

Ionic Equilibria:

Strong, moderate and weak electrolytes, degree of ionization, factors affecting degree of ionization, ionization constant and ionic product of water. Ionization of weak acids and bases, pH scale, common ion effect. Salt hydrolysis-calculation of hydrolysis constant, degree of hydrolysis and pH for different salts. Buffer solutions. Solubility and solubility product of sparingly soluble salts – applications of solubility product principle.

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



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

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]} \quad \dots(5)$$

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

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

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

$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}] \quad \dots(7)$$

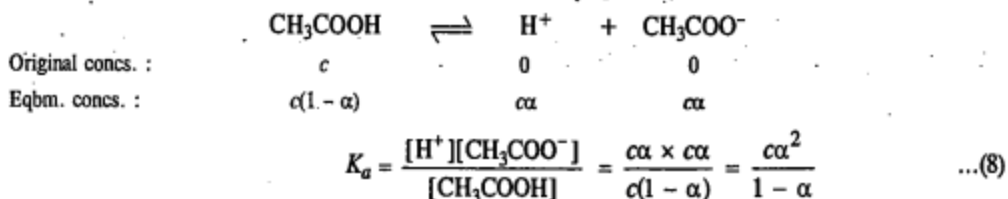
The significance of Eq. 7 is that the product of the concentrations of the hydrogen ion and the anion, irrespective of their source (*i.e.*, whether furnished by the acid itself or by any other substance present in the solution) divided by the concentration of the undissociated acid, is equal to a constant. 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



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 :



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

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

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

$$\alpha_1/\alpha_2 = \sqrt{K_{a_1}/K_{a_2}} \quad \dots(10)$$

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.

$$\frac{\text{Strength of one acid, HA}_1}{\text{Strength of another acid, HA}_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}} \quad \dots(11)$$

Example 4. The dissociation constants of formic and acetic acids are 1.77×10^{-4} and 1.75×10^{-5} , respectively. Calculate the relative strengths of the two acids.

Solution : According to Eq. 11,

$$\frac{\text{Strength of formic acid}}{\text{Strength of acetic acid}} = \sqrt{\frac{K_a \text{ formic acid}}{K_a \text{ acetic acid}}} = \sqrt{\frac{1.77 \times 10^{-4}}{1.75 \times 10^{-5}}} = 3.18$$

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: $\alpha = \Lambda_m / \Lambda_m^\circ$.

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

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

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

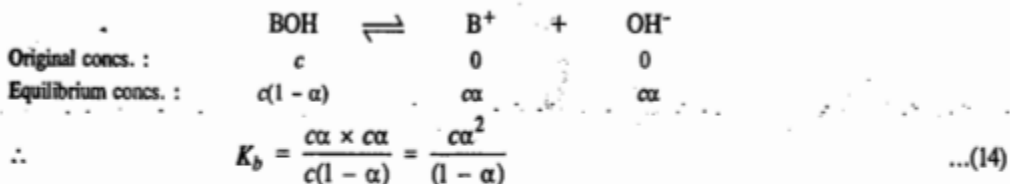


Applying the equilibrium law equation, the dissociation constant, K_b , of the base, will be given by

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

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,

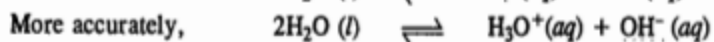
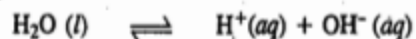


Since, for a weak base, α is very small as compared to 1, Eq. 14, as before, is reduced to

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

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

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



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

$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \quad \dots(16)$$

Since dissociation takes place to a very small extent, the concentration of the undissociated water molecules, $[\text{H}_2\text{O}]$, may be regarded as constant, say k .

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

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

Hence, Eq. 17 is written as

$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ at } 25^\circ\text{C} \quad \dots(18)$$

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

$$[\text{H}^+] = [\text{OH}^-] = \sqrt{K_w} = \sqrt{1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}} = 1 \times 10^{-7} \text{ mol dm}^{-3}$$

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.

pH 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 $25^\circ C$. 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 pH scale was introduced by the Danish biochemist S.P. Sørensen (1868-1939) in 1909. As defined by him, the pH of a solution is the negative logarithm (to the base 10) of the concentration (in moles per litre) of hydrogen ions which it contains.

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

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

Example 7. Calculate the pH 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

$$[H^+] = 0.0001 \text{ mol dm}^{-3}$$

$$\therefore \quad \text{pH} = -\log [H^+] = -\log [0.0001] = 4$$

(b) Concentration of HNO_3 = 0.04 M

Since HNO_3 is completely dissociated, hence

$$[H^+] = 0.04 \text{ mol dm}^{-3}$$

$$\therefore \quad \text{pH} = -\log [H^+] = -\log [0.04] = 1.398$$

Example 8. Calculate the hydrogen ion concentration in moles per litre of a solution whose pH is 5.4.

Solution : pH of the solution = 5.4

$$\text{pH} = -\log [H^+]$$

$$\text{or } \quad \log [H^+] = -5.4 = \bar{6}.600$$

$$\therefore \quad [H^+] = 3.98 \times 10^{-6} \text{ mol dm}^{-3}$$

Example 9. Calculate the pH 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

$$\text{Number of millimoles of the acid in the solution} = 50 \times 0.2 = 10$$

$$\text{Number of millimoles of the alkali in the solution} = 50 \times 0.1 = 5$$

$$\text{Number of millimoles of the acid left in the solution after the addition of alkali} = 10 - 5 = 5$$

$$\text{Total volume of the solution} = 50 + 50 = 100 \text{ ml}$$

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.

$$\therefore \quad \text{Concentration of } H^+ \text{ ions} = 0.05 \text{ mol dm}^{-3}$$

$$\therefore \quad \text{pH of the solution} = -\log [H^+] = -\log (0.05) = 1.30$$

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,



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 a 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



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**.

BUFFER SOLUTIONS

For many purposes in chemistry, industry and biology, it is necessary to have solutions whose *pH* does not change much even on the addition of appreciable amounts of strong acids or strong alkalis. 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.

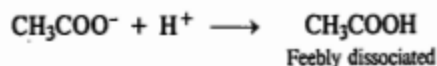
Consider a solution of sodium chloride in water. Its *pH* is 7. The addition of even 1 ml of 1 M HCl solution to one litre of sodium chloride solution lowers the *pH* of the solution from 7 to about 3. Similarly, the addition of 1 ml of 1 M NaOH solution to one litre of sodium chloride solution raises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

The *pH* 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 pH of ammonium acetate solution. Thus, ammonium acetate solution is a buffer as it can resist alterations in its pH on the addition of an acid or a base.

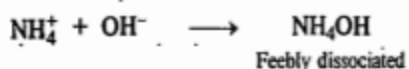
Let us see why a solution of ammonium acetate is a buffer while that of sodium chloride is not.

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 :



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 pH) 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 :



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 pH 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 pH 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 pH 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 pH , is known as its *buffer capacity*.

HYDROLYSIS OF SALTS

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



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.

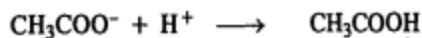
1. Salts of Strong Acids and Strong Bases. Salts of strong acids and strong bases *do not hydrolyse*. Consider, for example, potassium chloride. When it is dissolved in water, its ions, K^+ and Cl^- , have no tendency to react with the H^+ and OH^- ions of water. This is because the possible products 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.



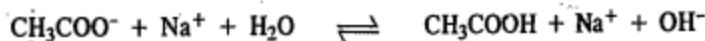
The acetate ions will take up some of the H^+ ions furnished by the slightly dissociated water to form the feebly dissociated acetic acid :



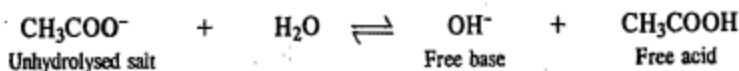
The undissociated water further dissociates so as to maintain the constant value of $K_w = [H^+][OH^-]$. The H^+ ions are again taken up by CH_3COO^- ions. This leads to an increase in the concentration of hydroxyl ions and decrease in the concentration of hydrogen ions. The solution, therefore, becomes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



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

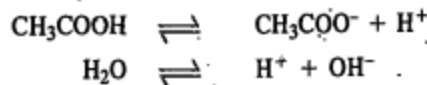


Applying the law of chemical equilibrium and taking the concentration of water as constant (since it is present in large excess), we have

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

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 equilibria have also to be satisfied :



Therefore, the following equations should also hold good :

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

where K_a is the dissociation constant of the acid and

$$K_w = [H^+][OH^-] \quad \dots(33)$$

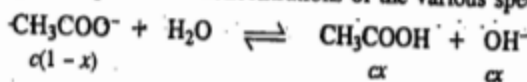
Dividing Eq. 33 by Eq. 32, we get

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

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

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



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

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

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

But,

$$K_h = K_w/K_a \quad \text{(Eq. 34)}$$

\therefore

$$x = \sqrt{K_w/(K_a \times c)} \quad \dots(36)$$

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. $K_a = 1.75 \times 10^{-5}$ and $K_w = 1.008 \times 10^{-14}$.

Solution :
$$K_h = K_w/K_a = \frac{1.008 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.76 \times 10^{-10}$$

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

$$x = \sqrt{K_h/c} = \sqrt{\frac{5.76 \times 10^{-10}}{0.10}} = 7.589 \times 10^{-5}$$

Thus, the degree of hydrolysis = 7.589×10^{-5}

pH of the Hydrolysed Salt Solution. As shown above, in the hydrolysis of CH_3COONa , $[\text{OH}^-] = cx$. Substituting the value of x from Eq. 36, we have

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

Taking negative logs of both sides, we get

$$p\text{OH} = \frac{1}{2} pK_w - \frac{1}{2} \log c - \frac{1}{2} pK_a$$

But

$$p\text{H} + p\text{OH} = 14$$

\therefore

$$p\text{H} = 14 - \frac{1}{2} pK_w + \frac{1}{2} \log c + \frac{1}{2} pK_a \quad \dots(37)$$

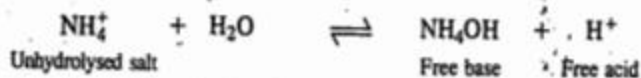
3. Salts of Weak Bases and Strong Acids. Consider ammonium chloride as an example of this category of salts. In water, it undergoes almost complete dissociation into NH_4^+ and Cl^- ions. The ammonium ions take up OH^- ions furnished by water to form the feebly dissociated base, ammonium hydroxide (NH_4OH). 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



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



Applying the law of chemical equilibrium, we have

$$K_h = [\text{H}^+][\text{NH}_4\text{OH}]/[\text{NH}_4^+] \quad \dots(38)$$

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 :



and



Accordingly, the following equations should also hold good :

$$K_b = [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_4\text{OH}] \quad \dots(39)$$

where K_b is the dissociation constant of the base and

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

Dividing Eq. 40 by Eq. 39, we get

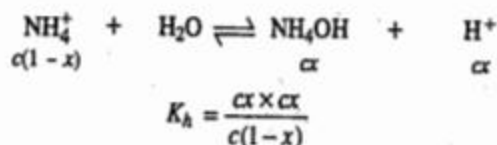
$$K_w/K_b = [\text{H}^+][\text{NH}_4\text{OH}]/[\text{NH}_4^+] = K_h \quad (\text{from Eq. 38})$$

Thus,

$$K_h = K_w/K_b \quad \dots(41)$$

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 :



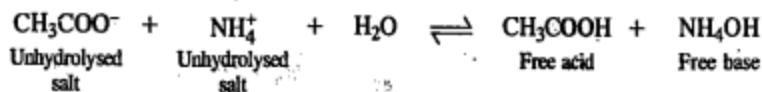
If, as before, x is too small as compared to unity

$$K_h = cx^2 \quad \dots(42)$$

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

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.

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



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

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} \quad \dots(46)$$

The following other equilibria also exist in the solution :



Accordingly, the following equations should hold good :

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \quad \dots(47)$$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \dots(48)$$

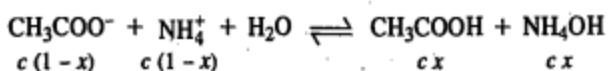
$$K_w = [\text{H}^+][\text{OH}^-] \quad \dots(49)$$

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

$$\frac{K_w}{K_a \times K_b} = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} = K_h \quad \text{(from Eq. 46)}$$

Thus, in this case,
$$K_h = \frac{K_w}{K_a \times K_b} \quad \dots(50)$$

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 :



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

Neglecting x as compared to unity, we have

$$K_h = x^2 \quad \dots(52)$$

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

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.

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

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \dots(54)$$

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

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

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

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

$$= \left(\frac{K_w K_a}{K_b} \right)^{1/2} \quad \dots(56)$$

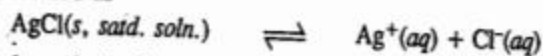
Taking negative logs of both sides,

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} pK_b \quad \dots(57)$$

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.

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



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

$$K = \frac{a_{\text{Ag}^+} \times a_{\text{Cl}^-}}{a_{\text{AgCl}}} \quad \dots(64)$$

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

$$K_{sp} = a_{\text{Ag}^+} \times a_{\text{Cl}^-} \quad \dots(65)$$

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,

$$K'_{sp} = [\text{Ag}^+][\text{Cl}^-] \quad \dots(66)$$

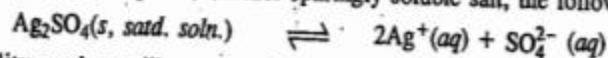
where the square brackets, as usual, represent the concentrations of the entities enclosed within. In the case of sparingly soluble salts since the ionic concentrations are very low, activity of each ion is almost equal to its concentration. Hence,

$$K_{sp} = K'_{sp} \quad \dots(67)$$

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

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

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

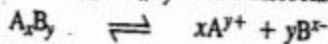


The solubility product will now be given by the expression

$$K_{sp} = [\text{Ag}^+]^2[\text{SO}_4^{2-}]$$

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

Consider, in general, a salt of the type A_xB_y which dissociates as



The solubility product of the salt is now given by

$$K_{sp} = [\text{A}^{y+}]^x [\text{B}^{x-}]^y \quad \dots(68)$$

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 :



The true solubility product constant is given by the equation

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

and the concentration solubility product is given by the expression

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

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.

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 :



If the molar solubility of the salt is s , then

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

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

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

$$\dots \dots \dots \text{ g mol}^{-1} = 5.842 \times 10^{-7} \text{ g dm}^{-3}$$

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

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

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 $2.4 \times 10^{-5} \text{ M}^2$. 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



$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = 2.4 \times 10^{-5} \text{ M}^2$$

$$[\text{Ca}^{2+}] \text{ in water} = 0.01 \text{ M}$$

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

$$[\text{Ca}^{2+}] \text{ in the mixture} = 0.01/2 = 0.005 \text{ M}$$

$$\text{Concentration of sulphuric acid} = 0.001 \text{ M}$$

$$\therefore [\text{SO}_4^{2-}] = 0.001 \text{ M}$$

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

$$[\text{SO}_4^{2-}] \text{ in the mixture} = 0.001/2 = 0.0005 \text{ M}$$

The product of concentrations of ions

$$[\text{Ca}^{2+}][\text{SO}_4^{2-}] = 0.005 \text{ M} \times 0.0005 \text{ M} = 2.5 \times 10^{-6} \text{ M}^2$$

Evidently, the ionic product is less than the solubility product of CaSO_4 which is equal to $2.4 \times 10^{-5} \text{ M}^2$. 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).

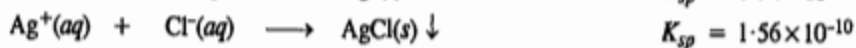
$$[\text{Ca}^{2+}] \text{ in the mixture} = 0.01/2 = 0.005 \text{ M}$$

$$[\text{SO}_4^{2-}] \text{ in the mixture} = 0.02/2 = 0.01 \text{ M}$$

$$\text{The ionic product } [\text{Ca}^{2+}][\text{SO}_4^{2-}] = 0.005 \text{ M} \times 0.01 \text{ M} = 5 \times 10^{-5} \text{ M}^2$$

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

3. Fractional Precipitation. Consider an aqueous solution of KCl and KI to which AgNO₃ solution is added. Since $K_{sp}(\text{AgI})$ is less than $K_{sp}(\text{AgCl})$, hence, $K_{sp}(\text{AgI})$ will be exceeded and AgI will be precipitated first :



$$\frac{[\text{I}^-]}{[\text{Cl}^-]} = \frac{K_{sp}(\text{AgI})}{K_{sp}(\text{AgCl})} = \frac{0.94 \times 10^{-16}}{1.56 \times 10^{-10}} = 6.0 \times 10^{-7} \approx 10^{-6}$$

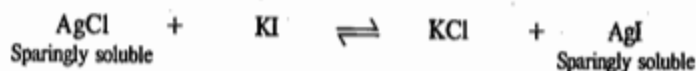
Thus, AgI will start precipitating out when $[\text{I}^-]$ is approximately one-millionth part of $[\text{Cl}^-]$.

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

$$[\text{Ag}^+] = \frac{K_{sp}(\text{AgCl})}{[\text{Cl}^-]} = \frac{1.56 \times 10^{-10}}{[\text{Cl}^-]}$$

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



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

$$K_{sp}(\text{AgCl}) = [\text{Ag}^+][\text{Cl}^-] = 1.56 \times 10^{-10} \quad (\text{Table 7})$$

and that of silver iodide,

$$K_{sp}(\text{AgI}) = [\text{Ag}^+][\text{I}^-] = 0.94 \times 10^{-16} \quad (\text{Table 7})$$

$$\therefore \frac{[\text{Cl}^-]}{[\text{I}^-]} = \frac{1.56 \times 10^{-10}}{0.94 \times 10^{-16}} = 1.66 \times 10^6$$

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 :

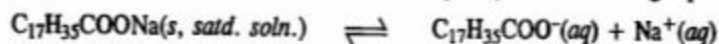


$$K_{sp} = [\text{Na}^+][\text{Cl}^-]$$

HCl gas is passed through this solution. The $[\text{Cl}^-]$, 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 :

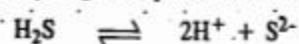


$$K'_{sp} = [C_{17}H_{35}COO^-][Na^+]$$

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



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



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

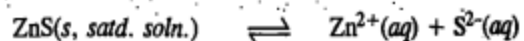
calcium nitrate. The reaction in this case is



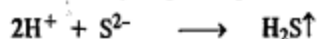
The concentration of oxalate ion ($\text{C}_2\text{O}_4^{2-}$) is sufficient to make the ionic product $[\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}]$ greater than the solubility product of calcium oxalate. The acetic acid that is formed is very slightly ionised and, therefore, it cannot alter the ionisation 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 :

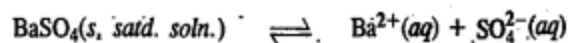


If a largely dissociated acid such as hydrochloric acid or nitric acid is added, the hydrogen ions combine with sulphide ions to form hydrogen sulphide,



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 :



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.