\times x\text{ mol dm}^{-3}$$

which reduces to the quadratic equation

$$x^2 + 10^{-7}x - 10^{-14} = 0$$

The roots of this equation are given by

$$x = \frac{-10^{-7} \pm \sqrt{(10^{-7})^2 + 4\times10^{-14}}}{2}$$

Neglecting the negative root which has no physical meaning,

$$x = \frac{-10^{-7} + \sqrt{10^{-14} + 4\times10^{-14}}}{2} = \frac{-10^{-7} + 2{\cdot}24\times10^{-7}}{2} = 0{\cdot}62\times10^{-7}\text{ mol dm}^{-3}$$
$$\therefore \quad [H^+] = 10^{-7} + x = 10^{-7} + 0{\cdot}62\times10^{-7} = 1{\cdot}62\times10^{-7}\text{ mol dm}^{-3}$$
$$\therefore \quad pH = -\log[H^+] = -\log(1{\cdot}62\times10^{-7}) = 6{\cdot}79$$

We conclude that the dissociation of H_2O increases the $[H^+]$ above that due to the acid alone. *Regardless of how dilute the solution, the pH of an acid solution is always less than 7.*

Example 12. Calculate the *p*H of a 2×10^{-5} M aqueous solution of phenol at 25°C. $K_a = 1{\cdot}30\times10^{-10}$, $K_w = 1{\cdot}008\times10^{-14}$.

Solution : The dissociation of phenol may be represented as

$$\begin{array}{ccccc} C_6H_5OH & \rightleftharpoons & C_6H_5O^- & + & H^+ \\ 2\times10^{-5}-x & & x & & x \end{array}$$

$$K_a = \frac{x^2}{2 \times 10^{-5} - x}$$

Neglecting x in the denominator, we have

$$K_a = x^2/2\times10^{-5} \text{ so that } x = (2\times10^{-5}\times K_a)^{1/2}$$

$$x = [H^+] = (2\times10^{-5}\times K_a)^{1/2} = (2\times10^{-5}\times1\cdot30\times10^{-10})^{1/2}$$

$$= \mathbf{5\cdot1\times10^{-8}\ mol\ dm^{-3}}$$

The above answer is obviously incorrect because phenol, even though it is a very weak acid, must have $[H^+]$ greater than 10^{-7}. The error lies in the assumption that $[H^+] = [C_6H_5O^-] = x$. This would normally be true in the absence of any other source of hydrogen ions. To obtain the correct value for $[H^+]$, we make use of the concept of *electroneutrality of the solution, viz.*,

$$[H^+] = [C_6H_5O^-] + [OH^-]$$

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

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

$$\therefore \quad [C_6H_5O^-] = [H^+] - [OH^-] = \left\{[H^+] - \frac{K_w}{[H^+]}\right\}$$

Since phenol is present either as C_6H_5OH or partly as $C_6H_5O^-$. Hence

$$[C_6H_5OH] + [C_6H_5O^-] = 2\times10^{-5} \text{ mol dm}^{-3}$$

Assuming that $[C_6H_5O^-] << [C_6H_5OH]$,

$$[C_6H_5OH] = 2\times10^{-5} \text{ mol dm}^{-3}$$

$$K_a = \frac{[C_6H_5O^-][H^+]}{[C_6H_5OH]} = \frac{\left\{[H^+] - \frac{K_w}{[H^+]}\right\}[H^+]}{2\times10^{-5}} = 1\cdot3\times10^{-10}$$

$$\text{or} \quad [H^+]^2 - K_w = 2\times10^{-5}\times K_a = 2\times10^{-5}\times1\cdot3\times10^{-10} = 2\cdot60\times10^{-15}$$

$$\text{or} \quad [H^+]^2 - 1\cdot008\times10^{-14} = 2\cdot60\times10^{-15}$$

$$\therefore \quad [H^+]^2 = 1\cdot268\times10^{-14}$$

$$\text{or} \quad [H^+] = 1\cdot126\times10^{-7} \text{ mol dm}^{-3}$$

$$\therefore \quad pH = -\log [H^+] = -\log (1\cdot126\times10^{-7}) = \mathbf{6\cdot95}$$

The value for $[H^+]$, *viz.*, $1\cdot126\times10^{-7}$ mol dm^{-3} is acceptable since it is greater than 10^{-7}, as we would expect it to be.

This example shows that in calculating the *p*H of dilute solution of a very weak acid (or a very weak base), care must be exercised and one must check the validity of the assumption that the given acid or base is the only source of $[H^+]$ or $[OH^-]$.

Some Other Logarithmic Expressions. Just as *p*H is used to indicate hydrogen ion concentration, *p*OH is used to indicate hydroxyl ion concentration. Thus,

$$pOH = -\log [OH^-] \qquad \text{...(20)}$$

Ionic product of water, K_w, is also frequently expressed in a similar manner as

$$pK_w = -\log K_w \qquad \text{...(21)}$$

Remembering that $[H^+][OH^-] = K_w$ and taking logs and reversing signs, we have

$$-\log [H^+] - \log [OH^-] = -\log K_w \qquad \text{...(22)}$$

$$\text{or} \quad pH + pOH = pK_w \qquad \text{...(23)}$$

This relationship holds good for water as well as for any aqueous solution.

Since K_w at 25°C is about 10^{-14}, pK_w is 14·0. Hence,

$$pH + pOH = 14 \qquad \text{...(24)}$$

In other words, the sum of *p*H and *p*OH is equal to 14 in water or in any aqueous solution at 25°C.

We may also represent dissociation constants of acids and bases (K_a and K_b) in the form of the following expressions :

$$pK_a = -\log K_a \qquad \text{...(25)}$$

$$\text{and} \quad pK_b = -\log K_b \qquad \text{...(26)}$$

Example 13. Calculate the *p*H and *p*OH of 0·03 M aqueous solution of HCl at 25°C.

Solution : HCl, being a strong electrolyte, is completely dissociated in aqueous solution. Hence, the hydrogen ion concentration, $[H^+]$, is equal to the given concentration of HCl in solution :

$$[H^+] = 0\cdot03 \text{ M} = 3\times10^{-2} \text{ mol dm}^{-3}$$

$$pH = -\log [H^+] = -\log (3\times10^{-2}) = \mathbf{1\cdot52}$$

$$\text{Since} \quad pH + pOH = 14 \text{ at } 25°C,$$

$$\therefore \quad pOH = 14 - 1\cdot52 = \mathbf{12\cdot48}$$

Example 14. Calculate the *p*H and the hydrogen and hydroxyl ion concentrations of a $3\cdot2\times10^{-3}$ M solution of $Ba(OH)_2$ in water at 25°C.

Solution : $Ba(OH)_2$ is a strong base which dissociates to furnish two moles of OH^- ions for one mole of the base :

$$Ba(OH)_2 \longrightarrow Ba^{2+} + 2OH^-$$

$$\text{Hence,} \quad [OH^-] = 2\times3\cdot2\times10^{-3} \text{ M} = \mathbf{6\cdot4\times10^{-3}\ mol\ dm^{-3}}$$

$$pOH = -\log [OH^-] = -\log (6\cdot4\times10^{-3}) = -\log 6\cdot4 - \log 10^{-3}$$

$$= -0\cdot8062 - (-3) = -0\cdot8062 + 3 = \mathbf{2\cdot19}$$

$$\text{Since} \quad pH + pOH = 14 \text{ at } 25°C$$

$$\therefore \quad pH = 14 - 2\cdot19 = \mathbf{11\cdot81}$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1\cdot008 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{6\cdot4 \times 10^{-3} \text{ mol dm}^{-3}} = \mathbf{1\cdot57\times10^{-12}\ mol\ dm^{-3}}$$

Common Ion Effect. If a salt of a weak acid is added to a solution of the acid itself, the dissociation of the acid is diminished further. For example, the addition of sodium acetate to a solution of acetic acid suppresses the dissociation of acetic acid which is already very small. Consider the equilibrium,

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

The addition of one of the products of dissociation (*e.g.*, acetate ions) supplied by the largely dissociated salt (*e.g.*, sodium acetate) pushes the equilibrium to the left. In other words, the dissociation of acetic acid is suppressed. Similarly, the addition of hydrogen ions furnished by the addition of largely dissociated acid such as hydrochloric acid, also suppresses the dissociation of acetic acid.

Likewise the dissociation of a weak base, such as ammonium hydroxide, represented by the equilibrium

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

is suppressed on the addition of a salt like ammonium chloride which supplies ammonium ions. The addition of a strong base like sodium hydroxide which supplies hydroxyl ions, also suppresses the dissociation of ammonium hydroxide.

The suppression of the dissociation of a weak acid or a weak base on the addition of its own ions is called **common ion effect.**

Mixtures of Weak Acids and Salts. The hydrogen ion concentration of a mixture of a weak acid and its highly dissociated salt can be calculated from the simple equilibrium law considerations.

Suppose a monobasic weak acid, say, HA, is dissociated as

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

The dissociation constant K_a is given by the expression

$$K_a = [H^+][A^-]/[HA]$$

or $$[H^+] = K_a[HA]/[A^-] \qquad ...(27)$$

Although the above equation has been derived on the basis of the dissociation of the acid HA alone, it holds good whatever be the source from which H^+ or A^- ions are derived.

Suppose there is a mixture of a weak acid HA and its almost completely dissociated sodium salt NaA. Let c_1 and c_2 represent the molar concentrations of acid and salt, respectively. Since the dissociation of the acid, which is very small by itself, is further suppressed by the presence of A^- ion (common ion effect), while the salt is presumed to be almost entirely dissociated, it follows that the anionic concentration

$$[A^-] = c_2$$

and concentration of undissociated acid, being the same as that of the total acid, is given by

$$[HA] = c_1$$

Hence, Eq. 27 becomes $[H^+] = K_a c_1/c_2$

or, in general, $$[H^+] = K_a\ [Acid]/[Salt] \qquad ...(28)$$

Thus, the hydrogen ion concentration is determined by the dissociation constant of the acid, K_a and the ratio of the concentrations of acid and salt in the mixture. Since K_a is constant, it follows that the hydrogen ion concentration of a weak acid decreases as the ratio [acid]/[salt] in the mixture decreases. This is illustrated in the following table in the case of acetic acid–sodium acetate mixtures.

Ratio [Acid]/[Salt]	16	4	2	1	0·5	0·25	0·062
$[H^+]\times10^5$	28·80	7·21	3·60	1·81	0·91	0·45	0·11

Thus, the hydrogen ion concentration of acetic acid–sodium acetate mixture can be made to decrease from $28{\cdot}8\times10^{-5}$ mole per litre to $0{\cdot}11\times10^{-5}$ mole per litre, simply by adding increasing amounts of sodium acetate.

Example 15. What will be the hydrogen ion concentration of a solution obtained by mixing 500 ml of 0·20 M acetic acid and 500 ml of 0·30 M sodium acetate ? (Dissociation constant of acetic acid = $1{\cdot}75\times10^{-5}$).

Solution : Concentration of acetic acid in the mixture = $500\times0{\cdot}20/1000 = 0{\cdot}10$ mol dm^{-3}

Concentration of sodium acetate = $500\times0{\cdot}30/1000 = 0{\cdot}15$ mol dm^{-3}

$$[H^+] = K_a\ [Acid]/[Salt] \qquad (Eq.\ 28)$$

$$= 1{\cdot}75\times10^{-5}\ \text{mol dm}^{-3}\times0{\cdot}10\ \text{mol dm}^{-3}/0{\cdot}15\ \text{mol dm}^{-3} = \mathbf{1{\cdot}17\times10^{-5}\ mol\ dm^{-3}}$$

BUFFER SOLUTIONS

For many purposes in chemistry, industry and biology, it is necessary to have solutions whose *p*H does not change much even on the addition of appreciable amounts of strong acids or strong alkalies. Such solutions are called buffer solutions.

A **buffer solution** *is one which can resist change in its* pH *on the addition of an acid or a base.*

Consider a solution of sodium chloride in water. Its *p*H is 7. The addition of even 1 ml of 1 M HCl solution to one litre of sodium chloride solution lowers the *p*H of the solution from 7 to about 3. Similarly, the addition of 1 ml of 1 M NaOH solution to one litre of sodium chloride solution raises the *p*H of the solution from 7 to about 11. Sodium chloride solution, therefore, is *not* a buffer.

The *p*H of an aqueous solution of ammonium acetate is also 7. But the addition of the same amount of acid or alkali, as the one added in the case of sodium chloride solution, does not cause any appreciable alteration in the *p*H of ammonium acetate solution. Thus, ammonium acetate solution is a buffer as it can resist alterations in its *p*H on the addition of an acid or a base.

Let us see why a solution of ammonium acetate is a buffer while that of sodium chloride is not.

Ammonium acetate, like any other salt, exists almost entirely in the form of its ions, *viz.*, NH_4^+ and CH_3COO^- ions. If an acid is added to this solution, the H^+ ions furnished by the acid combine with acetate ions to form feebly dissociated molecules of acetic acid :

$$CH_3COO^- + H^+ \longrightarrow \underset{\text{Feebly dissociated}}{CH_3COOH}$$

Since most of the H^+ ions added are taken up by acetate ions to form acetic acid which itself is only slightly dissociated, the H^+ ion concentration (and hence the *p*H) of ammonium acetate solution changes only slightly.

Now, suppose a base is added to ammonium acetate solution. The OH^- ions furnished by the base will be taken up by NH_4^+ ions to form feebly dissociated NH_4OH :

$$NH_4^+ + OH^- \longrightarrow \underset{\text{Feebly dissociated}}{NH_4OH}$$

Since most of the OH^- ions added are taken up by NH_4^+ ions to form weakly dissociated NH_4OH, there is very little change in the *p*H of ammonium acetate solution.

Buffer solutions are considered to possess *reserve acidity* as well as *reserve alkalinity*. Thus, ammonium acetate has reserve acidity due to the presence of NH_4^+ ions and reserve alkalinity due to the presence of CH_3COO^- ions.

Now let us see why a solution of sodium chloride is not a buffer. In aqueous solution it is almost entirely dissociated into Na^+ and Cl^- ions. If H^+ ions are added to this solution, the hydrogen ion concentration increases, *i.e.*, the *p*H falls immediately. The reason is that HCl, likely to be formed, is itself almost completely dissociated. If OH^- ions are added to the solution, the hydrogen ion concentration falls, *i.e.*, the *p*H rises. The reason is that NaOH, likely to be formed, is itself almost completely dissociated.

The capacity of a solution to resist alteration in its *p*H, is known as its **buffer capacity**.

Buffer Capacity and Buffer Index. Van Slyke introduced a quantity called **buffer index,** β, as a quantitative measure of the buffer capacity. It is defined as

$$\beta = dB/d(pH)$$

where dB is the increment of a strong base added to a buffer solution and $d(pH)$ is the resulting increment in *p*H. The quantity dB is given in moles per 1000 gram of the solvent. β is always a positive quantity. Addition of a strong acid is equivalent to $-dB$, *i.e.*, a negative increment of base and to $-dp$H (since *p*H decreases on the addition of the acid). Hence, β remains positive.

Most of the important buffer solutions usually consist of mixtures of either weak acids and their salts or weak bases and their salts.

Buffer Mixture of a Weak Acid and its Salt. A very common buffer is prepared by mixing equimolar aqueous solutions of acetic acid and sodium acetate. Acetic acid is very slightly dissociated while sodium acetate, being a salt, is almost completely dissociated. The mixture thus contains CH_3COOH molecules as well as CH_3COO^- and Na^+ ions. Let us consider the buffer action of this mixture.

Suppose a strong acid is added to the above mixture. The H^+ ions added will be taken up immediately by CH_3COO^- ions to form very slightly dissociated CH_3COOH :

$$H^+ + CH_3COO^- \longrightarrow \underset{\text{Feebly dissociated}}{CH_3COOH}$$

Thus, the H^+ ions added are neutralised by the acetate ions present in the mixture. There is very little change in the *p*H of the mixture.

If, on the other hand, a strong base is added, the OH^- ions added are neutralised by the acetic acid present in the mixture :

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

Thus, again, there is very little change in the *p*H of the mixture.

It should be clear from the above mechanism of buffer action that reserve acidity of CH_3COOH-CH_3COONa buffer is due to the presence of CH_3COOH and reserve alkalinity is due to the presence of CH_3COO^- ions.

It may be of interest to note that while addition of 1 ml of 1 M HCl to 10 ml of a sodium chloride solution lowers the *p*H from 7·0 to about 1·0, the addition of the same amount of HCl to 10 ml of a buffer containing 1 mole of CH_3COOH and 1 mole of CH_3COONa will lower the *p*H from 4·75 to 4·66 only.

Buffer Mixture of a Weak Base and its Salt. A mixture containing equimolar aqueous solutions of ammonium hydroxide and its almost completely dissociated salt, ammonium chloride, constitutes another good buffer. The mixture contains undissociated NH_4OH as well as NH_4^+ and Cl^- ions. The buffer action of this mixture may now be considered.

If a strong acid is added, the H^+ ions added are neutralised by the base NH_4OH :

$$H^+ + NH_4OH \longrightarrow H_2O + NH_4^+$$

If a strong base is added, the OH^- ions added are neutralised by NH_4^+ ions forming very slightly dissociated NH_4OH.

In this case, evidently, reserve acidity is due to the presence of NH_4^+ ions and reserve alkalinity is due to the presence of NH_4OH.

Calculation of *p*H of Buffer Mixtures

A. Buffer Mixture of a Weak Acid and its Salt. Henderson-Hasselbalch Equation. Consider first a buffer solution containing a weak acid HA and its highly dissociated salt NaA. The hydrogen ion concentration of such a solution is given by the equation

$$[H^+] = K_a\,[\text{Acid}]/[\text{Salt}] \qquad \text{(Eq. 28)}$$

Taking logs and reversing the signs, we have

$$-\log [H^+] = -\log K_a + \log ([\text{Salt}]/[\text{Acid}])$$

or

$$pH = pK_a + \log ([\text{Salt}]/[\text{Acid}]) \qquad ...(29)$$

This equation, known as **Henderson-Hasselbalch equation**, enables the calculation of *p*H of a buffer solution made by mixing known quantities of a weak acid and its salt. Alternatively, it enables calculation of the ratio in which acid and salt must be mixed in order to get a buffer solution of a definite *p*H.

Example 16. What would be the *p*H of an aqueous solution obtained by mixing 5 gram of acetic acid and 7·5 gram of sodium acetate and making the volume equal to 500 ml ? Dissociation constant of acetic acid at 25°C is $1{\cdot}75\times10^{-5}$.

Solution : $\quad pH = pK_a + \log ([\text{Salt}]/[\text{Acid}]) \qquad$ (Eq. 29)

In this case, $\quad pK_a = -\log K_a = -\log (1{\cdot}75\times10^{-5}) = 4{\cdot}76$

$$[\text{Salt}] = \left(\frac{7{\cdot}5}{82}\times\frac{1000}{500}\right) = 0{\cdot}1829 \text{ mol dm}^{-3}$$

$$[\text{Acid}] = \left(\frac{5}{60}\times\frac{1000}{500}\right) = 1{\cdot}666 \text{ mol dm}^{-3}$$

$$pH = 4{\cdot}76 + \log\frac{0{\cdot}1829}{0{\cdot}1666} = 4{\cdot}80$$

Example 17. A buffer solution contains 0·2 mole of acetic acid and 0·25 mole of potassium acetate per litre. Calculate the change in *p*H of the solution if 0·5 ml of 1 M HCl is added to it. The dissociation constant of acetic acid at room temperature is $1{\cdot}75\times10^{-5}$. (The volume change on the addition of HCl may be neglected).

Solution : $\quad pH = pK_a + \log ([\text{Salt}]/[\text{Acid}]) \qquad$ (Eq. 29)

$$pK_a = -\log K_a = -\log 1{\cdot}75\times10^{-5} = 4{\cdot}76$$

*p*H of the solution before adding HCl will be given by

$$pH = pK_a + \log\frac{0{\cdot}25}{0{\cdot}20} = 4{\cdot}76 + 0{\cdot}0969 = 4{\cdot}8569$$

Amount of HCl added = 0·5 ml of 1M HCl = 0·5 millimole = 0·0005 mole

Assuming HCl to be completely dissociated, the amount of H^+ ions added will be = 0·0005 mole

The addition of H^+ ion will result in the reaction

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

i.e., the amount of acetic acid will increase and that of the salt will correspondingly decrease by 0·0005 mole.

∴ After adding HCl,

$$[CH_3COOH] = 0{\cdot}20 + 0{\cdot}0005 = 0{\cdot}2005 \text{ mol dm}^{-3}$$

and

$$[CH_3COOK] = 0{\cdot}25 - 0{\cdot}0005 = 0{\cdot}2495 \text{ mol dm}^{-3}$$

(The change of volume resulting from the addition of HCl is negligible)

$$pH = pK_a + \log ([\text{Salt}]/[\text{Acid}]) = 4{\cdot}76 + \log\frac{0{\cdot}2495}{0{\cdot}2005} = 4{\cdot}8549$$

∴ Change of *p*H = 4·8569 − 4·8549 = **0·002**

We see that there is only a slight change in the *p*H.

Example 18. Calculate the *p*H before and after the addition of 0·01 mole of NaOH to 1 litre of a buffer solution that is 0·1 M in acetic acid and 0·1 M in sodium acetate. The dissociation constant of acetic acid is $1{\cdot}75\times10^{-5}$.

Solution : Prior to the addition of NaOH,

$$[CH_3COOH] = 0{\cdot}1 \text{ M} ; \qquad [CH_3COO^-] = 0{\cdot}1 \text{ M}$$

Using Eq. 29, $\quad pH = pK_a + \log\dfrac{[CH_3COO^-]}{[CH_3COOH]}$

$$pK_a = -\log K_a = -\log (1{\cdot}75\times10^{-5}) = 4{\cdot}76$$

$$\therefore \quad pH = 4{\cdot}76 + \log\frac{0{\cdot}1}{0{\cdot}1} = 4{\cdot}76 + \log 1 = 4{\cdot}76 + 0 = 4{\cdot}76$$

After the addition of 0·01 mole of NaOH, some of the acetic acid is neutralized so that the concentration of the weak acid is diminished while that of the salt (the acetate ion) is increased. Thus, we have

$$[CH_3COOH] = 0{\cdot}1 - 0{\cdot}01 = 0{\cdot}09 \text{ mol dm}^{-3}$$

$$[CH_3COO^-] = 0{\cdot}1 + 0{\cdot}01 = 0{\cdot}11 \text{ mol dm}^{-3}$$

Hence, the *p*H of the buffer is given by

$$pH = 4{\cdot}76 + \log\frac{0{\cdot}11}{0{\cdot}09} = 4{\cdot}76 + 0{\cdot}087 = 4{\cdot}847$$

We see that the *p*H of the buffer solution increases *very slightly*.

B. Buffer Mixture of a Weak Base and its Salt. If a buffer solution consists of a mixture of a weak base and its salt, it can be easily shown that

$$[OH^-] = K_b\,[Base]/[Salt]$$

$$\therefore \quad pOH = pK_b + \log\,([Salt]/[Base]) \qquad ...(30)$$

Knowing pOH, the pH can be easily calculated from the well known relationship : $pH + pOH = pK_w = 14$.

Example 19. A buffer solution contains 0·20 mole of NH_4OH and 0·25 mole of NH_4Cl per litre. Calculate the pH of the solution. Dissociation constant of NH_4OH at the room temperature is $1{\cdot}81\times10^{-5}$.

Solution :

$$pOH = pK_b + \log\,([Salt]/[Base]) \qquad \text{(Eq. 30)}$$

$$pK_b = -\log K_b = -\log(1{\cdot}81\times10^{-5}) = 4{\cdot}7423$$

$$pOH = 4{\cdot}7423 + \log\frac{0{\cdot}25}{0{\cdot}20} = 4{\cdot}839$$

$$pH = 14 - 4{\cdot}839 = \mathbf{9{\cdot}161}$$

HYDROLYSIS OF SALTS

Water is dissociated to a very small extent into H^+ and OH^- ions :

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

In pure water, the concentrations of H^+ ions and OH^- ions are equal to each other, *i.e.*,

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

Pure water, therefore, is neutral.

Salts are strong electrolytes. When dissolved in water, they dissociate almost completely into positively charged ions (cations) and negatively charged ions (anions). In some of the salts, the anions of the salt react with H^+ ions furnished by water thereby lowering the concentration of H^+ ions in solution. Since the product of $[H^+]$ and OH^- ions is constant $\{[H^+][OH^-]=K_w\}$, therefore, the concentration of OH^- ions in the solution increases. The solution, therefore, becomes alkaline.

In the case of some other salts, the cations of the salt react with OH^- ions furnished by water thereby lowering the concentration of OH^- ions in solution. Since K_w is constant, the concentration of H^+ ions in the solution increases. The solution, therefore, becomes **acidic.**

The phenomenon of the interaction of anions and cations of the salt with the H^+ and OH^- ions furnished by water yielding acidic or alkaline (or sometimes even neutral) solutions is known as **salt hydrolysis.**

Hydrolysis may also be considered as the reverse of neutralisation. Neutralisation, as we know, involves combination of H^+ and OH^- ions yielding undissociated water, *i.e.*, it involves almost complete disappearance of H^+ and OH^- ions. Hydrolysis, on the other hand, leads to the formation of H^+ or OH^- ions, as discussed above.

For a study of hydrolysis, it is convenient to divide the salts into four categories :

1. Salts of strong acids and strong bases such as potassium chloride and sodium nitrate.
2. Salts of weak acids and strong bases, such as potassium cyanide and sodium acetate.
3. Salts of strong acids and weak bases, such as ammonium chloride and aniline hydrochloride.
4. Salts of weak acids and weak bases, such as ammonium acetate.

1. Salts of Strong Acids and Strong Bases. Salts of strong acids and strong bases *do not hydrolyse.* Consider, for example, potassium chloride. When it is dissolved in water, its ions, K^+ and Cl^-, have no tendency to react with the H^+ and OH^- ions of water. This is because the possible products of such interactions, namely, KOH and HCl, are themselves almost completely dissociated. Consequently, there is no change in the concentration of H^+ or OH^- ions and the solution continues to remain neutral. Thus, salts of strong acids and strong bases do not undergo hydrolysis.

2. Salts of Weak Acids and Strong Bases. Salts of this category undergo hydrolysis to give alkaline solutions. Consider sodium acetate as an example of this category. When dissolved in water it undergoes almost complete dissociation into Na^+ and CH_3COO^- ions.

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

The acetate ions will take up some of the H^+ ions furnished by the slightly dissociated water to form the feebly dissociated acetic acid :

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

The undissociated water further dissociates so as to maintain the constant value of $K_w = [H^+][OH^-]$. The H^+ ions are again taken up by CH_3COO^- ions. This leads to an increase in the concentration of hydroxyl ions and decrease in the concentration of hydrogen ions. The solution, therefore, becomes alkaline.

Thus, the aqueous solution of the salt of a weak acid and a strong base is alkaline because of hydrolysis.

Hydrolysis Constant. The hydrolytic reaction of sodium acetate may be written as

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

Since, Na^+ ion is common on both sides of the equation, it may be left out and the equation may be represented as

$$\underset{\text{Unhydrolysed salt}}{CH_3COO^-} + H_2O \rightleftharpoons \underset{\text{Free base}}{OH^-} + \underset{\text{Free acid}}{CH_3COOH}$$

Applying the law of chemical equilibrium and taking the concentration of water as constant (since it is present in large excess), we have

$$K_h = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]} \qquad ...(31)$$

K_h is known as **hydrolysis constant.**

Relation between K_h, K_a and K_w. It should be noted that ultimately when the equilibrium of hydrolytic reaction of CH_3COONa is established, the following two equilibra have also to be satisfied :

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

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

Therefore, the following equations should also hold good :

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \qquad ...(32)$$

where K_a is the dissociation constant of the acid and

$$K_w = [H^+][OH^-] \qquad ...(33)$$

Dividing Eq. 33 by Eq. 32, we get

$$\frac{K_w}{K_a} = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]} = K_h \qquad \text{(from Eq. 31)}$$

$$\text{Thus,} \quad K_h = K_w/K_a \qquad ...(34)$$

Evidently, the hydrolysis constant K_h of the salt varies inversely as the dissociation constant K_a of the weak acid. Therefore, the weaker the acid, the greater is the hydrolysis constant of the salt.

Degree of Hydrolysis. Let c moles per litre be the initial concentration of sodium acetate in aqueous solution and let x be the **degree of hydrolysis** which is defined as the fraction of the total salt that has undergone hydrolysis on the attainment of equilibrium. Rewriting the hydrolysis equation as before and putting the equilibrium concentrations of the various species, we have

$$\underset{c(1-x)}{CH_3COO^-} + H_2O \rightleftharpoons \underset{cx}{CH_3COOH} + \underset{cx}{OH^-}$$

$$K_h = \frac{cx \times cx}{c(1-x)} = \frac{cx^2}{1-x}$$

If x is small as compared to unity, $(1 - x)$ in the above equation may be replaced by 1 so that

$$K_h = cx^2 \quad \text{or} \quad x = \sqrt{K_h/c} \qquad \text{...(35)}$$

But, $K_h = K_w/K_a$ (Eq. 34)

$$\therefore \quad x = \sqrt{K_w/(K_a \times c)} \qquad \text{...(36)}$$

By means of Eq. 36 it is possible to calculate the degree of hydrolysis of a salt of a weak acid and a strong base at any concentration c of the salt provided the dissociation constant K_a of the acid is known.

It also follows from Eq. 36 that the weaker the acid (*i.e.*, the smaller the value of K_a), the greater is x, the degree of hydrolysis. Also, since K_w increases rapidly with temperature and K_a changes only slightly, it is evident that the degree of hydrolysis increases considerably with rise of temperature. Lastly, it is seen that the degree of hydrolysis increases when concentration (c) decreases, *i.e.*, when dilution increases.

Example 20. Calculate the degree of hydrolysis of 0·10 M solution of sodium acetate at 25°C. $K_a = 1{\cdot}75 \times 10^{-5}$ and $K_w = 1{\cdot}008 \times 10^{-14}$.

Solution :

$$K_h = K_w/K_a = \frac{1{\cdot}008 \times 10^{-14}}{1{\cdot}75 \times 10^{-5}} = 5{\cdot}76 \times 10^{-10}$$

Assuming that the degree of hydrolysis (x) is small,

$$x = \sqrt{K_h/c} = \sqrt{\frac{5{\cdot}75 \times 10^{-10}}{0{\cdot}10}} = 7{\cdot}589 \times 10^{-5}.$$

Thus, the degree of hydrolysis $= 7{\cdot}589 \times 10^{-5}$

***p*H of the Hydrolysed Salt Solution.** As shown above, in the hydrolysis of CH_3COONa, $[OH^-] = cx$. Substituting the value of x from Eq. 36, we have

$$[OH^-] = c\left(\frac{K_w}{K_a c}\right)^{\frac{1}{2}} = \left(\frac{K_w c}{K_a}\right)^{\frac{1}{2}}$$

Taking negative logs of both sides, we get

$$pOH = \tfrac{1}{2}\, pK_w - \tfrac{1}{2}\log c - \tfrac{1}{2}\, pK_a$$

But $\quad pH + pOH = 14$

$$\therefore \quad pH = 14 - \tfrac{1}{2}\, pK_w + \tfrac{1}{2}\log c + \tfrac{1}{2}\, pK_a \qquad \text{...(37)}$$

Example 21. Calculate the *p*H of 0·01 M aqueous solution of CH_3COONa at 25°C (K_a for $CH_3COOH = 1{\cdot}75 \times 10^{-5}$). $K_w = 1{\cdot}008 \times 10^{-14}$.

Solution :

$$pK_w = -\log K_w = -\log(1{\cdot}008 \times 10^{-14}) = 13{\cdot}997 = 14$$
$$pK_a = -\log K_a = -\log(1{\cdot}75 \times 10^{-5}) = 4{\cdot}76$$
$$\log c = \log(10^{-2}) = -2$$

Substituting in Eq. 37, we have

$$pH = 14 - \tfrac{1}{2}(14{\cdot}0) + \tfrac{1}{2}(-2) + \tfrac{1}{2}(4{\cdot}76) = 8{\cdot}38$$

The *p*H shows that the solution is **alkaline**, as expected.

3. Salts of Weak Bases and Strong Acids. Consider ammonium chloride as an example of this category of salts. In water, it undergoes almost complete dissociation into NH_4^+ and Cl^- ions. The ammonium ions take up OH^- ions furnished by water to form the feebly dissociated base, ammonium hydroxide (NH_4OH). The undissociated water further dissociates so as to maintain the constant value of K_w. This causes an increase in the concentration of hydrogen ions and a decrease in the concentration of hydroxyl ions. The solution, therefore, becomes *acidic*.

Thus, an aqueous solution of a salt of a weak base and a strong acid is **acidic** because of hydrolysis.

Hydrolysis Constant. The hydrolytic reaction of ammonium chloride may be represented as

$$NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + Cl^- + H^+$$

Since Cl^- ion is common on both sides of the equation, it may be left out and the equation may be represented as

$$\underset{\text{Unhydrolysed salt}}{NH_4^+} + H_2O \rightleftharpoons \underset{\text{Free base}}{NH_4OH} + \underset{\text{Free acid}}{H^+}$$

Applying the law of chemical equilibrium, we have

$$K_h = [H^+]\,[NH_4OH]/[NH_4^+] \qquad \text{...(38)}$$

K_h, as already mentioned, is known as hydrolysis constant.

Relation between K_h, K_b and K_w. The following other equilibria also exist in the solution :

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

and

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

Accordingly, the following equations should also hold good :

$$K_b = [NH_4^+][OH^-]/[NH_4OH] \qquad \text{...(39)}$$

where K_b is the dissociation constant of the base and

$$K_w = [H^+][OH^-] \qquad \text{...(40)}$$

Dividing Eq. 40 by Eq. 39, we get

$$K_w/K_b = [H^+][NH_4OH]/[NH_4^+] = K_h \qquad \text{(from Eq. 38)}$$

Thus, $\quad K_h = K_w/K_b \qquad$ ...(41)

It is evident that the weaker the base, the greater is the hydrolysis constant of the salt.

Degree of Hydrolysis. If c is the initial concentration of the salt in moles per litre and x is the degree of hydrolysis on the attainment of equilibrium, then the concentrations of the various species at equilibrium will be as represented below :

$$\underset{c(1-x)}{NH_4^+} + H_2O \rightleftharpoons \underset{cx}{NH_4OH} + \underset{cx}{H^+}$$

$$K_h = \frac{cx \times cx}{c(1-x)}$$

If, as before, x is too small as compared to unity

$$K_h = cx^2 \qquad \ldots(42)$$

or

$$x = \sqrt{K_h/c} = \sqrt{K_w/(K_b \times c)} \quad \text{(from Eq. 41)} \qquad \ldots(43)$$

As in the previous case, the degree of hydrolysis of a salt, at a given temperature, is more if the base is weaker, *i.e.*, if K_b is smaller. Also, x increases when concentration decreases, *i.e.*, when dilution increases. Further, since K_w increases much more with temperature than K_b, the degree of hydrolysis at a given concentration increases with rise in temperature.

Example 22. The dissociation constant of NH_4OH at 25°C is $1{\cdot}81\times10^{-5}$. Calculate the degree of hydrolysis of a 0·01 M solution of ammonium chloride. K_w at 25°C=$1{\cdot}008\times10^{-14}$.

Solution :

$$K_h = \frac{K_w}{K_b} = \frac{1{\cdot}008 \times 10^{-14}}{1{\cdot}81 \times 10^{-5}} = 5{\cdot}569 \times 10^{-10}$$

Assuming that the degree of hydrolysis x is very small,

$$x = \sqrt{K_h/c} \qquad \text{(Eq. 43)}$$

$$= \sqrt{\frac{5{\cdot}569 \times 10^{-10}}{0{\cdot}01}} = 2{\cdot}359\times10^{-6}$$

***p*H of the Hydrolysed Salt Solution.** As shown above, in the hydrolysis of NH_4Cl,

$$[H^+] = cx$$

Substituting the value of x from Eq. 43, we have

$$[H^+] = c\left(\frac{K_w}{K_b c}\right)^{1/2} = \left(\frac{K_w c}{K_b}\right)^{1/2} \qquad \ldots(44)$$

Taking negative logs of both sides,

$$pH = \tfrac{1}{2}\,pK_w - \tfrac{1}{2}\log c - \tfrac{1}{2}\,pK_b \qquad \ldots(45)$$

Example 23. What would be the *p*H of 0·01 M solution of NH_4Cl in water at 25°C ? (K_b for $NH_4OH=1{\cdot}81\times10^{-5}$).

Solution :

$$pK_w = -\log K_w = -\log 1{\cdot}008\times10^{-14} = 13{\cdot}997 = 14$$

$$pK_b = -\log K_b = -\log(1{\cdot}81\times10^{-5}) = 4{\cdot}74$$

$$\log c = \log(10^{-2}) = -2$$

Using Eq. 45,

$$pH = \tfrac{1}{2}(14{\cdot}0) - \tfrac{1}{2}(-2) - \tfrac{1}{2}(4{\cdot}74) = 5{\cdot}63$$

The *p*H shows that the solution is acidic, as expected.

4. Salts of Weak Acids and Weak Bases. Salts of this category may be exemplified by ammonium acetate. The NH_4^+ and CH_3COO^- ions furnished by the salt combine with OH^- and H^+ ions of water, respectively, to form feebly dissociated NH_4OH and CH_3COOH. The reaction may be represented as

$$\underset{\substack{\text{Unhydrolysed}\\ \text{salt}}}{CH_3COO^-} + \underset{\substack{\text{Unhydrolysed}\\ \text{salt}}}{NH_4^+} + H_2O \rightleftharpoons \underset{\text{Free acid}}{CH_3COOH} + \underset{\text{Free base}}{NH_4OH}$$

In this case, both H^+ and OH^- ions are removed simultaneously and if they are removed in equivalent amounts, as in the present case, the solution remains neutral although hydrolysis of the salt has taken place.

The equilibrium law equation for hydrolysis constant in the present case may be written as

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \qquad \ldots(46)$$

The following other equilibria also exist in the solution :

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

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

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

Accordingly, the following equations should hold good :

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \qquad \ldots(47)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \qquad \ldots(48)$$

$$K_w = [H^+][OH^-] \qquad \ldots(49)$$

Dividing Eq. 49 by Eq. 48 as well as by Eq. 47, we have

$$\frac{K_w}{K_a \times K_b} = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} = K_h \qquad \text{(from Eq. 46)}$$

Thus, in this case,

$$K_h = \frac{K_w}{K_a \times K_b} \qquad \ldots(50)$$

If the initial concentration of the salt is c moles per litre and x is its degree of hydrolysis, then, at the equilibrium point, the concentrations of the various species will be as shown below :

$$\underset{c(1-x)}{CH_3COO^-} + \underset{c(1-x)}{NH_4^+} + H_2O \rightleftharpoons \underset{cx}{CH_3COOH} + \underset{cx}{NH_4OH}$$

$$\therefore \quad K_h = \frac{c^2x^2}{c^2(1-x)^2} = \frac{x^2}{(1-x)^2} \qquad \ldots(51)$$

Neglecting x as compared to unity, we have

$$K_h = x^2 \qquad \ldots(52)$$

or

$$x = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a \times K_b}} \quad \text{(from Eq. 50)} \qquad \ldots(53)$$

It is evident from Eq. 53 that the weaker the acid and the base, the greater is the degree of hydrolysis of the salt. It should be noted that in this case *the degree of hydrolysis is independent of the concentration of the solution.* Further, as before, since K_w increases with temperature much more rapidly than either K_a or K_b, the degree of hydrolysis increases with rise of temperature.

Example 24. Calculate the degree of hydrolysis of decimolar solution of ammonium acetate at 25°C. Dissociation constants of acetic acid and ammonium hydroxide are $1{\cdot}75\times10^{-5}$ and $1{\cdot}81\times10^{-5}$, respectively, at 25°C. K_w at 25°C = $1{\cdot}008\times10^{-14}$.

Solution :

$$K_h = \frac{K_w}{K_a \times K_b} \qquad \text{(Eq. 50)}$$

$$= \frac{1{\cdot}008\times10^{-14}}{1{\cdot}75\times10^{-5}\times1{\cdot}81\times10^{-5}} = 3{\cdot}182\times10^{-5}$$

In the present case,

$$K_h = \frac{x^2}{(1-x)^2} \qquad \text{(Eq. 51)}$$

or

$$3{\cdot}182\times10^{-5} = \frac{x^2}{(1-x)^2}$$

$$\frac{x}{1-x} = \sqrt{3\cdot182 \times 10^{-5}}$$

If x is very small, it may be neglected as compared to unity.

$\therefore$ Degree of hydrolysis, $x = \sqrt{3\cdot182 \times 10^{-5}} = 5\cdot64\times10^{-3}$

***pH* of the Hydrolysed Salt Solution.** For the dissociation of a weak acid HA,

$$K_a = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \qquad \ldots(54)$$

If the initial concentration of the acid is c and x is the degree of dissociation, then

$$[\mathrm{H^+}] = K_a\frac{[\mathrm{HA}]}{[\mathrm{A^-}]} = K_a\frac{cx}{c(1-x)} = K_a\frac{x}{1-x} \qquad \ldots(55)$$

From Eq. 51, $x/(1-x) = \sqrt{K_h}$

$$\therefore \quad [\mathrm{H^+}] = K_a\sqrt{K_h} = K_a\left(\frac{K_w}{K_aK_b}\right)^{1/2} \qquad \text{(from Eq. 50)}$$

$$= \left(\frac{K_wK_a}{K_b}\right)^{1/2} \qquad \ldots(56)$$

Taking negative logs of both sides,

$$pH = \tfrac{1}{2}\,pK_w + \tfrac{1}{2}\,pK_a - \tfrac{1}{2}\,pK_b \qquad \ldots(57)$$

From Eq. 57 we see that if K_a and K_b are equal, then $pH = \frac{1}{2}pK_w = 7$, that is, the solution is neutral in spite of the fact that the extent of hydrolysis may be considerable.

Determination of Degree of Hydrolysis. A number of methods for determining degree of hydrolysis are available. Some of these have been discussed below.

1. Indirect Method. The simplest though indirect method makes use of the relationships that exist between degree of hydrolysis of a salt, the ionic product of water and the dissociation constant of the weak acid or weak base from which the salt is obtained. The various equations have been reproduced below :

$$x = \sqrt{\frac{K_w}{K_a \times c}} \quad \text{(for a salt of a weak acid and a strong base)} \qquad \text{(Eq. 36)}$$

$$x = \sqrt{\frac{K_w}{K_b \times c}} \quad \text{(for a salt of a weak base and a strong acid)} \qquad \text{(Eq. 43)}$$

$$x = \sqrt{\frac{K_w}{K_a \times K_b}} \quad \text{(for a salt of a weak acid and a weak base)} \qquad \text{(Eq. 53)}$$

Knowing dissociation constant of acid or base (K_a or K_b) or both, as the case may be, it is a simple matter to calculate the degree of hydrolysis of a given salt at a given concentration. The concentration, however, has no effect if the salt is of a weak acid and a weak base.

Example 25. Calculate the percentage hydrolysis of sodium acetate in 0·1 M solution at 25°C assuming that the salt is completely dissociated. K_a of acetic acid at 25°C = $1\cdot75\times10^{-5}$. Ionic product of water at 25°C = $1\cdot008\times10^{-14}$.

Solution : The degree of hydrolysis x of a salt of a weak acid and a strong base is given by

$$x = \sqrt{\frac{K_w}{K_a \times c}} \qquad \text{(Eq. 36)}$$

$$= \sqrt{\frac{1\cdot008 \times 10^{-14}}{1\cdot75 \times 10^{-5} \times 0\cdot1}} = 7\cdot589 \times 10^{-5}$$

$\therefore$ Percentage hydrolysis = $7\cdot589\times10^{-3}$

Example 26. The dissociation constant of aniline as a base at 25°C is $5\cdot93\times10^{-10}$. The ionic product of water at 25°C is $1\cdot008\times10^{-14}$. Calculate the percentage hydrolysis of aniline hydrochloride in 0·1 M solution at 25°C.

Solution : The degree of hydrolysis x of the salt of a strong acid and a weak base is given by

$$x = \sqrt{\frac{K_w}{K_b \times c}} \qquad \text{(Eq. 43)}$$

$$x = \sqrt{\frac{1\cdot008 \times 10^{-14}}{5\cdot93 \times 10^{-10} \times 0\cdot1}} = 1\cdot30 \times 10^{-2}$$

$\therefore$ Percentage hydrolysis = $1\cdot30$

Example 27. The dissociation constants of aniline, acetic acid and water at 25°C are, respectively, $3\cdot83\times10^{-10}$, $1\cdot75\times10^{-5}$ and $1\cdot008\times10^{-14}$. Calculate the percentage hydrolysis of aniline acetate in a decimolar solution.

Solution : The degree of hydrolysis x of a salt of a weak acid and a weak base is given by

$$x = \sqrt{\frac{K_w}{K_a \times K_b}} \qquad \text{(Eq. 53)}$$

$$= \sqrt{\frac{1\cdot008 \times 10^{-14}}{1\cdot75 \times 10^{-5} \times 3\cdot83 \times 10^{-10}}} = 1\cdot219$$

But, x cannot be greater than 1. This indicates that the degree of hydrolysis in this case is very large and, therefore, the above formula, which is based on the assumption that x is small, is not applicable

In the present case, therefore, we have to calculate x as follows :

$$K_h = \frac{K_w}{K_a \times K_b} \qquad \text{(Eq. 50)}$$

But
$$K_h = \frac{x^2}{(1-x)^2} \qquad \text{(Eq. 51)}$$

i.e.,
$$\frac{x}{1-x} = \sqrt{\frac{K_w}{K_a \times K_b}} = 1\cdot219 \quad \text{or} \quad x = 0\cdot5495$$

$\therefore$ Percentage hydrolysis = $54\cdot95$

2. Electrical Conductance Method. The electrical conductance of an aqueous solution of a salt of a weak acid or a weak base is due partly to the ions of the unhydrolysed salt and partly to the ions (particularly $\mathrm{H^+}$ or $\mathrm{OH^-}$ ions) formed by hydrolysis. Consider, for example, a salt of a weak base and a strong acid, say, ammonium chloride. If x is the degree of hydrolysis, then, for every one mole of the salt, the number of moles of the various species at equilibrium will be as shown in the equation below :

$$\underset{1-x}{\mathrm{NH_4Cl}} + \mathrm{H_2O} \rightleftharpoons \underset{x}{\mathrm{NH_4OH}} + \underset{x}{\mathrm{HCl}}$$

Ammonium hydroxide, being a weak base, may be taken as undissociated and to contribute little or nothing towards the total conductance of the solution. The molar conductance of this solution Λ_m, as determined experimentally, will be the sum of the conductance of $1-x$ moles of ammonium chloride and x moles of hydrochloric acid.

$$\Lambda_m = (1-x)\Lambda'_m + x\,\overset{\circ}{\Lambda}_{m(\mathrm{HCl})} \qquad \ldots(58)$$

where $\overset{\circ}{\Lambda}_{m(\mathrm{HCl})}$ is the molar conductance of hydrochloric acid at infinite dilution and Λ'_m is the molar conductance of the unhydrolysed salt at the given concentration. The value of Λ'_m is obtained by adding *excess* of the nonconducting or very slightly conducting ammonium hydroxide (base) to the salt solution. This suppresses the hydrolysis of ammonium chloride to such a large extent that the molar conductance of the solution can be taken as Λ_m, *i.e.*, the conductance of the unhydrolysed salt.

From Eq. 58 it follows that

$$x = \frac{\Lambda_m - \Lambda'_m}{\overset{\circ}{\Lambda}_{m(HCl)} - \Lambda'_m} \qquad \text{...(59)}$$

Thus, all that is to be done is to measure the conductance of the salt solution before (Λ_m) and after the addition of excess of ammonia (Λ'_m). Then knowing the value of $\overset{\circ}{\Lambda}_{m(HCl)}$ $(= \overset{\circ}{\lambda}_{H^+} + \overset{\circ}{\lambda}_{Cl^-})$, x can be evaluated.

This is known as **Bredig's method.**

3. From Freezing Point Depression. Freezing point depression, as is well known, is a colligative property depending only upon the *number* of molecules and ions present in the dissolved state. Suppose that the salt under examination is sodium acetate and that one mole of it is dissolved in a given amount of the solvent. Let x be the degree of hydrolysis. Then the number of moles at equilibrium will be as shown below :

$$\begin{matrix} CH_3COO^- & + & Na^+ & + & H_2O & \rightleftharpoons & CH_3COOH & + & Na^+ & + & OH^- \\ 1-x & & 1-x & & & & x & & x & & x \end{matrix}$$

Total number of moles $= 1 - x + 1 - x + 3x = 2 + x$

$$\therefore \quad \frac{\text{Observed freezing point depression}}{\text{Calculated freezing point depression}} = \frac{2+x}{2}$$

Thus, by determining the freezing point depression of a solution of a known concentration experimentally, the degree of hydrolysis x can be easily calculated.

Example 28. 10 gram of ammonium chloride (molar mass=53·5 g mol^{-1}) when dissolved in 1000 gram of water lowered the freezing point by 0·350°C. Calculate the degree of hydrolysis of the salt. The unhdrolysed salt may be taken as completely dissociated. The molal freezing point depression constant K_f of water is 1·86 K kg mol^{-1}.

Solution : We know that the freezing point depression, $\Delta T_f = \dfrac{K_f w_2}{M_2 w_1}$ (Chapter 22)

$$= \frac{(1{\cdot}86\,\text{K kg mol}^{-1})(10 \times 10^{-3}\,\text{kg})}{(53{\cdot}5 \times 10^{-3}\,\text{kg mol}^{-1})(1000 \times 10^{-3}\,\text{kg})} = 0{\cdot}347\,\text{K}$$

Let x be the degree of hydrolysis of ammonium chloride. Then, the number of moles of various species at equilibrium will be as shown below :

$$\begin{matrix} NH_4^+ & + & Cl^- & + & H_2O & \rightleftharpoons & NH_4OH & + & H^+ & + & Cl^- \\ 1-x & & 1-x & & & & x & & x & & x \end{matrix}$$

Total number of moles $= 1 - x + 1 - x + 3x = 2 + x$

$$\frac{\text{Observed freezing point depression}}{\text{Calculated freezing point depression}} = \frac{2+x}{2}$$

$$\frac{0{\cdot}350}{0{\cdot}347} = \frac{2+x}{2}$$

$$\therefore \quad x = 0{\cdot}017$$

Thus, the degree of hydrolysis of NH_4Cl = **0·017**

4. From Distribution Law. The degree of hydrolysis of a salt can be determined by the application of distribution law, provided the free acid or free base formed during hydrolysis is soluble in an immiscible solvent like benzene. The hydrolysis of aniline hydrochloride may be taken as an example.

The salt on hydrolysis yields free aniline which is soluble in water as well as in benzene and hydrochloric acid which remains soluble only in water. On adding a small amount of benzene, the free aniline distributes itself between the two solvents, as shown in Fig. 1, in accordance with the distribution law. The concentration of aniline in the benzene layer can be determined experimentally (by evaporating a known amount of the solution or by titrating against an acid) and its concentration in the aqueous layer is calculated knowing the value of its partition coefficient between water and benzene. The amount of free hydrochloric acid must be equal to the *total* amount of free aniline produced and is, therefore, obtained by taking the *total* of aniline in benzene and in aqueous layer. This, divided by the volume of water, gives the concentration of free hydrochloric acid in the aqueous layer. Subtracting this value from the initial concentration of the salt, the concentration of the unhydrolysed salt is obtained.

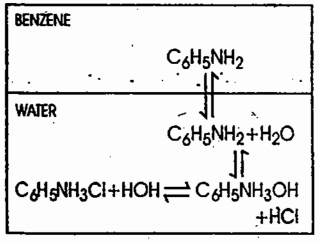


Fig. 1: Hydrolysis of aniline hydrochloride.

The hydrolysis constant K_h is then calculated by the usual equation, *viz.*,

$$K_h = \frac{[\text{Free aniline in aqueous layer}][\text{Free HCl}]}{[\text{Unhydrolysed salt}]}$$

Knowing K_h, the degree of hydrolysis x can be calculated by the relation,

$$x = \sqrt{K_h/c}$$

where c is the initial concentration of the salt in moles per litre.

Acid-Base Indicators

A hydrogen ion (or acid-base) indicator is a substance which changes its colour within limits with variation in pH of the solution to which it is added. This gives an easy method of determining pH of a solution by simply adding a ***suitable*** indicator and noting the colour. The pH range, over which the colour change occurs, varies considerably from one indicator to another. For example, methyl orange gives full acid colour (red) when added to a solution the pH of which is 3 or below and full basic colour (yellow) in a solution whose pH is 4·4 or above. In solutions having pH between 3 and 4·4, methyl orange gives a colour intermediate between red and yellow. Thus, the pH range over which methyl orange can be used as an indicator lies between 3 and 4·4.

Phenolphthalein, another common indicator, gives acid colour (colourless) in a solution of pH 8·3 or less and full basic colour (pink) in a solution of pH 10 or above. Thus, phenolphthalein can be used to determine pH over the range 8·3—10.

Theory of Acid-Base Indicators

Ostwald developed a theory of acid-base indicators which, though incomplete, offers a simple explanation for the colour change with change in pH. According to this theory, a hydrogen ion indicator is either a weak organic acid or a base. The undissociated molecule has one colour and the ion furnished by it, on dissociation, has another colour.

Let the indicator be an acid of formula HIn. Then, its dissociation in solution may be represented as

$$\underset{\text{Colour } A}{HIn} \rightleftharpoons H^+ + \underset{\text{Colour } B}{In^-} \qquad \text{...(60)}$$

The undissociated molecule HIn has one colour, say, colour A, while the ion In^- has another colour, say, colour B.

The equation for the above equilibrium may be written as

$$K_{In} = \frac{[H^+][In^-]}{[HIn]} \qquad \text{...(61)}$$

K_{In} is known as the **indicator constant.**

Since the species In^- and HIn have different colours, the actual colour shown by the indicator will depend upon the hydrogen ion concentration of the solution. Thus, if the solution is acidic, *i.e.*, it contains excess of H^+ ions, the equilibrium in Eq. 60 will shift towards the left. The indicator will, therefore, show predominantly colour *A* (acidic colour).

On the other hand, if the solution is alkaline, *i.e.*, it contains excess of OH^- ions, the H^+ ions furnished by the indicator will be taken up to form undissociated water. Therefore, the equilibrium in Eq. 60 will shift towards the right and there will be larger concentration of the ions In^-. The indicator will, therefore, show predominantly colour *B* (basic colour). Eq. 60, thus, successfully explains the change of colour of an indicator when the solution changes from acidic to alkaline.

Action of Phenolphthalein. Phenolphthalein is a colourless weak acid. It dissolves in water and dissociates to some extent to give colourless hydrogen ions and pink coloured anions. The equilibrium may be represented as :

$$\underset{\text{(Colourless)}}{HPh} \rightleftharpoons \underset{\text{(Colourless)}}{H^+} + \underset{\text{(Pink)}}{Ph^-} \qquad ...(62)$$

The actual state of affairs is not so simple. Phenolphthalein, or any other indicator, first undergoes a reversible tautomeric change into a substance of a different colour which then dissociates almost completely to give the coloured anions or cations, as the case may be. The process in the case of phenolphthalein may be represented as

$$\underset{\text{Colourless}}{HPh} \rightleftharpoons \underset{\text{Coloured tautomeric form}}{HPh^*} \rightleftharpoons \underset{\text{Colourless}}{H^+} + \underset{\text{Pink}}{Ph^-} \qquad ...(63)$$

But, since the concentration of the undissociated molecules of the tautomeric form is usually very small, the simple dissociation equation (Eq. 62) given above is sufficient for most purposes.

If the solution is acidic, the hydrogen ions furnished by the acid suppress the dissociation of phenolphthalein, shifting the equilibrium towards the left (common ion effect). The solution, therefore, remains colourless. In the presence of an alkali, however, the hydroxyl ions combine with the H^+ ions furnished by the indicator to form undissociated water. The equilibrium, therefore, shifts towards the right giving more of the coloured anions. The solution, therefore, turns pink. Thus, the indicator appears colourless in acidic and pink in alkaline solution.

The reason why phenolphthalein is not a suitable indicator for titrating a weak base, like ammonium hydroxide, against a strong acid is that the hydroxyl ions furnished by the weak base at the end point of the titration are too few to shift the equilibrium sufficiently towards the right to raise the *p*H to 8·3 at least and, therefore, pink colour does not appear just at the end point. A sufficient excess of the weak base has to be added to get the end point.

Action of Methyl Orange. Methyl orange is a weak base which, for simplicity, may be represented as MeOH. It dissolves in water and undergoes dissociation to a small extent. The undissociated molecules are yellow while the cations Me^+ are red in colour. The dissociation may be written as

$$\underset{\text{Yellow}}{MeOH} \rightleftharpoons \underset{\text{Red}}{Me^+} + \underset{\text{Colourless}}{OH^-}$$

If the solution is acidic, the hydrogen ions furnished by the acid combine with OH^- ions furnished by the indicator to form undissociated water. This shifts the equilibrium towards the right giving more of the red coloured Me^+ ions. Therefore, in acidic solution, this indicator gives red colour. In the presence of an alkali, the OH^- ions suppress the dissociation of methyl orange. Hence, the solution in alkaline medium remains yellow in colour.

Methyl orange cannot be used as indicator for titrating a weak acid, like acetic acid, against a strong base because the hydrogen ions furnished by the weak acid at the end point are too few to combine with a sufficient number of hydroxyl ions of methyl orange to shift the equilibrium in favour of the red coloured Me^+ ions. A sufficient excess of the weak acid has to be added to get the end point.

Some common indicators together with their useful ranges and extreme colours in acidic and alkaline solutions are given in Table 4.

TABLE 4
Some Useful Indicators

Indicator	*p*H range	Colour in acidic solution	Colour in alkaline solution
Cresol red (acid)	1·2–1·8	Red	Yellow
m-Cresol purple	1·2–1·8	Red	Yellow
Thymol blue (acid)	1·2–2·8	Red	Yellow
Bromophenol blue	3·1–4·6	Yellow	Purple
Methyl orange	3·1–4·5	Red	Yellow
Methyl red	4·2–6·3	Red	Yellow
Bromothymol blue	6·0–7·6	Yellow	Blue
Phenol red	6·4–8·2	Yellow	Red
Cresol red (base)	7·0–8·1	Yellow	Red
Thymol blue (base)	8·1–9·6	Yellow	Blue
Phenophthalein	8·0–9·8	Colourless	Pink
Thymolphthalein	9·3–10·5	Colourless	Blue
Alizarine yellow	10·1–12·1	Yellow	Lilac

Acid–Base Titrations and Use of Indicators. The process of acid–base titrations is accompanied by a change in *p*H. A plot between *p*H of the solution during titration and the amount of acid (or alkali) added from a burette is called a **titration curve.**

Indicators are frequently employed in detecting end points in acid–base titrations. Since, on account of hydrolysis, the *p*H at the end point depends upon the relative strengths of the acid and the base being titrated and since different indicators have different *p*H ranges within which they can be used, the selection of a proper indicator for a given titration is very important. The *p*H changes occurring in some acid–base titrations may be first considered.

Titration of a strong acid against a strong base. The titration of a strong acid with a strong base may be illustrated by the reaction of hydrochloric acid and sodium hydroxide. Suppose, 25 ml of 0·1 M HCl is to be titrated against 0·1 M NaOH. The equivalence or end point will, evidently, occur on the addition of 25 ml of the alkali solution. The *p*H values of the solution at different stages of neutralization are plotted graphically as in Fig. 2 against the increasing amount of the alkali added. It is seen that *p*H changes very slowly at first and rises from 1 to only about 4 when such a large amount as about 24·99 ml of the alkali solution has been added, *i.e.*, when about 99·9 per cent of the acid has been neutralised. Further addition of such a small amount as 0·01 ml of the alkali raises the *p*H by about 3 units to 7. The acid is now completely neutralised. Further addition of such a small amount as 0·01 ml of the sodium hydroxide solution (0·1 M) will amount to adding free hydroxyl ions and the *p*H will jump to a value above 9. Thus, near the end point, the titration curve is almost vertical and there is a rapid change of *p*H from 4 to about 10.

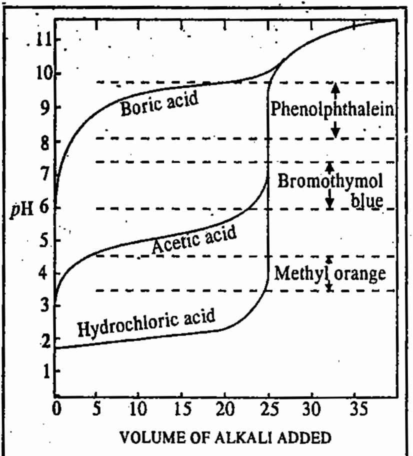


Fig. 2. The *p*H titration curves of different acids with sodium hydroxide. The *p*H ranges of the indicators involved are also shown in the figure.

Now an indicator is suitable only if it undergoes a change of colour at the *p*H prevailing near the end point. A reference to Table 4 shows that there are a number of indicators including methyl orange, methyl red, bromothymol blue and phenolphthalein which can undergo colour change within the *p*H range 3 to 10. Thus, while titrating a strong acid with a strong base, any of the above indicators may be used to detect the end point. The *p*H ranges of these indicators are also shown in Fig. 2 for convenience of reference.

Titration of a weak acid with strong base. The titration of a weak acid like acetic acid, against a strong base like sodium hydroxide, is included in Fig. 2. It will be seen that the vertical portion now does not begin until beyond *p*H 7 and the end point lies somewhere between *p*H 8 and 10. This is due to the hydrolysis of sodium acetate. This, being a salt of a weak acid and a strong base, gives excess of free OH^- ions in aqueous solution due to hydrolysis. Hence, phenolphthalein will be a satisfactory indicator but not methyl orange, methyl red or even bromothymol blue. Thymolphthalein (Table 4), though not so common, is another suitable indicator for such titrations.

Fig. 2 also includes a titration curve for the titration of boric acid against sodium hydroxide. This titration curve does not show any sharp rise in *p*H. This is because boric acid is so weak (its dissociation constant being $6{\cdot}0\times10^{-10}$) that its salt sodium borate formed during the reaction gets very largely hydrolysed giving alkaline solution. The *p*H, therefore, goes on rising *continuously* and there is no *sharp rise* at the equivalence point. Hence, there is no abrupt change in the colour of the indicator for the addition of a small amount of sodium hydroxide at the equivalence point. Thus, the acids with dissociation constants less than 10^{-7} cannot be successfully titrated.

Titration of sodium carbonate with hydrochloric acid. The titration curve obtained on reacting sodium carbonate with hydrochloric acid is shown in Fig. 3. It shows two inflection points. One of these indicates the conversion of sodium carbonate into bicarbonate :

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

This is completed at about *p*H 8·5 and phenolphthalein can be used to detect the end point. The second point of inflection indicates the neutralisation of sodium bicarbonate :

$$NaHCO_3 + HCl \longrightarrow NaCl + CO_2 + H_2O$$

This reaction gets completed at *p*H 4·3. Therefore, methyl orange is a highly suitable indicator in this case while phenolphthalein is not of any use.

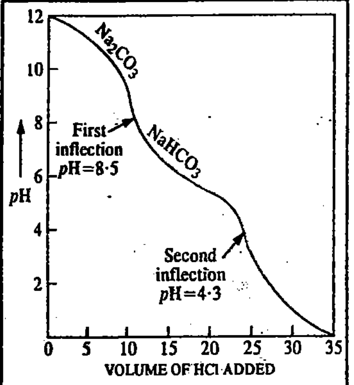


Fig. 3. The *p*H titration curves of sodium carbonate with a strong acid.

Mathematical Treatment of Acid-base Titrations

The *p*H values obtained experimentally at different stages of an acid–base titration can also be calculated mathematically, as illustrated below. (The value of K_w in these calculations is taken as 10^{-14}).

Suppose we are titrating 25 ml of a solution of HCl (0·1 M) against a standard (0·1 M) solution of NaOH and we want to calculate *p*H values of the titration solution after the addition of 20, 24·9, 24·95, 25·00, 25·05, 25·10 and 30 ml of NaOH solution. This is done as follows.

Initial *p*H of the titration solution, *viz.*, 0·1 M HCl $= -\log[H^+] = -\log(0{\cdot}1) = 1{\cdot}0$

Since the product of volume in ml and the concentration in mol dm^{-3} (*i.e.*, molarity) of a solute gives the amount of the solute in millimoles, hence,

Amount of HCl initially present in the titration solution $= 25\times0{\cdot}1 = 2{\cdot}5$ millimoles

The amount of NaOH in 20 ml of 0·1 M solution added during titration

$$= 20\times0{\cdot}1 = 2{\cdot}0 \text{ millimoles}$$

Amount of HCl left in the titration solution on adding 20 ml of NaOH $= 2{\cdot}5 - 2{\cdot}0 = 0{\cdot}5$ millimole

$\therefore$ Concentration of HCl or of H^+ ions in the solution $= \dfrac{0{\cdot}5}{1000}\times\dfrac{1000}{45}$ mol dm^{-3}

$\therefore$ *p*H of the titration solution $= -\log[H^+] = -\log\left(\frac{0{\cdot}5}{45}\right) = 1{\cdot}95$

Proceeding as above, the *p*H of titration solution on the addition of 24·9 and 24·95 ml of NaOH solution comes out to be **3·70** and **4·00**, respectively.

On the addition of 25 ml of NaOH, the acid is completely neutralised giving NaCl. The *p*H of the resulting solution is, therefore, 7.

On adding 25·05 ml of NaOH, the additional volume of NaOH = 0·05 ml

Amount of NaOH in 0·05 ml = 0·005 millimole

$$\therefore \quad \text{Concn. of NaOH or } OH^- \text{ ions} = \frac{0{\cdot}005}{1000}\times\frac{1000}{50{\cdot}05}\,\text{mol dm}^{-3}$$

$$[H^+][OH^-] = 10^{-14} \text{ at } 25°C$$

$$\therefore \quad [H^+] = \frac{10^{-14}\times50{\cdot}05}{0{\cdot}005} = 1{\cdot}00\times10^{-10}\,\text{mol dm}^{-3}$$

Hence, $\quad pH = -\log[H^+] = 10{\cdot}00$

Proceeding as above, the *p*H values of the titration solution after the addition of 25·10 and 30 ml of NaOH solution come out to be 10·30 and 10·96, respectively.

It is evident from the *p*H values calculated as above that the *p*H increases from 1 to 4 on the addition of 24·95 ml of NaOH. Around the point of equivalence, the *p*H increases from 4 to 7 by the addition of a single drop of NaOH and then from 7 to 10 by the addition of another drop of NaOH. In other words, *around the end point there is a sharp change in* pH *from* 4 *to* 10 *just by the addition of* 2 *drops of NaOH solution.* We shall, thus, select an indicator which undergoes a change in colour in the *p*H range 4 to 10. As can be seen from Table 4, methyl orange as well as phenolphthalein are suitable indicators in this case.

Now suppose that we are titrating 25 ml solution of acetic acid (0·1 M) against 0·1 M solution of NaOH and we want to calculate the *p*H values of the titration solution after the addition of 20, 24·90, 24·95, 25·00, 25·05, 25·10 and 30 ml of NaOH solution. This is now done as follows.

Amount of CH_3COOH present in solution $= 25\times0{\cdot}1 = 2{\cdot}5$ millimoles

Since acetic acid is a weak acid, its H^+ ion concentration is given by the relation $[H^+]=\sqrt{cK_a}$, where *c* is the molar concentration of the acid and K_a is its dissociation constant.

$\therefore$ The initial concentration of H^+ ion in 0·1 M CH_3COOH solution

$$= \sqrt{0{\cdot}1\times1{\cdot}75\times10^{-5}} = 1{\cdot}32\times10^{-3}\,\text{mol dm}^{-3}$$

$$\therefore \quad pH = -\log[H^+] = -\log(1{\cdot}32\times10^{-3}) = 2{\cdot}88$$

During titration, CH_3COOH gets converted into CH_3COONa. The *p*H of the titration solution would thus depend upon the concentration of CH_3COOH left and of CH_3COONa formed during titration. In a mixture of a weak acid and its salt, the *p*H is given by the relation

$$pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} \qquad \text{(Eq. 29)}$$

With the addition of 20 ml of NaOH solution, the amount of NaOH added to the titration solution $= 20\times0{\cdot}1 = 2{\cdot}0$ millimoles

Amount of CH_3COONa formed = 2·0 millimoles

Since volume of the solution is the same for both CH_3COOH and CH_3COONa, the ratio of their amounts in millimoles can be taken as the ratio of their molar concentrations.

$$\therefore \quad pH \text{ of the titration solution} = 4{\cdot}76 + \log\frac{2{\cdot}0}{0{\cdot}5} = 5{\cdot}36$$

$$(K_a \text{ of } CH_3COOH = 1{\cdot}75\times10^{-5} \;\therefore\; pK_a = -\log K_a = 4{\cdot}76)$$

Proceeding as above, the pH of the titration solution on the addition of 24·90 and 24·95 ml of NaOH solution comes out to be 7·16 and 7·46, respectively.

On the addition of 25 ml of NaOH solution, the acetic acid is completely neutralised, the resulting product being CH_3COONa. The amount of CH_3COONa formed would be $25 \times 0{\cdot}1 = 2{\cdot}5$ millimoles. Since the total volume of the titration solution is $25 + 25 = 50$ ml, hence the concentration of $CH_3COONa = \frac{2{\cdot}5 \times 1000}{1000 \times 50} = 0{\cdot}05$ mol dm^{-3}. Since CH_3COONa is a salt of a strong base and a weak acid, it would get hydrolysed to give an alkaline solution whose pH is given by the relation

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

$$= 14 - \tfrac{1}{2}(14) + \tfrac{1}{2}\log 0{\cdot}05 + \tfrac{1}{2}(4{\cdot}76) = 8{\cdot}73$$

With the addition of 25·05 ml of NaOH, the amount of free NaOH added to the titration solution

$$= 0{\cdot}1 \times 0{\cdot}05 = 0{\cdot}005 \text{ millimole}$$

$\therefore$ Concentration of OH^- ions due to this addition $= \frac{0{\cdot}005}{1000} \times \frac{1000}{50{\cdot}05} = 0{\cdot}0001$ mol dm^{-3}

Concentration of OH^- ions due to the hydrolysis of CH_3COONa is given by the expression

$$[OH^-] = \left(\frac{K_w c}{K_a}\right)^{1/2} = \left(\frac{10^{-14} \times 0{\cdot}05}{1{\cdot}75 \times 10^{-5}}\right) \text{mol dm}^{-3}$$

$$= 0{\cdot}534 \times 10^{-5} \text{ mol dm}^{-3} \text{ which is negligible as compared to } 0{\cdot}0001 \text{ mol dm}^{-3}.$$

$\therefore$ Total concentration of $[OH^-] = 0{\cdot}0001$ mol dm^{-3}

$$[H^+][OH^-] = 10^{-14} \text{ at } 25°C$$

$$\therefore \quad [H^+] = 10^{-14}/0{\cdot}0001 = 10^{-10} \text{ mol dm}^{-3}$$

$$\therefore \quad pH = 10$$

The pH of the titration solution on the addition of 25·10 and 30 ml of NaOH solution would be 10·30 and 10·96, respectively.

The data obtained for the titration of 0·1 M HCl and 0·1 M CH_3COOH solutions against 0·1 M NaOH solution have been summed up in Table 5.

As can be seen, the pH in the case of CH_3COOH is higher at each stage upto the end point. This is evidently due to the hydrolysis of CH_3COONa formed during the titration.

If we plot the above data graphically, the pH titration curves obtained would be exactly similar to those shown earlier in Fig. 2.

TABLE 5

Titrations of 0·1 M HCl and 0·1 M CH_3COOH solutions against 0·1 M NaOH solution

Volume of NaOH added (ml)	*p*H values in the titration of :	
	HCl solution	CH_3COOH solution
0·00	1·00	2·88
20·00	1·95	5·36
24·90	3·70	7·16
24·95	4·00	7·46
25·00	7·00	8·73
25·05	10·00	10·00
25·10	10·30	10·30
30·00	10·96	10·96

Example 29. 50 ml of a solution of acetic acid (0·1 M) is being titrated against a standard (0·125 M) solution of NaOH. Calculate the *p*H values of the titration solution on the addition of 30, 39·9, 39·95, 40·00, 40·05, 40·10 and 50 ml of NaOH solution. Comment on your result.

Solution : The H^+ ion concentration of a weak acid which is only partially dissociated is given by $[H^+] = \sqrt{cK_a}$

$\therefore$ Initial $[H^+]$ furnished by acetic acid $= (0{\cdot}1 \times 1{\cdot}75 \times 10^{-5})^{1/2} = 1{\cdot}32 \times 10^{-3}$ mol dm^{-3}

$$\therefore \quad pH = -\log(1{\cdot}32 \times 10^{-3}) = \mathbf{2{\cdot}88}$$

Thus, the initial pH of the titration solution is 2·88.

The amount of acetic acid initially present in the titraion solution $= 50 \times 0{\cdot}1 = 5$ millimole. During titration, CH_3COOH gets converted into CH_3COONa. The pH of the titration solution would thus depend upon the amount of the acetic acid left and the sodium acetate formed during titration. In the case of a mixture of a weak acid and its salt, the pH is given by the well known relation :

$$pH = pK_a + \log [\text{Salt}]/[\text{Acid}]$$

With the addition of 30 ml of NaOH solution, the amount of NaOH added to the titration solution $= 30 \times 0{\cdot}125 = 3{\cdot}75$ millimole.

$\therefore$ Amount of CH_3COONa formed $= 3{\cdot}75$ millimoles

Amount of CH_3COOH left behind $= 1{\cdot}25$ millimoles

$$\therefore \quad pH \text{ of the titration solution} = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

Since the volume of solution is the same for both the acid and the salt, hence the ratio of their amounts in millimoles can be taken as the ratio of their molar concentrations.

Thus, $$pH = 4{\cdot}76 + \log\frac{3{\cdot}75}{1{\cdot}25} = \mathbf{5{\cdot}24}$$

Proceeding as above, the pH of the titration solution, on the addition of 39·9 ml and 39·95 ml of NaOH solution would be **7·34** and **7·46**, respectively. On the addition of 40 ml of NaOH solution, the acetic acid is completely neutralised, the resulting product being CH_3COONa. The amount of CH_3COONa formed would, evidently, be $40 \times 0{\cdot}125 = 5{\cdot}0$ millimoles. Since the total volume of the titration solution is $50 + 40 = 90$ ml, hence the concentration of CH_3COONa would be $\frac{5 \times 1000}{1000 \times 90} = 5/90$ mol dm^{-3}. Since CH_3COONa is a salt of a strong base and a weak acid, it would get hydrolysed to give an alkaline solution whose pH is given by the relation

$$pH = 14 - \tfrac{1}{2}pK_w + \tfrac{1}{2}\log c + \tfrac{1}{2}pK_a$$

$$= 14 - \tfrac{1}{2}(14) + \tfrac{1}{2}\log(5/90) + \tfrac{1}{2}(4{\cdot}76) = \mathbf{8{\cdot}75}$$

With the addition of 40·05 ml of NaOH solution, the amount of free NaOH added to the titration solution $= 0{\cdot}125 \times 0{\cdot}05 = 0{\cdot}00625$ millimole. Hence, concentration of OH^- ions due to this addition $= \frac{0{\cdot}00625}{1000} \times \frac{1000}{90{\cdot}05} = 0{\cdot}000069$ mol dm^{-3}. Concentration of OH^- ions due to the hydrolysis of CH_3COONa is given by the expression

$$[OH^-] = \left(\frac{K_w c}{K_a}\right)^{1/2} = \left(\frac{10^{-14} \times (5/90)}{1{\cdot}75 \times 10^{-5}}\right)^{1/2} = 0{\cdot}563 \times 10^{-5} \text{ mol dm}^{-3}$$

$\therefore$ Total concentration of OH^- ions in titration solution $= 0{\cdot}0000746$ mol dm^{-3}

$$[H^+[OH^-] = 10^{-14} \text{ at } 25°C$$

$$\therefore \quad [H^+] = \frac{10^{-14}}{0{\cdot}0000746} \text{ mol dm}^{-3}$$

$$\therefore \quad pH \text{ of titration solution} = -\log[H^+] = 9{\cdot}87$$

Proceeding as above, the pH of titration solution on the addition of 40·10 and 50 ml of NaOH solution would be **10·16** and **12·10**, respectively.

Comments. It is evident from the calculations made as above that the pH increases from 2·88 to 7·46 on the addition of 39·95 ~~ml~~ of NaOH solution. Around the end point, the pH increases from 7·46 to 8·75 by the addition of a single drop of NaOH and then from 8·75 to 9·87 by the addition of another drop of NaOH. Thus, around the end point, there is considerable increase in pH from 7·34 to 9·87 by the addition of just 2 drops of NaOH. An indicator which changes colour in the pH range 7·34 to 9·87 would be a suitable indicator in this titration. As can be seen from Table 4, phenolphthalein would be a suitable indicator but not methyl orange.

TABLE 6

Titration of 0·1 M CH_3COOH against 0·125 M NaOH

Volume of CH_3COOH solution = 50 ml

Strength of NaOH solution = 0·125 M

Volume of NaOH solution added (ml)	*p*H of titration solution
0·00	2·88
30·00	5·24
39·00	7·34
39·95	7·46
40·00	8·75
40·05	9·87
40·10	10·16
50·00	12·10

The data obtained for the titration of 0·1 M CH_3COOH against 0·125 M NaOH have been summed up in Table 6.

SOLUBILITY PRODUCT

Solubility Product. In a saturated solution of a salt, there exists a dynamic equilibrium between the excess of the solute and the ions furnished by that part of the solute which has gone in solution. Consider, for example, the case when a sparingly soluble salt, like silver chloride, is added to water. A very small amount dissolves and the rest of it remains in the solid state. Here the solid silver chloride is in equilibrium with silver and chloride ions furnished by the dissolved silver chloride. This may be represented as

$$\mathrm{AgCl}(s,\ \textit{satd. soln.}) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq)$$

Applying the law of chemical equilibrium, the equilibrium constant would be given by

$$K = \frac{a_{\mathrm{Ag^+}} \times a_{\mathrm{Cl^-}}}{a_{\mathrm{AgCl}}} \qquad \ldots(64)$$

Since activity of a solid is taken as unity by convention, the above expression may be put as

$$K_{sp} = a_{\mathrm{Ag^+}} \times a_{\mathrm{Cl^-}} \qquad \ldots(65)$$

K_{sp} is known as the **solubility product** of silver chloride. It is constant at a given temperature.

Very often, in practice, it is more convenient to use concentration terms instead of activities. The constant is then known as **concentration solubility product**, denoted by K'_{sp}. Thus,

$$K'_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}] \qquad \ldots(66)$$

where the square brackets, as usual, represent the concentrations of the entities enclosed within. In the case of sparingly soluble salts since the ionic concentrations are very low, activity of each ion is almost equal to its concentration. Hence,

$$K_{sp} = K'_{sp} \qquad \ldots(67)$$

i.e., solubility product is almost equal to concentration solubility product. Therefore, without introducing any serious error, we may write :

$$K_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}]$$

In the case of silver sulphate, another sparingly soluble salt, the following equilibrium exists :

$$\mathrm{Ag_2SO_4}(s,\ \textit{satd. soln.}) \rightleftharpoons 2\mathrm{Ag^+}(aq) + \mathrm{SO_4^{2-}}\ (aq)$$

The solubility product will now be given by the expression

$$K_{sp} = [\mathrm{Ag^+}]^2[\mathrm{SO_4^{2-}}]$$

Similarly, the solubility products in the case of $\mathrm{Al(OH)_3}$ and $\mathrm{As_2S_3}$ would be given by the expressions $K_{sp}=[\mathrm{Al^{3+}}][\mathrm{OH^-}]^3$ and $K_{sp} = [\mathrm{As^{3+}}]^2[\mathrm{S^{2-}}]^3$, respectively.

Consider, in general, a salt of the type $\mathrm{A}_x\mathrm{B}_y$ which dissociates as

$$\mathrm{A}_x\mathrm{B}_y \rightleftharpoons x\mathrm{A}^{y+} + y\mathrm{B}^{x-}$$

The solubility product of the salt is now given by

$$K_{sp} = [\mathrm{A}^{y+}]^x\,[\mathrm{B}^{x-}]^y \qquad \ldots(68)$$

Thus, the solubility product of a sparingly soluble salt forming a saturated solution in water is given by the product of the concentrations of the ions raised to a power equal to the number of times the ions occur in the equation representing the dissociation of the electrolyte.

It may be mentioned in particular that the *solubility product principle can also be applied to saturated solutions of freely soluble salts*. For example, in the case of a saturated solution of sodium chloride in which some solid NaCl is also present, the following equilibrium exists :

$$\mathrm{NaCl}(s,\ \textit{satd. soln}). \rightleftharpoons \mathrm{Na^+}(aq) + \mathrm{Cl^-}(aq)$$

The true solubility product constant is given by the equation

$$K_{sp} = a_{\mathrm{Na^+}} \times a_{\mathrm{Cl^-}}$$

and the concentration solubility product is given by the expression

$$K'_{sp} = [\mathrm{Na^+}][\mathrm{Cl^-}]$$

However, in this case, the activities are considerably less than the concentrations. This is due to high ionic concentrations which enhance interionic effects. K'_{sp} is, therefore, no longer equal to K_{sp}. Apart from this mathematical difference, the solubility product principle is as valid for sparingly soluble as for freely soluble electrolytes.

The solubility products of some of the common sparingly soluble substances are given in Table 7.

TABLE 7

Solubility Products of Some Sparingly Soluble Substances

Substance	K_{sp} at 25°C	Substance	K_{sp} at 25°C	Substance	K_{sp} at 25°C
PbS	$3{\cdot}4\times10^{-28}$	$\mathrm{CaCO_3}$	$4{\cdot}8\times10^{-9}$	$\mathrm{Al(OH)_3}$	$8{\cdot}5\times10^{-32}$
CdS	$3{\cdot}6\times10^{-28}$	$\mathrm{SrCO_3}$	$1{\cdot}1\times10^{-10}$	$\mathrm{Zn(OH)_2}$	$1{\cdot}8\times10^{-17}$
CuS	$8{\cdot}5\times10^{-36}$	$\mathrm{Ag_2CO_3}$	$6{\cdot}15\times10^{-12}$	$\mathrm{Mn(OH)_2}$	$4{\cdot}0\times10^{-14}$
HgS	$4{\cdot}1\times10^{-53}$	$\mathrm{Ag_2S}$	$1{\cdot}6\times10^{-50}$	$\mathrm{Mg(OH)_2}$	$1{\cdot}2\times10^{-11}$
MnS	$1{\cdot}4\times10^{-10}$	$\mathrm{HgBr_2}$	$8{\cdot}0\times10^{-18}$	AgCl	$1{\cdot}56\times10^{-10}$
ZnS	$1{\cdot}2\times10^{-28}$	AgBr	$7{\cdot}7\times10^{-13}$	$\mathrm{Ag_2CrO_4}$	$9{\cdot}0\times10^{-12}$
NiS	$1{\cdot}5\times10^{-24}$	$\mathrm{PbI_2}$	$1{\cdot}39\times10^{-8}$	$\mathrm{BaSO_4}$	$1{\cdot}08\times10^{-10}$
CoS	$3{\cdot}0\times10^{-25}$	$\mathrm{HgI_2}$	$3{\cdot}2\times10^{-29}$	TlCl	$2{\cdot}0\times10^{-4}$
$\mathrm{Fe(OH)_3}$	$1{\cdot}1\times10^{-38}$	AgI	$0{\cdot}94\times10^{-16}$		

Relation between Solubility Product and Molar Solubility of a Sparingly Soluble Salt. For the saturated solution of a sparingly soluble salt AB, the following solubility equilibrium would exist :

$$\mathrm{AB}(s,\ \textit{satd. soln.}) \rightleftharpoons \mathrm{A^+}(aq) + \mathrm{B^-}(aq)$$

If the molar solubility of the salt is s, then

$$[\mathrm{A^+}] = s\ \mathrm{mol\ dm^{-3}}$$

$$[\mathrm{B^-}] = s\ \mathrm{mol\ dm^{-3}}$$

Hence, $$K_{sp} = [\mathrm{A^+}][\mathrm{B^-}] = (s\ \mathrm{mol\ dm^{-3}})(s\ \mathrm{mol\ dm^{-3}}) = s^2\ \mathrm{mol^2\ dm^{-6}}$$

Example 30. The solubility of silver chloride in water at 25°C is 0·00179 g per litre. Calculate its solubility product at 25°C.

Solution : Solubility of silver chloride $= 0{\cdot}00179\ \mathrm{g\ dm^{-3}} = \dfrac{0{\cdot}00179\ \mathrm{g\ dm^{-3}}}{143{\cdot}5\ \mathrm{g\ mol^{-1}}} = 0{\cdot}0000125\ \mathrm{mol\ dm^{-3}}$

The dissolved salt would be present in the form of ions so that

$$[\mathrm{Ag^+}] = [\mathrm{Cl^-}] = 0{\cdot}0000125\ \mathrm{mol\ dm^{-3}}$$

$$K_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}] = (0{\cdot}0000125\ \mathrm{mol\ dm^{-3}})^2 = \mathbf{1{\cdot}56\times10^{-10}\ mol^2\ dm^{-6}}$$

Example 31. The solubility product of magnesium hydroxide $\mathrm{Mg(OH)_2}$ at 25°C is $1{\cdot}4\times10^{-11}$. Calculate the solubility of magnesium hydroxide in grams per litre ? (Mg=24, O=16, H=1)

Solution : The solubility equilibrium in this case will be

$$\mathrm{Mg(OH)_2}(s,\ \textit{satd. soln.}) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\mathrm{OH^-}(aq)$$

Let the solubility of $\mathrm{Mg(OH)_2}$ be s mol $\mathrm{dm^{-3}}$.

$\therefore$ Concentration of $\mathrm{Mg^{2+}} = s\ \mathrm{mol\ dm^{-3}}$

Now, for each Mg^{2+} ion, two OH^- ions are produced.

∴ Concentration of OH^- ions = $2s$ mol dm^{-3}

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$\therefore \quad s(2s)^2 = 1{\cdot}2\times10^{-11} \quad \text{or} \quad 4s^3 = 1{\cdot}2\times10^{-11} \quad \text{or} \quad s = 1{\cdot}44\times10^{-4} \text{ mol dm}^{-3}$$

∴ Solubility of $Mg(OH)_2 = 1{\cdot}44\times10^{-4}$ mol $dm^{-3} = 1{\cdot}44\times10^{-4}$ mol $dm^{-3}\times58$ g $mol^{-1} = \mathbf{0{\cdot}00835}$ **g** dm^{-3}

Example 32. Calculate the solubility in grams per litre of $Al(OH)_3$ in water at 25°C if $K_{sp}=8{\cdot}5\times10^{-32}$.

Solution : The solubility equilibrium in this case would be written as

$$Al(OH)_3\ (s,\ satd,\ soln.) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$$

If s mol dm^{-3} is the solubility of the salt, then

$$K_{sp} = [Al^{3+}][OH^-]^3 = (s)(3s)^3 = 27\ s^4$$

$$\therefore \quad s = [K_{sp}/27]^{1/4} = [8{\cdot}5\times10^{-32}/27]^{1/4} = 0{\cdot}749\times10^{-8} \text{ mol dm}^{-3}$$

$$= 0{\cdot}749\times10^{-8} \text{ mol dm}^{-3}\times78 \text{ g mol}^{-1} = 5{\cdot}842\times10^{-7} \text{ g dm}^{-3}$$

Applications of Solubility Product Principle

1. Determination of Solubilities of Sparingly Soluble Salts. Suppose, solubility of a sparingly soluble salt, say, silver chloride, is s mole per litre. Since its concentration will be quite small, it may be taken as completely dissociated so that the concentration of both silver and chloride ions will be s mole per litre each.

Therefore, solubility product K_{sp} of silver chloride will be given by

$$K_{sp} = [Ag^+][Cl^-] = s^2$$

Hence, solubility of silver chloride is related to the solubility product by the expression

$$s = \sqrt{K_{sp}}$$

The solubility product of silver chloride at a given temperature is determined by adding silver chloride in a solution of potassium chloride of a known concentration, say, b moles per litre. The concentration of Ag^+ ions in the solution produced by the dissociation of that part of AgCl which dissolves in water is determined by an EMF method. Suppose it is a mole per litre. The concentration of chloride ions in solution will be $(a+b)$ moles per litre due to silver chloride and potassium chloride both. Therefore, solubility product of silver chloride, K_{sp}, is given by

$$K_{sp} = a(a+b)$$

Since, both a and b are known, the solubility product of silver chloride can easily be obtained.

Hence, solubility of silver chloride = $\sqrt{K_{sp}}$ mole per litre

2. Predicting Precipitation Reactions. With the knowledge of solubility product of a sparingly soluble substance, we can predict whether under certain given conditions that substance would be precipitated or not. It may be remembered that a substance gets precipitated when the ionic product, *i.e.*, the product of concentrations of its ions present in a solution, exceeds the solubility product of the substance. We may take an example.

The solubility product of calcium sulphate in water in 25°C is $2{\cdot}4\times10^{-5}$ M^2. A sample of hard water contains 0·01 mole of $CaCl_2$ per litre. It is required to precipitate calcium sulphate by the addition of dilute sulphuric acid. Two solutions of sulphuric acid of concentrations 0·001 M and 0·02 M are given.

Suppose we mix, in the first instance, equal volumes of the hard water and sulphuric acid of lower concentration. Will calcium sulphate be precipitated ?

The solubility equation for calcium sulphate may be written as

$$CaSO_4(s,\ satd.\ soln.) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}\ (aq)$$

$$K_{sp} = [Ca^{2+}][SO_4^{2-}] = 2{\cdot}4\times10^{-5}\ M^2$$

$[Ca^{2+}]$ in water = 0·01 M

Since volume is doubled on the addition of sulphuric acid solution, hence,

$[Ca^{2+}]$ in the mixture = 0·01/2 = 0·005 M

Concentration of sulphuric acid = 0·001 M

$$\therefore \quad [SO_4^{2-}] = 0{\cdot}001\ M$$

Since volume is doubled when mixed with equal volume of hard water, hence,

$[SO_4^{2-}]$ in the mixture = 0·001/2 = 0·0005 M

The product of concentrations of ions

$$[Ca^{2+}][SO_4^{2-}] = 0{\cdot}005\ M\times0{\cdot}0005\ M = 2{\cdot}5\times10^{-6}\ M^2$$

Evidently, the ionic product is less than the solubility product of $CaSO_4$ which is equal to $2{\cdot}4\times10^{-5}$ M^2. Therefore, precipitation of calcium sulphate will **not** occur.

Now, suppose we mix equal volumes of hard water and sulphuric acid solution of the higher concentration (0·02 M).

$[Ca^{2+}]$ in the mixture = 0·01/2 = 0·005 M

$[SO_4^{2-}]$ in the mixture = 0·02/2 = 0·01 M

The ionic product $[Ca^{2+}][SO_4^{2-}] = 0{\cdot}005\ M\times0{\cdot}01\ M = 5\times10^{-5}\ M^2$

The ionic product now exceeds the solubility product of $CaSO_4$. Hence, calcium sulphate **will be precipitated.**

Example 33. 25 ml of 0·01 $AgNO_3$ solution is mixed with 25 ml of 0·0005 M aqueous NaCl solution. Determine if the precipitate of AgCl will be formed. Given K_{sp}(AgCl)=$1{\cdot}7\times10^{-10}$ M^2.

Solution : Since the volume of the solution *after mixing* is doubled and $AgNO_3$ and NaCl are strong electrolytes which are completely dissociated in solution, we have

$$[Ag^+] = 1/2(0{\cdot}01\ M) = 5\times10^{-3}\ M$$

$$[Cl^-] = 1/2(0{\cdot}0005\ M) = 2{\cdot}25\times10^{-4}\ M$$

$$\text{Ionic product} = [Ag^+][Cl^-] = (5\times10^{-3}\ M)(2{\cdot}25\times10^{-4}\ M) = 1{\cdot}125\times10^{-6}\ M^2$$

Since ionic product > K_{sp}(AgCl), **the precipitate of AgCl will be formed.**

Example 34. 25 ml of 4×10^{-5} M solution of $Ba(NO_3)_2$ is mixed with 500 ml of 5×10^{-5} M solution of Na_2SO_4. Will a precipitate of $BaSO_4$ be formed ? $K_{sp}(BaSO_4)$ = $1{\cdot}08\times10^{-10}$ M^2.

Solution : After mixing, the total volume of the solution is 525 ml.

Since $Ba(NO_3)_2$ and Na_2SO_4 are strong electrolytes, they are completely dissociated. Therefore, we have

$$[Ba^{2+}] = 4\times10^{-5}\ M\times(25/525) = 1{\cdot}90\times10^{-6}\ M$$

$$[SO_4^{2-}] = 5\times10^{-5}\ M\times(500/525) = 4{\cdot}76\times10^{-5}\ M$$

$$\text{Ionic product} = [Ba^{2+}][SO_4^{2-}] = [1{\cdot}90\times10^{-6}\ M]\ [4{\cdot}76\times10^{-5}\ M] = 9{\cdot}04\times10^{-11}\ M^2$$

Since ionic product is less then $K_{sp}(BaSO_4)$, **the precipitate of $BaSO_4$ will not be formed.**

3. Fractional Precipitation. Consider an aqueous solution of KCl and KI to which $AgNO_3$ solution is added. Since $K_{sp}(AgI)$ is less than $K_{sp}(AgCl)$, hence, $K_{sp}(AgI)$ will be exceeded and AgI will be precipitated first :

$$Ag^+(aq) + I^-(aq) \longrightarrow AgI(s)\downarrow \qquad K_{sp} = 0{\cdot}94\times10^{-16}$$

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)\downarrow \qquad K_{sp} = 1{\cdot}56\times10^{-10}$$

$$\frac{[I^-]}{[Cl^-]} = \frac{K_{sp}(AgI)}{K_{sp}(AgCl)} = \frac{0{\cdot}94\times10^{-16}}{1{\cdot}56\times10^{-10}} = 6{\cdot}0\times10^{-7} \approx 10^{-6}$$

Thus, AgI will start precipitating out when $[I^-]$ is approximately one-millionth part of $[Cl^-]$.

AgCl will precipitate only when $[Ag^+]$ is greater than the value given below :

$$[Ag^+] = \frac{K_{sp}(AgCl)}{[Cl^-]} = \frac{1{\cdot}56\times10^{-10}}{[Cl^-]}$$

At that point both AgI and AgCl will start precipitating *simultaneously.*

4. Preferential Precipitation of an Insoluble Salt. Silver chloride is 'insoluble' or sparingly soluble, to be more accurate. So is silver iodide. The question arises as to what would happen if potassium iodide solution is added to silver chloride. Would the reaction

$$\underset{\text{Sparingly soluble}}{AgCl} + KI \rightleftharpoons KCl + \underset{\text{Sparingly soluble}}{AgI}$$

take place towards the right, *i.e.*, would the precipitate of silver chloride change into the precipitate of silver iodide ?

For answer, it is necessary to look to their respective solubility products.

Solubility product of silver chloride

$$K_{sp(AgCl)} = [Ag^+][Cl^-] = 1{\cdot}56\times10^{-10} \qquad \text{(Table 7)}$$

and that of silver iodide,

$$K_{sp(AgI)} = [Ag^+][I^-] = 0{\cdot}94\times10^{-16} \qquad \text{(Table 7)}$$

$$\therefore \quad \frac{[Cl^-]}{[I^-]} = \frac{1{\cdot}56\times10^{-10}}{0{\cdot}94\times10^{-16}} = 1{\cdot}66\times10^{6}$$

This means that at equilibrium, the concentration of Cl^- ions in solution is more than a million times greater than that of I^- ions. In other words, practically nothing of the I^- ions can remain in solution at equilibrium. As the I^- ions can only be removed as AgI, it means that the reaction proceeds virtually to completion towards the right.

As a rule, the compound with the lower solubility product gets precipitated in preference. Silver iodide has lower solubility product than silver chloride. Therefore, the former gets precipitated in preference to the latter.

5. Precipitation of Soluble Salts. ***(a) Purification of common salt.*** The principle of solubility product is also applied in the precipitation of soluble salts in pure state from their saturated solutions. This phenomenon, known as *salting out*, is used in the purification of sodium chloride. This is done by preparing a saturated solution of commercial (impure) sodium chloride in water when the following equilibrium exists :

$$NaCl(s,\ \textit{satd. soln.}) \rightleftharpoons Na^+(aq) + Cl^-(aq)$$

$$K'_{sp} = [Na^+][Cl^-]$$

HCl gas is passed through this solution. The $[Cl^-]$, therefore, increases considerably. Hence, the ionic product exceeds the concentration solubility product of NaCl and, therefore, it precipitates out from the solution in pure state. The soluble impurities remain in solution.

(b) Salting out of soap. The same principle is made use of in the *salting out* of soap which may be considered as sodium salt of stearic acid for simplicity. The following equilibrium exists :

$$C_{17}H_{35}COONa(s,\ \textit{satd. soln.}) \rightleftharpoons C_{17}H_{35}COO^-(aq) + Na^+(aq)$$

$$K'_{sp} = [C_{17}H_{35}COO^-][Na^+]$$

Some sodium chloride is now added. The $[Na^+]$, therefore, increases. Hence, the ionic product exceeds the concentration solubility product of sodium stearate. The soap, therefore, separates out from solution.

6. Inorganic Analysis. The application of solubility product principle to inorganic analysis is of great importance. A few illustrations are given below.

a. Precipitation of sulphides. Hydrogen sulphide is a weak acid. Its small dissociation

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

is further suppressed by the addition of dilute hydrochloric acid (common ion effect). Therefore, the concentration of S^{2-} ions which was already small, becomes smaller still. But even then it is larger than that required for the solubility products of sulphides of copper, cadmium, bismuth, arsenic, antimony and tin, to be exceeded. Therefore, these cations get precipitated as sulphides in acidic solution in the Second Group of qualitative analysis.

But, as the solubility products of sulphides of nickel, cobalt, manganese and zinc are comparatively higher, the sulphide ion concentration in the presence of hydrochloric acid is smaller than that required to cause their precipitation. These cations, therefore, do not get precipitated in Group II. Since they require a larger concentration of sulphide ions, a highly ionised sulphide, such as ammonium sulphide, is added (or which is the same thing as passing hydrogen sulphide through ammoniacal solution). By this means, the product $[Zn^{2+}][S^{2-}]$, for example, in solution exceeds the solubility product of zinc sulphide. Therefore, zinc sulphide gets precipitated. Similarly, the sulphides of nickel, cobalt and manganese, which all appear in Group IV of qualitative analysis, get precipitated.

The solubility product of cadmium sulphide is greater than that of the other sulphides of the Second Group. Therefore, the sulphide ion concentration in this case should not be made very low. In other words, excess of hydrochloric acid should be avoided or the solution should be diluted before passing hydrogen sulphide for the detection of Cd^{2+} in the Second Group of qualitative analysis.

b. Precipitation of hydroxides. Advantage is taken of the fact that solubility products of hydroxides of iron, aluminium and chromium are much smaller than those of magnesium, zinc, etc.

Ammonium hydroxide is a weak base. Its ionisation

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

is further suppressed by the addition of largely ionised ammonium chloride (**common ion effect**). But the OH^- ion concentration, although extremely small, is larger than is required to exceed the solubility product of hydroxide of iron, aluminium or chromium. These cations, therefore, get precipitated as hydroxides in Group III of qualitative analysis in the presence of excess of ammonium chloride. But zinc or magnesium cations do not get precipitated (as hydroxides) in the presence of ammonium chloride since their solubility products are much higher.

7. Other Precipitation Reactions. The concept of solubility product also helps in explaining why a moderately weak acid is able to produce a precipitate when added to a solution of a salt of a weak acid but not when added to a solution of a salt of a strong acid. For example, oxalic acid will cause complete precipitation of calcium acetate as calcium oxalate but not that of calcium chloride or calcium nitrate. The reaction in this case is

$$(CH_3COO)_2Ca + H_2C_2O_4 \longrightarrow CaC_2O_4 + 2CH_3COOH$$

The concentration of oxalate ion ($C_2O_4^{2-}$) is sufficient to make the ionic product $[Ca^{2+}][C_2O_4^{2-}]$ greater than the solubility product of calcium oxalate. The acetic acid that is formed is very slightly ionised and, therefore, it cannot alter the ionisation of oxalic acid which is much stronger than acetic acid. If, however, oxalic acid is added to a solution of calcium chloride, the hydrochloric acid that is formed is largely ionised and the increase in the hydrogen ion concentration will suppress the ionisation of oxalic acid. Therefore, the oxalate ion concentration falls below the value required to exceed the solubility product of calcium oxalate. As a result, the precipitation of calcium oxalate is incomplete.

8. Dissolution of Precipitates of Phosphates, Carbonates, Sulphides, etc., in Acid Solutions. It is well known that the precipitates of salts of weak acids, such as phosphates, carbonates, sulphides, are soluble in dilute hydrochloric or nitric acid but the precipitates of salts of strong acids, such as chlorides and sulphates, are not.

Consider zinc sulphide as a representative of the first category of precipitates. When suspended in water, the following equilibrium exists :

$$ZnS(s,\ satd.\ soln.) \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq)$$

If a largely dissociated acid such as hydrochloric acid or nitric acid is added, the hydrogen ions combine with sulphide ions to form hydrogen sulphide,

$$2H^+ + S^{2-} \longrightarrow H_2S\uparrow$$

which, being a sparingly soluble gas, will escape into the atmosphere. Therefore, the dynamic equilibrium between solid zinc sulphide and its ions will be disturbed and more of the solid ZnS will pass into solution as Zn^{2+} and S^{2-} ions. The sulphide ions will again be taken up by hydrogen ions to form hydrogen sulphide gas, and so on. In this way the whole of zinc sulphide passes into solution ultimately.

Consider barium sulphate as a representative of the second category of precipitates, *i.e.*, sparingly soluble salts of strong acids. When added to water, the following equilibrium exists :

$$BaSO_4(s,\ satd.\ soln.) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

The added H^+ ions (through the addition of hydrochloric acid or nitric acid) will not be able to remove sulphate ions since sulphuric acid formed is very largely ionised and, therefore, the above equilibrium is not materially disturbed. Consequently, barium sulphate does not dissolve in hydrochloric acid or nitric acid.

Ionic Equilibria Involving Complex Ions

As is well known, AgCl, which is only sparingly soluble in water, dissolves completely in aqueous ammonia solution. The increased solubility is due to the formation of a soluble complex $[Ag(NH_3)_2]Cl$. The various equilibria involved in the dissolution of AgCl in aqueous ammonia solution are as follows :

(i) $$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$K_{sp} = [Ag^+][Cl^-]$$

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

(Complex ion)

The equilibrium constant for reaction *(ii)*, designated as **stability constant**, K_{stab}, of the complex ion, is given by

$$K_{stab} = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2}$$

Adding reactions *(i)* and *(ii)*, we have

(iii) $$AgCl(s) + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-$$

The equilibrium constant for the overall reaction *(iii)* is given by

$$K_{eq} = \frac{[Ag(NH_3)_2]^+[Cl^-]}{[NH_3]^2} = \frac{[Ag^+][Cl^-][Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2} = K_{sp}\,K_{stab}$$

The complex ion formed in reaction *(ii)* is highly stable, the stability constant being as high as $1{\cdot}67\times10^7$. The formation of a stable complex ion in reaction *(ii)* upsets equilibrium *(i)* thereby causing it to shift to the right according to Le Chatelier's principle. As a result, AgCl(*s*) dissolves completely on the addition of excess of aqueous ammonia.

Example 35. Calculate the molar solubility of $Zn(OH)_2$ in 1 M ammonia solution at room temperature. $K_{sp}(Zn(OH)_2) = 1{\cdot}8\times10^{-17}$; K_{stab} of $[Zn(NH_3)_4]^{2+} = 1{\cdot}64\times10^{10}$.

Solution : The solubility equilibrium in this case is represented as

(i) $$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$$

$$K_{sp} = [Zn^{2+}][OH^-]^2 = 1{\cdot}18\times10^{-17}$$

(ii) $$Zn^{2+} + 4NH_3(aq) \rightleftharpoons [Zn(NH_3)_4]^{2+}$$

$$K_{stab} = \frac{[Zn(NH_3)_4]^{2+}}{[Zn^{2+}][NH_3]^4}$$

The overall reaction is obtained by adding reactions *(i)* and *(ii)* :

$$\underset{1-4x}{Zn(OH)_2(s) + 4NH_3(aq)} \rightleftharpoons \underset{x}{[Zn(NH_3)_4]^{2+}} + \underset{2x}{2OH^-(aq)}$$

$$K_{eq} = \frac{[Zn(NH_3)_4]^{2+}[OH^-]^2}{[NH_3]^4} = \frac{[Zn^{2+}][OH^-]^2[Zn(NH_3)_4]^{2+}}{[Zn^{2+}][NH_3]^4} = K_{sp}\,K_{stab}$$

If x is the molar solubility of $Zn(OH)_2$ in 1 M NH_3 solution, then, at equilibrium,

$$[NH_3] = 1 - 4x\ ;\quad [OH^-] = 2x \quad \text{and} \quad [Zn(NH_3)_4]^{2+} = x.$$

$$K_{eq} = \frac{x(2x)^2}{(1-4x)^4} = 4x^3 \ (\text{since } 4x \ll 1)$$

$$4x^3 = K_{eq} = K_{sp}\,K_{stab} = (1{\cdot}8\times10^{-17})\,(1{\cdot}64\times10^{10})$$

$$x = 4{\cdot}19\times10^{-3}\ \text{mol dm}^{-3}$$

Example 36. Calculate the solubility of $Mg(OH)_2$ in *(i)* pure water *(ii)* 0·01 M NaOH and *(iii)* 0·01 M $Ba(OH)_2$. Given K_{sp} of $Mg(OH)_2 = 1{\cdot}2\times10^{-11}\ M^3$.

Solution : *(i)* The solubility equilibrium in this case is represented as

$$Mg(OH)_2\ (s,\ satd.\ soln.) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

$$K_{sp} = [Mg^{2+}][OH^-]^2 = s(2s)^2 = 4s^3$$

Hence, the molar solubility s is given by

$$s = (K_{sp}/4)^{1/3} = (1{\cdot}2\times10^{-11}\ M^3/4)^{1/3} = \mathbf{1{\cdot}442\times10^{-4}\ M}$$

(ii) NaOH, being a strong electrolyte, will suppress the dissociation of $Mg(OH)_2$ due to common ion effect, thereby decreasing its solubility.

Let s' be the new molar solubility of $Mg(OH)_2$ in the presence of NaOH. Then

$$[Mg^{2+}] = s'\ ;\ [OH^-] = 0{\cdot}01 + 2s'$$