that in weak electrolytes, equilibrium is established between ions and the unionized molecules. This type of equilibrium involving ions in aqueous solution is called **ionic equilibrium**. Acids, bases and salts come under the category of electrolytes and may act as either strong or weak electrolytes.

6.10 ACIDS, BASES AND SALTS

Acids, bases and salts find widespread occurrence in nature. Hydrochloric acid present in the gastric juice is secreted by the lining of our stomach in a significant amount of 1.2-1.5 L/day and is essential for digestive processes. Acetic acid is known to be the main constituent of vinegar. Lemon and orange juices contain citric and ascorbic acids, and tartaric acid is found in tamarind paste. As most of the acids taste sour, the word "acid" has been derived from a latin word "*acidus*" meaning sour. Acids are known to turn blue litmus paper into red and liberate dihydrogen on reacting with some metals. Similarly, bases are known to turn red litmus paper blue, taste bitter and feel soapy. A common example of a base is washing soda used for washing purposes. When acids and bases are mixed in the right proportion they react with each other to give *salts*. Some commonly known examples of salts are sodium chloride, barium sulphate, sodium nitrate. Sodium chloride (common salt) is an important component of our diet and is formed by reaction between hydrochloric acid and sodium hydroxide. It exists in solid state as a cluster of positively charged sodium ions and negatively charged chloride ions which are held together due to electrostatic interactions between oppositely charged species (Fig.6.10). The electrostatic forces between two charges are inversely proportional to dielectric constant of the medium. Water, a universal solvent, possesses a very high dielectric constant of 80. Thus, when sodium chloride is dissolved in water, the electrostatic interactions are reduced by a factor of 80 and this facilitates the ions to move freely in the solution. Also, they are well-separated due to hydration with water molecules.
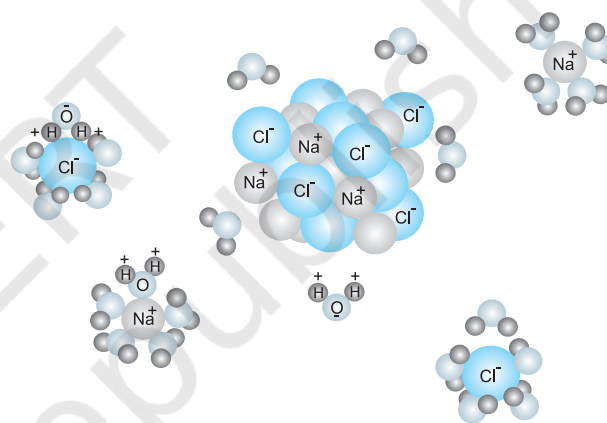

Fig.6.10 *Dissolution of sodium chloride in water. Na⁺ and Cl⁻ ions are stablised by their hydration with polar water molecules.*

Comparing, the ionization of hydrochloric acid with that of acetic acid in water we find that though both of them are polar covalent

molecules, former is completely ionized into its constituent ions, while the latter is only partially ionized (< 5%). The extent to which ionization occurs depends upon the strength of the bond and the extent of solvation of ions produced. The terms dissociation and ionization have earlier been used with different meaning. Dissociation refers to the process of separation of ions in water already existing as such in the solid state of the solute, as in sodium chloride. On the other hand, ionization corresponds to a process in which a neutral molecule splits into charged ions in the solution. Here, we shall not distinguish between the two and use the two terms interchangeably.

6.10.1 Arrhenius Concept of Acids and Bases

According to Arrhenius theory, *acids are substances that dissociates in water to give hydrogen ions $H^+(aq)$ and bases are substances that produce hydroxyl ions $OH^-(aq)$.* The ionization of an acid HX (aq) can be represented by the following equations:

$$HX (aq) \rightarrow H^+(aq) + X^- (aq)$$
$$or$$
$$HX(aq) + H_2O(l) \rightarrow H_3O^+(aq) + X^-(aq)$$
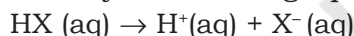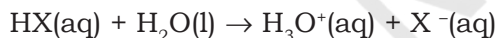
A bare proton, H^+ is very reactive and cannot exist freely in aqueous solutions. Thus, it bonds to the oxygen atom of a solvent water molecule to give *trigonal pyramidal* **hydronium ion**, H_3O^+ {$[H (H_2O)]^+$} (see box). In this chapter we shall use $H^+(aq)$ and $H_3O^+(aq)$ interchangeably to mean the same i.e., a hydrated proton.

Similarly, a base molecule like MOH ionizes in aqueous solution according to the equation:

$$MOH(aq) \rightarrow M^+(aq) + OH^-(aq)$$
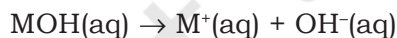
The hydroxyl ion also exists in the hydrated form in the aqueous solution. Arrhenius concept of acid and base, however, suffers from the limitation of being applicable only to aqueous solutions and also, does not account for the basicity of substances like, ammonia which do not possess a hydroxyl group.

Hydronium and Hydroxyl Ions

Hydrogen ion by itself is a bare proton with very small size (~10^{-15} m radius) and intense electric field, binds itself with the water molecule at one of the two available lone pairs on it giving H_3O^+. This species has been detected in many compounds (e.g., $H_3O^+Cl^-$) in the solid state. In aqueous solution the hydronium ion is further hydrated to give species like $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$. Similarly the hydroxyl ion is hydrated to give several ionic species like $H_3O_2^-$, $H_5O_3^-$ and $H_7O_4^-$ etc.
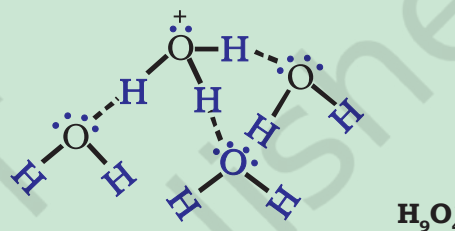
6.10.2 The Brönsted-Lowry Acids and Bases

The Danish chemist, Johannes Brönsted and the English chemist, Thomas M. Lowry gave a more general definition of acids and bases. According to Brönsted-Lowry theory, *acid is a substance that is capable of donating a hydrogen ion H^+ and bases are substances capable of accepting a hydrogen ion, H^+.* In short, acids are proton donors and bases are proton acceptors.

Consider the example of dissolution of NH_3 in H_2O represented by the following equation:
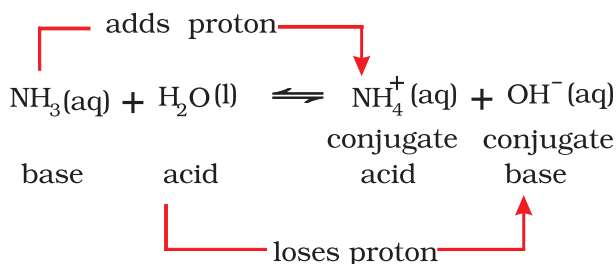
The basic solution is formed due to the presence of hydroxyl ions. In this reaction, water molecule acts as proton donor and ammonia molecule acts as proton acceptor and are thus, called Lowry-Brönsted acid and

Arrhenius was born near Uppsala, Sweden. He presented his thesis, on the conductivities of electrolyte solutions, to the University of Uppsala in 1884. F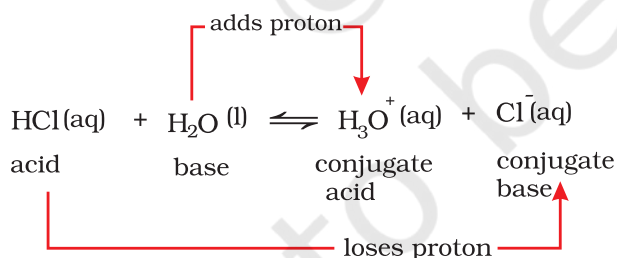or the next five years he travelled extensively and visited a number of research centers in Europe. In 1895 he was appointed professor of physics at the newly formed University of Stockholm, serving its rector from 1897 to 1902. From 1905 until his death he was Director of physical chemistry at the Nobel Institute in Stockholm. He continued to work for many years on electrolytic solutions. In 1899 he discussed the temperature dependence of reaction rates on the basis of an equation, now usually known as Arrhenius equation.

Svante Arrhenius (1859-1927)

He worked in a variety of fields, and made important contributions to immunochemistry, cosmology, the origin of life, and the causes of ice age. He was the first to discuss the 'green house effect' calling by that name. He received Nobel Prize in Chemistry in 1903 for his theory of electrolytic dissociation and its use in the development of chemistry.

base, respectively. In the reverse reaction, H^+ is transferred from NH_4^+ to OH^-. In this case, NH_4^+ acts as a Bronsted acid while OH^- acted as a Brönsted base. The acid-base pair that differs only by one proton is called a **conjugate acid-base pair**. Therefore, OH^- is called the conjugate base of an acid H_2O and NH_4^+ is called conjugate acid of the base NH_3. If Brönsted acid is a strong acid then **its conjugate base is a weak base and *vice-versa.*** It may be noted that conjugate acid has one extra proton and each conjugate base has one less proton.

Consider the example of ionization of hydrochloric acid in water. HCl(aq) acts as an acid by donating a proton to H_2O molecule which acts as a base.

$$\text{HCl(aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{H}_3\text{O}^+ \text{(aq)} + \text{Cl}^-\text{(aq)}$$

acid   base   conjugate   conjugate
                            acid   base

It can be seen in the above equation, that water acts as a base because it accepts the proton. The species H_3O^+ is produced when water accepts a proton from HCl. Therefore, Cl^- is a conjugate base of HCl and HCl is the conjugate acid of base Cl^-. Similarly, H_2O is a conjugate base of an acid H_3O^+ and H_3O^+ is a conjugate acid of base H_2O.

It is interesting to observe the dual role of water as an acid and a base. In case of reaction with HCl water acts as a base while

in case of ammonia it acts as an acid by donating a proton.

Problem 6.12

What will be the conjugate bases for the following Brönsted acids: HF, H_2SO_4 and HCO_3^-?

Solution

The conjugate bases should have one proton less in each case and therefore the corresponding conjugate bases are: F^-, HSO_4^- and CO_3^{2-} respectively.

Problem 6.13

Write the conjugate acids for the following Brönsted bases: NH_2^-, NH_3 and $HCOO^-$.

Solution

The conjugate acid should have one extra proton in each case and therefore the corresponding conjugate acids are: NH_3, NH_4^+ and HCOOH respectively.

Problem 6.14

The species: H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and conjugate base.

Solution

The answer is given in the following Table:

Species	Conjugate acid	Conjugate base
H_2O	H_3O^+	OH^-
HCO_3^-	H_2CO_3	CO_3^{2-}
HSO_4^-	H_2SO_4	SO_4^{2-}
NH_3	NH_4^+	NH_2^-

6.10.3 Lewis Acids and Bases

G.N. Lewis in 1923 defined an *acid as a species which accepts electron pair and base which donates an electron pair*. As far as bases are concerned, there is not much difference between Brönsted-Lowry and Lewis concepts, as the base provides a lone pair in both the cases. However, in Lewis concept many acids do not have proton. A typical example is reaction of electron deficient species BF_3 with NH_3.

BF_3 does not have a proton but still acts as an acid and reacts with NH_3 by accepting its lone pair of electrons. The reaction can be represented by,

$$BF_3 + :NH_3 \rightarrow BF_3:NH_3$$
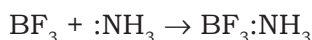
Electron deficient species like $AlCl_3$, Co^{3+}, Mg^{2+}, etc. can act as Lewis acids while species like H_2O, NH_3, OH^- etc. which can donate a pair of electrons, can act as Lewis bases.

Problem 6.15

Classify the following species into Lewis acids and Lewis bases and show how these act as such:

(a) HO^- (b) F^- (c) H^+ (d) BCl_3

Solution

(a) Hydroxyl ion is a Lewis base as it can donate an electron lone pair ($:OH^-$).

(b) Flouride ion acts as a Lewis base as it can donate any one of its four electron lone pairs.

(c) A proton is a Lewis acid as it can accept a lone pair of electrons from bases like hydroxyl ion and fluoride ion.

(d) BCl_3 acts as a Lewis acid as it can accept a lone pair of electrons from species like ammonia or amine molecules.

6.11 IONIZATION OF ACIDS AND BASES

Arrhenius concept of acids and bases becomes useful in case of ionization of acids and bases as mostly ionizations in chemical and biological systems occur in aqueous medium. Strong acids like perchloric acid

($HClO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), hyrdoiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) are termed *strong* because they are almost completely dissociated into their constituent ions in an aqueous medium, thereby acting as proton (H^+) donors. Similarly, strong bases like lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), caesium hydroxide (CsOH) and barium hydroxide $Ba(OH)_2$ are almost completely dissociated into ions in an aqueous medium giving hydroxyl ions, OH^-. According to Arrhenius concept they are strong acids and bases as they are able to completely dissociate and produce H_3O^+ and OH^- ions respectively in the medium. Alternatively, the strength of an acid or base may also be gauged in terms of Brönsted-Lowry concept of acids and bases, wherein a strong acid means a good proton donor and a strong base implies a good proton acceptor. Consider, the acid-base dissociation equilibrium of a weak acid HA,

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$
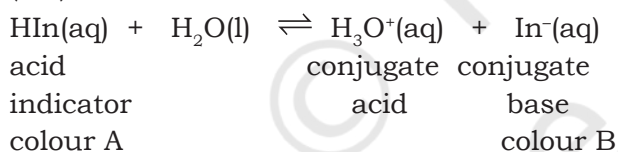conjugate   conjugate
acid   base   acid   base
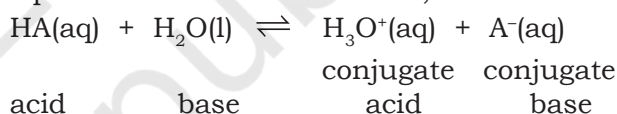
In section 6.10.2 we saw that acid (or base) dissociation equilibrium is dynamic involving a transfer of proton in forward and reverse directions. Now, the question arises that if the equilibrium is dynamic then with passage of time which direction is favoured? What is the driving force behind it? In order to answer these questions we shall deal into the issue of comparing the strengths of the two acids (or bases) involved in the dissociation equilibrium. Consider the two acids HA and H_3O^+ present in the above mentioned acid-dissociation equilibrium. We have to see which amongst them is a stronger proton donor. Whichever exceeds in its tendency of donating a proton over the other shall be termed as the stronger acid and the equilibrium will shift in the direction of weaker acid. Say, if HA is a stronger acid than H_3O^+, then HA will donate protons and not H_3O^+, and the solution will mainly contain A^- and H_3O^+ ions. The equilibrium moves in the direction of formation of weaker acid

and weaker base because **the stronger acid donates a proton to the stronger base**.

It follows that as a strong acid dissociates completely in water, the resulting base formed would be very weak i.e., **strong acids have very weak conjugate bases.** Strong acids like perchloric acid ($HClO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) will give conjugate base ions ClO_4^-, Cl, Br^-, I^-, NO_3^- and HSO_4^-, which are much weaker bases than H_2O. Similarly a very strong base would give a very weak conjugate acid. On the other hand, a weak acid say HA is only partially dissociated in aqueous medium and thus, the solution mainly contains undissociated HA molecules. Typical weak acids are nitrous acid (HNO_2), hydrofluoric acid (HF) and acetic acid (CH_3COOH). It should be noted that the *weak acids have very strong conjugate bases*. For example, NH_2^-, O^{2-} and H^- are very good proton acceptors and thus, much stronger bases than H_2O.
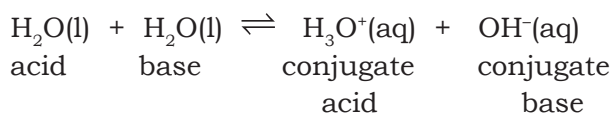
Certain water soluble organic compounds like phenolphthalein and bromothymol blue behave as weak acids and exhibit different colours in their acid (HIn) and conjugate base (In^-) forms.

HIn(aq) + H_2O(l) $\rightleftharpoons$ H_3O^+(aq) + In^-(aq)
acid   conjugate   conjugate
indicator   acid   base
colour A   colour B

Such compounds are useful as indicators in acid-base titrations, and finding out H^+ ion concentration.

6.11.1 The Ionization Constant of Water and its Ionic Product

Some substances like water are unique in their ability of acting both as an acid and a base. We have seen this in case of water in section 6.10.2. In presence of an acid, HA it accepts a proton and acts as the base while in the presence of a base, B^- it acts as an acid by donating a proton. In pure water, one H_2O molecule donates proton and acts as an acid and another water molecules accepts a proton and acts as a base at the same time. The following equilibrium exists:

H_2O(l) + H_2O(l) $\rightleftharpoons$ H_3O^+(aq) + OH^-(aq)
acid   base   conjugate   conjugate
                         acid   base

The dissociation constant is represented by,

$\quad K = [H_3O^+] [OH^-] / [H_2O]$ $\qquad$ (6.26)

The concentration of water is omitted from the denominator as water is a pure liquid and its concentration remains constant. [H_2O] is incorporated within the equilibrium constant to give a new constant, K_w, which is called the **ionic product of water**.

$\quad K_w = [H^+][OH^-]$ $\qquad\qquad$ (6.27)

The concentration of H^+ has been found out experimentally as 1.0×10^{-7} M at 298 K. And, as dissociation of water produces equal number of H^+ and OH^- ions, the concentration of hydroxyl ions, [OH^-] = [H^+] = 1.0×10^{-7} M. Thus, the value of K_w at 298K,

$K_w = [H_3O^+][OH^-] = (1 \times 10^{-7})^2 = 1 \times 10^{-14}$ M^2

$\qquad\qquad\qquad\qquad\qquad\qquad$ (6.28)

The value of K_w is temperature dependent as it is an equilibrium constant.

The density of pure water is 1000 g / L and its molar mass is 18.0 g /mol. From this the molarity of pure water can be given as,

[H_2O] = (1000 g /L)(1 mol/18.0 g) = 55.55 M. Therefore, the ratio of dissociated water to that of undissociated water can be given as:

10^{-7} / (55.55) = 1.8×10^{-9} or ~ 2 in 10^{-9} (thus, equilibrium lies mainly towards undissociated water)

We can distinguish acidic, neutral and basic aqueous solutions by the relative values of the H_3O^+ and OH^- concentrations:

Acidic: [H_3O^+] > [OH^-]

Neutral: [H_3O^+] = [OH^-]

Basic : [H_3O^+] < [OH^-]

6.11.2 The pH Scale

Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the **pH scale**. The pH of a solution is defined as the negative logarithm to base 10 of the activity $\left(a_{H^+}\right)$ of hydrogen

ion. In dilute solutions (< 0.01 M), activity of hydrogen ion (H⁺) is equal in magnitude to molarity represented by [H⁺]. It should be noted that activity has no units and is defined as:

a_{H^+} = [H⁺] / mol L⁻¹

From the definition of pH, the following can be written,

pH = – log a_{H+} = – log {[H⁺] / mol L⁻¹}

Thus, an acidic solution of HCl (10⁻² M) will have a pH = 2. Similarly, a basic solution of NaOH having [OH⁻] =10⁻⁴ M and [H₃O⁺] = 10⁻¹⁰ M will have a pH = 10. At 25 °C, pure water has a concentration of hydrogen ions, [H⁺] = 10⁻⁷ M. Hence, the pH of pure water is given as:

pH = –log(10⁻⁷) = 7

Acidic solutions possess a concentration of hydrogen ions, [H⁺] > 10⁻⁷ M, while basic solutions possess a concentration of hydrogen ions, [H⁺] < 10⁻⁷ M. thus, we can summarise that

Acidic solution has pH < 7

Basic solution has pH > 7

Neutral solution has pH = 7

Now again, consider the equation (6.28) at 298 K

K_w = [H₃O⁺] [OH⁻] = 10⁻¹⁴

Taking negative logarithm on both sides of equation, we obtain

–log K_w = – log {[H₃O⁺] [OH⁻]}
= – log [H₃O⁺] – log [OH⁻]
= – log 10⁻¹⁴

pK_w = pH + pOH = 14   (6.29)

Note that although K_w may change with temperature the variations in pH with temperature are so small that we often ignore it.

pK_w is a very important quantity for aqueous solutions and controls the relative concentrations of hydrogen and hydroxyl ions as their product is a constant. It should be noted that as the pH scale is logarithmic, a change in pH by just one unit also means change in [H⁺] by a factor of 10. Similarly,

when the hydrogen ion concentration, [H⁺] changes by a factor of 100, the value of pH changes by 2 units. Now you can realise why the change in pH with temperature is often ignored.

Measurement of pH of a solution is very essential as its value should be known when dealing with biological and cosmetic applications. The pH of a solution can be found roughly with the help of pH paper that has different colour in solutions of different pH. Now-a-days pH paper is available with four strips on it. The different strips have different colours (Fig. 6.11) at the same pH. The pH in the range of 1-14 can be determined with an accuracy of ~0.5 using pH paper.

Fig.6.11 pH-*paper with four strips that may have different colours at the same* pH

For greater accuracy pH meters are used. pH meter is a device that measures the pH-dependent electrical potential of the test solution within 0.001 precision. pH meters of the size of a writing pen are now available in the market. The pH of some very common substances are given in Table 6.5 (page 195).

Problem 6.16

The concentration of hydrogen ion in a sample of soft drink is 3.8 × 10⁻³M. what is its pH ?

Solution

pH = – log[3.8 × 10⁻³]
= – {log[3.8] + log[10⁻³]}
= – {(0.58) + (– 3.0)} = – { – 2.42} = 2.42

Therefore, the pH of the soft drink is 2.42 and it can be inferred that it is acidic.

**Problem 6.17**

Calculate pH of a 1.0 × 10⁻⁸ M solution of HCl.

Table 6.5 The pH of Some Common Substances

Name of the Fluid	pH	Name of the Fluid	pH
Saturated solution of NaOH	~15	Black Coffee	5.0
0.1 M NaOH solution	13	Tomato juice	~4.2
Lime water	10.5	Soft drinks and vinegar	~3.0
Milk of magnesia	10	Lemon juice	~2.2
Egg white, sea water	7.8	Gastric juice	~1.2
Human blood	7.4	1M HCl solution	~0
Milk	6.8	Concentrated HCl	~–1.0
Human Saliva	6.4		

Solution

$2H_2O\ (l) \rightleftharpoons H_3O^+\ (aq)\ +\ OH^-(aq)$
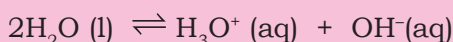
$K_w = [OH^-][H_3O^+]$

$\quad = 10^{-14}$

Let, $x = [OH^-] = [H_3O^+]$ from H_2O. The H_3O^+ concentration is generated (i) from the ionization of HCl dissolved i.e.,

$HCl(aq)\ +\ H_2O(l) \rightleftharpoons H_3O^+\ (aq)\ +\ Cl^-(aq)$,
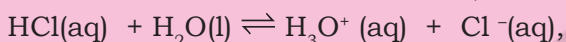
and (ii) from ionization of H_2O. In these very dilute solutions, both sources of H_3O^+ must be considered:

$[H_3O^+] = 10^{-8} + x$

$K_w = (10^{-8} + x)(x) = 10^{-14}$

or $x^2 + 10^{-8}\,x - 10^{-14} = 0$

$[OH^-] = x = 9.5 \times 10^{-8}$

So, pOH = 7.02 and pH = 6.98

6.11.3 Ionization Constants of Weak Acids

Consider a weak acid HX that is partially ionized in the aqueous solution. The equilibrium can be expressed by:

$HX(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + X^-(aq)$
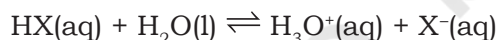
Initial
concentration (M)

c   0   0

Let α be the extent of ionization

Change (M)

-cα   +cα   +cα

Equilibrium concentration (M)

c-cα   cα   cα

Here, c = initial concentration of the undissociated acid, HX at time, t = 0. α = extent up to which HX is ionized into ions. Using these notations, we can derive the equilibrium constant for the above discussed acid-dissociation equilibrium:

$K_a = c^2\alpha^2\ /\ c(1-\alpha) = c\alpha^2\ /\ 1-\alpha$

K_a is called the **dissociation or ionization constant** of acid HX. It can be represented alternatively in terms of molar concentration as follows,

$K_a = [H^+][X^-]\ /\ [HX]$ \hfill (6.30)

At a given temperature *T*, K_a is a measure of the strength of the acid HX i.e., larger the value of K_a, the stronger is the acid. K_a is a dimensionless quantity with the understanding that the standard state concentration of all species is 1M.

The values of the ionization constants of some selected weak acids are given in Table 6.6.

Table 6.6   The Ionization Constants of Some Selected Weak Acids (at 298K)

Acid	Ionization Constant, K_a
Hydrofluoric Acid (HF)	3.5×10^{-4}
Nitrous Acid (HNO_2)	4.5×10^{-4}
Formic Acid (HCOOH)	1.8×10^{-4}
Niacin (C_5H_4NCOOH)	1.5×10^{-5}
Acetic Acid (CH_3COOH)	1.74×10^{-5}
Benzoic Acid (C_6H_5COOH)	6.5×10^{-5}
Hypochlorous Acid (HClO)	3.0×10^{-8}
Hydrocyanic Acid (HCN)	4.9×10^{-10}
Phenol (C_6H_5OH)	1.3×10^{-10}

The pH scale for the hydrogen ion concentration has been so useful that besides pK_w, it has been extended to other species and

quantities. Thus, we have:

$pK_a = -\log(K_a)$ (6.31)

Knowing the ionization constant, K_a of an acid and its initial concentration, c, it is possible to calculate the equilibrium concentration of all species and also the degree of ionization of the acid and the pH of the solution.

A general step-wise approach can be adopted to evaluate the pH of the weak electrolyte as follows:

Step 1. The species present before dissociation are identified as Brönsted-Lowry acids/bases.

Step 2. Balanced equations for all possible reactions i.e., with a species acting both as acid as well as base are written.

Step 3. The reaction with the higher K_a is identified as the primary reaction whilst the other is a subsidiary reaction.

Step 4. Enlist in a tabular form the following values for each of the species in the primary reaction

(a) Initial concentration, c.

(b) Change in concentration on proceeding to equilibrium in terms of α, degree of ionization.

(c) Equilibrium concentration.

Step 5. Substitute equilibrium concentrations into equilibrium constant equation for principal reaction and solve for α.

Step 6. Calculate the concentration of species in principal reaction.

Step 7. Calculate pH = $-\log[H_3O^+]$

The above mentioned methodology has been elucidated in the following examples.
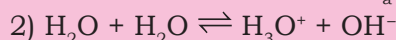
Problem 6.18

The ionization constant of HF is 3.2×10^{-4}. Calculate the degree of dissociation of HF in its 0.02 M solution. Calculate the concentration of all species present (H_3O^+, F^- and HF) in the solution and its pH.

Solution

The following proton transfer reactions are possible:

1) $HF + H_2O \rightleftharpoons H_3O^+ + F^-$

$K_a = 3.2 \times 10^{-4}$

2) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$
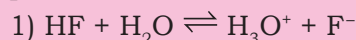
$K_w = 1.0 \times 10^{-14}$

As $K_a \gg K_w$, [1] is the principle reaction.

	HF	+	H_2O	$\rightleftharpoons$	H_3O^+	+	F^-
Initial concentration (M)	0.02				0		0
Change (M)	-0.02α				$+0.02\alpha$		$+0.02\alpha$
Equilibrium concentration (M)	$0.02 - 0.02\alpha$				0.02α		0.02α

Substituting equilibrium concentrations in the equilibrium reaction for principal reaction gives:

$K_a = (0.02\alpha)^2 / (0.02 - 0.02\alpha)$

$= 0.02\,\alpha^2 / (1 - \alpha) = 3.2 \times 10^{-4}$

We obtain the following quadratic equation:

$\alpha^2 + 1.6 \times 10^{-2}\alpha - 1.6 \times 10^{-2} = 0$

The quadratic equation in α can be solved and the two values of the roots are:

$\alpha = +0.12$ and -0.12

The negative root is not acceptable and hence,

$\alpha = 0.12$

This means that the degree of ionization, α = 0.12, then equilibrium concentrations of other species viz., HF, F^- and H_3O^+ are given by:

$[H_3O^+] = [F^-] = c\alpha = 0.02 \times 0.12$

$= 2.4 \times 10^{-3}$ M

$[HF] = c(1 - \alpha) = 0.02\,(1 - 0.12)$

$= 17.6 \times 10^{-3}$ M

$pH = -\log[H^+] = -\log(2.4 \times 10^{-3}) = 2.62$

Problem 6.19

The pH of 0.1M monobasic acid is 4.50. Calculate the concentration of species H^+, A^-

and HA at equilibrium. Also, determine the value of K_a and pK_a of the monobasic acid.

Solution

$$pH = - \log [H^+]$$

Therefore, $[H^+] = 10^{-pH} = 10^{-4.50}$

$$= 3.16 \times 10^{-5}$$

$[H^+] = [A^-] = 3.16 \times 10^{-5}$

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

$[HA]_{eqlbm} = 0.1 - (3.16 \times 10^{-5}) \simeq 0.1$

$K_a = (3.16 \times 10^{-5})^2 / 0.1 = 1.0 \times 10^{-8}$

$pK_a = - \log(10^{-8}) = 8$

Alternatively, "Percent dissociation" is another useful method for measure of strength of a weak acid and is given as:

Percent dissociation

$= [HA]_{dissociated}/[HA]_{initial} \times 100\%$ (6.32)

Problem 6.20

Calculate the pH of 0.08M solution of hypochlorous acid, HOCl. The ionization constant of the acid is 2.5×10^{-5}. Determine the percent dissociation of HOCl.

Solution

$HOCl(aq) + H_2O (l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$

Initial concentration (M)
 0.08   0   0

Change to reach

equilibrium concentration

(M)

  $- x$ $+ x$ $+x$

equilibrium concentartion (M)

$0.08 - x$ x   x

$K_a = \{[H_3O^+][ClO^-] / [HOCl]\}$

$= x^2 / (0.08 - x)$

As x << 0.08, therefore $0.08 - x \simeq 0.08$

$x^2 / 0.08 = 2.5 \times 10^{-5}$

$x^2 = 2.0 \times 10^{-6}$, thus, $x = 1.41 \times 10^{-3}$

$[H^+] = 1.41 \times 10^{-3}$ M.

Therefore,

Percent dissociation

$= \{[HOCl]_{dissociated} / [HOCl]_{initial}\} \times 100$

$= 1.41 \times 10^{-3} \times 10^2 / 0.08 = 1.76\%$.

pH = $-\log(1.41 \times 10^{-3}) = 2.85$.

6.11.4 Ionization of Weak Bases

The ionization of base MOH can be represented by equation:

$MOH(aq) \rightleftharpoons M^+(aq) + OH^-(aq)$

In a weak base there is partial ionization of MOH into M^+ and OH^-, the case is similar to that of acid-dissociation equilibrium. The equilibrium constant for base ionization is called **base ionization constant** and is represented by K_b. It can be expressed in terms of concentration in molarity of various species in equilibrium by the following equation:

$K_b = [M^+][OH^-] / [MOH]$ (6.33)

Alternatively, if c = initial concentration of base and α = degree of ionization of base i.e. the extent to which the base ionizes. When equilibrium is reached, the equilibrium constant can be written as:

$K_b = (c\alpha)^2 / c (1-\alpha) = c\alpha^2 / (1-\alpha)$

The values of the ionization constants of some selected weak bases, K_b are given in Table 6.7.

Table 6.7 The Values of the Ionization Constant of Some Weak Bases at 298 K

Base	K_b
Dimethylamine, $(CH_3)_2NH$	5.4×10^{-4}
Triethylamine, $(C_2H_5)_3N$	6.45×10^{-5}
Ammonia, NH_3 or NH_4OH	1.77×10^{-5}
Quinine, (A plant product)	1.10×10^{-6}
Pyridine, C_5H_5N	1.77×10^{-9}
Aniline, $C_6H_5NH_2$	4.27×10^{-10}
Urea, $CO (NH_2)_2$	1.3×10^{-14}

Many organic compounds like *amines* are weak bases. Amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by another group. For example, methylamine, codeine, quinine and

nicotine all behave as very weak bases due to their very small K_b. Ammonia produces OH^- in aqueous solution:
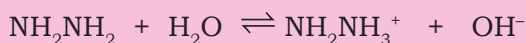
$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
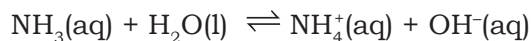
The pH scale for the hydrogen ion concentration has been extended to get:

$$pK_b = -\log(K_b) \tag{6.34}$$

Problem 6.21

The pH of 0.004M hydrazine solution is 9.7. Calculate its ionization constant K_b and pK_b.

Solution

$$NH_2NH_2 + H_2O \rightleftharpoons NH_2NH_3^+ + OH^-$$

From the pH we can calculate the hydrogen ion concentration. Knowing hydrogen ion concentration and the ionic product of water we can calculate the concentration of hydroxyl ions. Thus we have:

$[H^+]$ = antilog (–pH)

= antilog (–9.7) = 1.67×10^{-10}

$[OH^-] = K_w / [H^+] = 1 \times 10^{-14} / 1.67 \times 10^{-10}$

= 5.98×10^{-5}

The concentration of the corresponding hydrazinium ion is also the same as that of hydroxyl ion. The concentration of both these ions is very small so the concentration of the undissociated base can be taken equal to 0.004M.
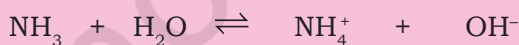
Thus,

$K_b = [NH_2NH_3^+][OH^-] / [NH_2NH_2]$

= $(5.98 \times 10^{-5})^2 / 0.004 = 8.96 \times 10^{-7}$

$pK_b = -\log K_b = -\log(8.96 \times 10^{-7}) = 6.04$.

Problem 6.22

Calculate the pH of the solution in which 0.2M NH_4Cl and 0.1M NH_3 are present. The pK_b of ammonia solution is 4.75.
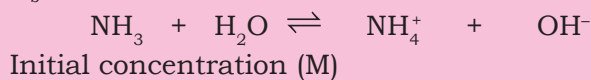
Solution

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The ionization constant of NH_3,

K_b = antilog (–pK_b) i.e.

$K_b = 10^{-4.75} = 1.77 \times 10^{-5}$ M

$$\begin{array}{ccccc} NH_3 & + & H_2O \rightleftharpoons & NH_4^+ & + & OH^- \end{array}$$

Initial concentration (M)

    0.10   0.20   0

Change to reach

equilibrium (M)

    –x   +x   +x

At equilibrium (M)

    0.10 – x   0.20 + x   x

$K_b = [NH_4^+][OH^-] / [NH_3]$

= (0.20 + x)(x) / (0.1 – x) = 1.77×10^{-5}

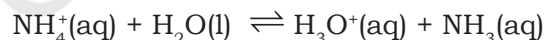As K_b is small, we can neglect x in comparison to 0.1M and 0.2M. Thus,

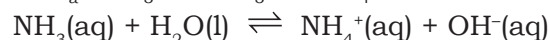$[OH^-] = x = 0.88 \times 10^{-5}$

Therefore, $[H^+] = 1.12 \times 10^{-9}$

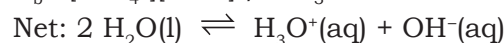pH = –log$[H^+]$ = 8.95.

6.11.5 Relation between K_a and K_b

As seen earlier in this chapter, K_a and K_b represent the strength of an acid and a base, respectively. In case of a conjugate acid-base pair, they are related in a simple manner so that if one is known, the other can be deduced. Considering the example of NH_4^+ and NH_3 we see,

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

$K_a = [H_3O^+][NH_3] / [NH_4^+] = 5.6 \times 10^{-10}$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$K_b = [NH_4^+][OH^-] / NH_3 = 1.8 \times 10^{-5}$

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

$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ M

Where, K_a represents the strength of NH_4^+ as an acid and K_b represents the strength of NH_3 as a base.

It can be seen from the net reaction that the equilibrium constant is equal to the product of equilibrium constants K_a and K_b for the reactions added. Thus,

$K_a \times K_b = \{[H_3O^+][NH_3] / [NH_4^+]\} \times \{[NH_4^+]$

$[OH^-] / [NH_3]\}$

= $[H_3O^+][OH^-] = K_w$

= $(5.6 \times 10^{-10}) \times (1.8 \times 10^{-5}) = 1.0 \times 10^{-14}$ M

This can be extended to make a generalisation. **The equilibrium constant for a net reaction obtained after adding two (or more) reactions equals the product of the equilibrium constants for individual reactions:**
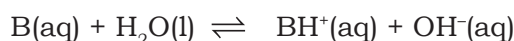
$$K_{NET} = K_1 \times K_2 \times \ldots\ldots \qquad (6.35)$$

Similarly, in case of a conjugate acid-base pair,

$$K_a \times K_b = K_w \qquad (6.36)$$

Knowing one, the other can be obtained. It should be noted that a *strong acid will have a weak conjugate base and vice-versa.*

Alternatively, the above expression $K_w = K_a \times K_b$, can also be obtained by considering the base-dissociation equilibrium reaction:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K_b = [BH^+][OH^-] / [B]$$

As the concentration of water remains constant it has been omitted from the denominator and incorporated within the dissociation constant. Then multiplying and dividing the above expression by $[H^+]$, we get:

$$K_b = [BH^+][OH^-][H^+] / [B][H^+]$$
$$= \{[OH^-][H^+]\}\{[BH^+] / [B][H^+]\}$$
$$= K_w / K_a$$

or $K_a \times K_b = K_w$

It may be noted that if we take negative logarithm of both sides of the equation, then pK values of the conjugate acid and base are related to each other by the equation:

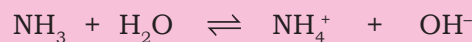$$pK_a + pK_b = pK_w = 14 \text{ (at 298K)}$$

Problem 6.23

Determine the degree of ionization and pH of a 0.05M of ammonia solution. The ionization constant of ammonia can be taken from Table 6.7. Also, calculate the ionization constant of the conjugate acid of ammonia.

Solution

The ionization of NH_3 in water is represented by equation:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

We use equation (6.33) to calculate hydroxyl ion concentration,

$$[OH^-] = c\,\alpha = 0.05\,\alpha$$

$$K_b = 0.05\,\alpha^2 / (1 - \alpha)$$

The value of α is small, therefore the quadratic equation can be simplified by neglecting α in comparison to 1 in the denominator on right hand side of the equation,

Thus,

$$K_b = c\,\alpha^2 \quad \text{or} \quad \alpha = \sqrt{(1.77 \times 10^{-5} / 0.05)}$$
$$= 0.018.$$

$$[OH^-] = c\,\alpha = 0.05 \times 0.018 = 9.4 \times 10^{-4}M.$$

$$[H^+] = K_w / [OH^-] = 10^{-14} / (9.4 \times 10^{-4})$$
$$= 1.06 \times 10^{-11}$$

$$pH = -\log(1.06 \times 10^{-11}) = 10.97.$$

Now, using the relation for conjugate acid-base pair,

$$K_a \times K_b = K_w$$

using the value of K_b of NH_3 from Table 6.7.

We can determine the concentration of conjugate acid NH_4^+

$$K_a = K_w / K_b = 10^{-14} / 1.77 \times 10^{-5}$$
$$= 5.64 \times 10^{-10}.$$

6.11.6 Di- and Polybasic Acids and Di- and Polyacidic Bases

Some of the acids like oxalic acid, sulphuric acid and phosphoric acids have more than one ionizable proton per molecule of the acid. Such acids are known as polybasic or polyprotic acids.

The ionization reactions for example for a *dibasic acid* H_2X are represented by the equations:

$$H_2X(aq) \rightleftharpoons H^+(aq) + HX^-(aq)$$

$$HX^-(aq) \rightleftharpoons H^+(aq) + X^{2-}(aq)$$
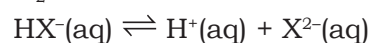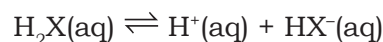
And the corresponding equilibrium constants are given below:

$$K_{a_1} = \{[H^+][HX^-]\} / [H_2X] \text{ and}$$

K_{a_2} = {[H$^+$][X^{2-}]} / [HX$^-$]

Here, K_{a_1} and K_{a_2} are called the first and second ionization constants respectively of the acid H$_2$X. Similarly, for tribasic acids like H$_3$PO$_4$ we have three ionization constants. The values of the ionization constants for some common polyprotic acids are given in Table 6.8.

Table 6.8   The Ionization Constants of Some Common Polyprotic Acids (298K)

Acid	K_{a_1}	K_{a_2}	K_{a_3}
Oxalic Acid	5.9×10^{-2}	6.4×10^{-5}	
Ascorbic Acid	7.4×10^{-4}	1.6×10^{-12}	
Sulphurous Acid	1.7×10^{-2}	6.4×10^{-8}	
Sulphuric Acid	Very large	1.2×10^{-2}	
Carbonic Acid	4.3×10^{-7}	5.6×10^{-11}	
Citric Acid	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Phosphoric Acid	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}

It can be seen that higher order ionization constants (K_{a_2}, K_{a_3}) are smaller than the lower order ionization constant (K_{a_1}) of a polyprotic acid. The reason for this is that it is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces. This can be seen in the case of removing a proton from the uncharged H$_2$CO$_3$ as compared from a negatively charged HCO$_3^-$. Similarly, it is more difficult to remove a proton from a doubly charged HPO$_4^{2-}$ anion as compared to H$_2$PO$_4^-$.

Polyprotic acid solutions contain a mixture of acids like H$_2$A, HA$^-$ and A^{2-} in case of a diprotic acid. H$_2$A being a strong acid, the primary reaction involves the dissociation of H$_2$A, and H$_3$O$^+$ in the solution comes mainly from the first dissociation step.

6.11.7 Factors Affecting Acid Strength

Having discussed quantitatively the strengths of acids and bases, we come to a stage where we can calculate the pH of a given acid solution. But, the curiosity rises about why should some acids be stronger than others? What factors are responsible for making them stronger? The answer lies in its being a complex phenomenon. But, broadly speaking we can say that the extent of dissociation of an acid depends on the **strength** and **polarity** of the H-A bond.

In general, when strength of H-A bond decreases, that is, the energy required to break the bond decreases, HA becomes a stronger acid. Also, when the H-A bond becomes more polar i.e., the electronegativity difference between the atoms H and A increases and there is marked charge separation, cleavage of the bond becomes easier thereby increasing the acidity.

But it should be noted that while comparing elements in the same *group* of the periodic table, H-A bond strength is a more important factor in determining acidity than its polar nature. As the size of A increases down the group, H-A bond strength decreases and so the acid strength increases. For example,

Size increases
$\longrightarrow$
HF << HCl << HBr << HI
$\longrightarrow$
Acid strength increases
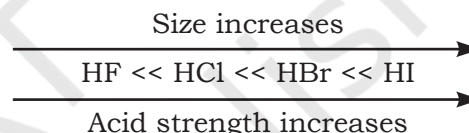
Similarly, H$_2$S is stronger acid than H$_2$O.

But, when we discuss elements in the same *row* of the periodic table, H-A bond polarity becomes the deciding factor for determining the acid strength. As the electronegativity of A increases, the strength of the acid also increases. For example,

Electronegativity of A increases
$\longrightarrow$
CH$_4$ < NH$_3$ < H$_2$O < HF
$\longrightarrow$
Acid strength increases
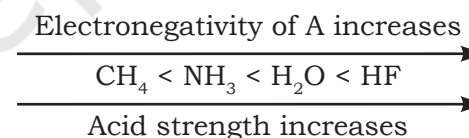
6.11.8 Common Ion Effect in the Ionization of Acids and Bases

Consider an example of acetic acid dissociation equilibrium represented as:

CH$_3$COOH(aq) $\rightleftharpoons$ H$^+$(aq) + CH$_3$COO$^-$(aq)

or HAc(aq) $\rightleftharpoons$ H$^+$(aq) + Ac$^-$(aq)
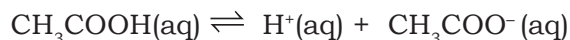
K_a = [H$^+$][Ac$^-$] / [HAc]

Addition of acetate ions to an acetic acid solution results in decreasing the concentration of hydrogen ions, [H$^+$]. Also, if H$^+$ ions are added from an external source then the equilibrium moves in the direction of undissociated acetic acid i.e., in a direction of reducing the concentration of hydrogen ions, [H$^+$]. This phenomenon is an example

of **common ion effect**. It can be defined as a shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium. Thus, we can say that common ion effect is a phenomenon based on the Le Chatelier's principle discussed in section 6.8.

In order to evaluate the pH of the solution resulting on addition of 0.05M acetate ion to 0.05M acetic acid solution, we shall consider the acetic acid dissociation equilibrium once again,

$$HAc(aq) \rightleftharpoons H^+(aq) + Ac^-(aq)$$
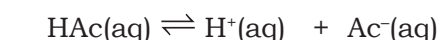
Initial concentration (M)

0.05   0   0.05

Let x be the extent of ionization of acetic acid.

Change in concentration (M)

−x   +x   +x

Equilibrium concentration (M)

0.05-x   x   0.05+x

Therefore,

$K_a = [H^+][Ac^-]/[HAc] = \{(0.05+x)(x)\}/(0.05-x)$

As K_a is small for a very weak acid, x<<0.05. Hence, $(0.05 + x) \approx (0.05 - x) \approx 0.05$

Thus,

$1.8 \times 10^{-5} = (x) (0.05 + x) / (0.05 - x)$

$= x(0.05) / (0.05) = x = [H^+] = 1.8 \times 10^{-5}M$

$pH = -\log(1.8 \times 10^{-5}) = 4.74$

Problem 6.24

Calculate the pH of a 0.10M ammonia solution. Calculate the pH after 50.0 mL of this solution is treated with 25.0 mL of 0.10M HCl. The dissociation constant of ammonia, $K_b = 1.77 \times 10^{-5}$

Solution

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

$K_b = [NH_4^+][OH^-] / [NH_3] = 1.77 \times 10^{-5}$

Before neutralization,

$[NH_4^+] = [OH^-] = x$

$[NH_3] = 0.10 - x \simeq 0.10$

$x^2 / 0.10 = 1.77 \times 10^{-5}$

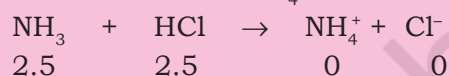Thus, $x = 1.33 \times 10^{-3} = [OH^-]$

Therefore, $[H^+] = K_w / [OH^-] = 10^{-14} /$

$(1.33 \times 10^{-3}) = 7.51 \times 10^{-12}$

$pH = -\log (7.5 \times 10^{-12}) = 11.12$

On addition of 25 mL of 0.1M HCl solution (i.e., 2.5 mmol of HCl) to 50 mL of 0.1M ammonia solution (i.e., 5 mmol of NH_3), 2.5 mmol of ammonia molecules are neutralized. The resulting 75 mL solution contains the remaining unneutralized 2.5 mmol of NH_3 molecules and 2.5 mmol of NH_4^+.

$$NH_3 + HCl \rightarrow NH_4^+ + Cl^-$$
2.5   2.5   0   0

At equilibrium

0   0   2.5   2.5

The resulting 75 mL of solution contains 2.5 mmol of NH_4^+ ions (i.e., 0.033 M) and 2.5 mmol (i.e., 0.033 M) of uneutralised NH_3 molecules. This NH_3 exists in the following equilibrium:

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
0.033M − y   y   y
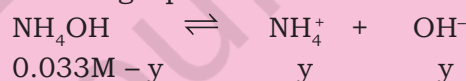
where, $y = [OH^-] = [NH_4^+]$

The final 75 mL solution after neutralisation already contains 2.5 m mol NH_4^+ ions (i.e. 0.033M), thus total concentration of NH_4^+ ions is given as:

$[NH_4^+] = 0.033 + y$

As y is small, $[NH_4OH] \simeq 0.033$ M and $[NH_4^+] \simeq 0.033M$.

We know,

$K_b = [NH_4^+][OH^-] / [NH_4OH]$

$= y (0.033)/(0.033) = 1.77 \times 10^{-5}$ M

Thus, $y = 1.77 \times 10^{-5} = [OH^-]$

$[H^+] = 10^{-14} / 1.77 \times 10^{-5} = 0.56 \times 10^{-9}$

Hence, pH = 9.24

6.11.9 Hydrolysis of Salts and the pH of their Solutions

Salts formed by the reactions between acids and bases in definite proportions, undergo ionization in water. The cations/anions

formed on ionization of salts either exist as hydrated ions in aqueous solutions or interact with water to reform corresponding acids/ bases depending upon the nature of salts. The later process of interaction between water and cations/anions or both of salts is called hydrolysis. The pH of the solution gets affected by this interaction. The cations (e.g., Na^+, K^+, Ca^{2+}, Ba^{2+}, etc.) of strong bases and anions (e.g., Cl^-, Br^-, NO_3^-, ClO_4^- etc.) of strong acids simply get hydrated but do not hydrolyse, and therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7. However, the other category of salts do undergo hydrolysis.

We now consider the hydrolysis of the salts of the following types :

(i)   salts of weak acid and strong base e.g., CH_3COONa.

(ii) salts of strong acid and weak base e.g., NH_4Cl, and

(iii) salts of weak acid and weak base, e.g., CH_3COONH_4.

In the first case, CH_3COONa being a salt of weak acid, CH_3COOH and strong base, NaOH gets completely ionised in aqueous solution.

$$CH_3COONa(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

Acetate ion thus formed undergoes hydrolysis in water to give acetic acid and OH^- ions

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$
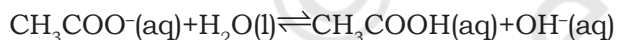
Acetic acid being a weak acid ($K_a = 1.8 \times 10^{-5}$) remains mainly unionised in solution. This results in increase of OH^- ion concentration in solution making it alkaline. The pH of such a solution is more than 7.

Similarly, NH_4Cl formed from weak base, NH_4OH and strong acid, HCl, in water dissociates completely.

$$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

Ammonium ions undergo hydrolysis with water to form NH_4OH and H^+ ions

$$NH_4^+(aq) + H_2O(1) \rightleftharpoons NH_4OH(aq) + H^+(aq)$$
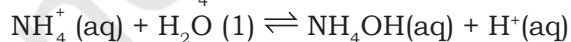
Ammonium hydroxide is a weak base ($K_b = 1.77 \times 10^{-5}$) and therefore remains almost unionised in solution. This results in

increased of H^+ ion concentration in solution making the solution acidic. Thus, the pH of NH_4Cl solution in water is less than 7.

Consider the hydrolysis of CH_3COONH_4 salt formed from weak acid and weak base. The ions formed undergo hydrolysis as follow:

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$
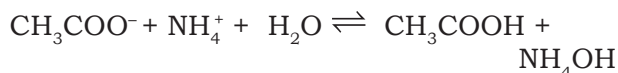
CH_3COOH and NH_4OH, also remain into partially dissociated form:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
$$H_2O \rightleftharpoons H^+ + OH^-$$
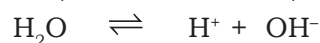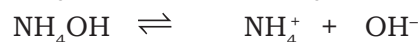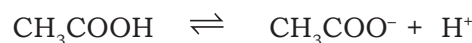
Without going into detailed calculation, it can be said that degree of hydrolysis is independent of concentration of solution, and pH of such solutions is determined by their pK values:

$$pH = 7 + \frac{1}{2}(pK_a - pK_b) \qquad (6.38)$$

The pH of solution can be greater than 7, if the difference is positive and it will be less than 7, if the difference is negative.

Problem 6.25

The pK_a of acetic acid and pK_b of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the pH of ammonium acetate solution.

Solution

$pH = 7 + \frac{1}{2}[pK_a - pK_b]$
$= 7 + \frac{1}{2}[4.76 - 4.75]$
$= 7 + \frac{1}{2}[0.01] = 7 + 0.005 = 7.005$

6.12 BUFFER SOLUTIONS

Many body fluids e.g., blood or urine have definite pH and any deviation in their pH indicates malfunctioning of the body. The control of pH is also very important in many chemical and biochemical processes. Many medical and cosmetic formulations require that these be kept and administered at a particular pH. **The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.** Buffer

solutions of known pH can be prepared from the knowledge of pK_a of the acid or pK_b of base and by controlling the ratio of the salt and acid or salt and base. A mixture of acetic acid and sodium acetate acts as buffer solution around pH 4.75 and a mixture of ammonium chloride and ammonium hydroxide acts as a buffer around pH 9.25. You will learn more about buffer solutions in higher classes.

6.12.1 Designing Buffer Solution

Knowledge of pK_a, pK_b and equilibrium constant help us to prepare the buffer solution of known pH. Let us see how we can do this.

Preparation of Acidic Buffer

To prepare a buffer of acidic pH we use weak acid and its salt formed with strong base. We develop the equation relating the pH, the equilibrium constant, K_a of weak acid and ratio of concentration of weak acid and its conjugate base. For the general case where the weak acid HA ionises in water,

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
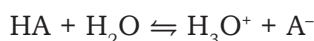
For which we can write the expression

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Rearranging the expression we have,

$$[H_3O^+] = K_a \frac{[HA]}{[A^-]}$$

Taking logarithm on both the sides and rearranging the terms we get —

$$pK_a = pH - \log \frac{[A^-]}{[HA]}$$

Or

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \qquad (6.39)$$

$$pH = pK_a + \log \frac{[\text{Conjugate base, } A^-]}{[\text{Acid, HA}]}$$
$$(6.40)$$

The expression (6.40) is known as **Henderson–Hasselbalch equation.** The quantity $\dfrac{[A^-]}{[HA]}$ is the ratio of concentration of conjugate base (anion) of the acid and the

acid present in the mixture. Since acid is a weak acid, it ionises to a very little extent and concentration of [HA] is negligibly different from concentration of acid taken to form buffer. Also, most of the conjugate base, [A$^-$], comes from the ionisation of salt of the acid. Therefore, the concentration of conjugate base will be negligibly different from the concentration of salt. Thus, equation (6.40) takes the form:

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

In the equation (6.39), if the concentration of [A$^-$] is equal to the concentration of [HA], then pH = pK_a because value of log 1 is zero. Thus if we take molar concentration of acid and salt (conjugate base) same, the pH of the buffer solution will be equal to the pK_a of the acid. So for preparing the buffer solution of the required pH we select that acid whose pK_a is close to the required pH. For acetic acid pK_a value is 4.76, therefore pH of the buffer solution formed by acetic acid and sodium acetate taken in equal molar concentration will be around 4.76.

A similar analysis of a buffer made with a weak base and its conjugate acid leads to the result,

$$pOH = pK_b + \log \frac{[\text{Conjugate acid, BH}^+]}{[\text{Base, B}]}$$
$$(6.41)$$

pH of the buffer solution can be calculated by using the equation pH + pOH = 14.

We know that pH + pOH = pK_w and $pK_a + pK_b = pK_w$. On putting these values in equation (6.41) it takes the form as follows:

$$pK_w - pH = pK_w - pK_a + \log \frac{[\text{Conjugate acid, BH}^+]}{[\text{Base, B}]}$$

or

$$pH = pK_a + \log \frac{[\text{Conjugate acid, BH}^+]}{[\text{Base, B}]}$$
$$(6.42)$$

If molar concentration of base and its conjugate acid (cation) is same then pH of the buffer solution will be same as pK_a for the base. pK_a value for ammonia is s9.25; therefore a buffer of pH close to 9.25 can be obtained by taking ammonia solution and ammonium

chloride solution of same molar concentration. For a buffer solution formed by ammonium chloride and ammonium hydroxide, equation (6.42) becomes:

$$pH = 9.25 + \log \frac{[\text{Conjugate acid}, BH^+]}{[\text{Base}, B]}$$

pH of the buffer solution is not affected by dilution because ratio under the logarithmic term remains unchanged.

## 6.13 SOLUBILITY EQUILIBRIA OF SPARINGLY SOLUBLE SALTS

We have already known that the solubility of ionic solids in water varies a great deal. Some of these (like calcium chloride) are so soluble that they are hygroscopic in nature and even absorb water vapour from atmosphere. Others (such as lithium fluoride) have so little solubility that they are commonly termed as insoluble. The solubility depends on a number of factors important amongst which are the lattice enthalpy of the salt and the solvation enthalpy of the ions in a solution. For a salt to dissolve in a solvent the strong forces of attraction between its ions (lattice enthalpy) must be overcome by the ion-solvent interactions. The solvation enthalpy of ions is referred to in terms of solvation which is always negative i.e. energy is released in the process of solvation. The amount of solvation enthalpy depends on the nature of the solvent. In case of a non-polar (covalent) solvent, solvation enthalpy is small and hence, not sufficient to overcome lattice enthalpy of the salt. Consequently, the salt does not dissolve in non-polar solvent. As a general rule, for a salt to be able to dissolve in a particular solvent its solvation enthalpy must be greater than its lattice enthalpy so that the latter may be overcome by former. Each salt has its characteristic solubility which depends on temperature. We classify salts on the basis of their solubility in the following three categories.

Category I	Soluble	Solubility > 0.1M
Category II	Slightly Soluble	0.01M<Solubility< 0.1M
Category III	Sparingly Soluble	Solubility < 0.01M

We shall now consider the equilibrium between the sparingly soluble ionic salt and its saturated aqueous solution.

6.13.1 Solubility Product Constant

Let us now have a solid like barium sulphate in contact with its saturated aqueous solution. The equilibrium between the undisolved solid and the ions in a saturated solution can be represented by the equation:

$$BaSO_4(s) \underset{\text{in water}}{\overset{\text{Saturated Solution}}{\rightleftharpoons}} Ba^{2+}(aq) + SO_4^{2-}(aq),$$
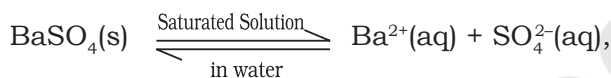
The equilibrium constant is given by the equation:

$$K = \{[Ba^{2+}][SO_4^{2-}]\} / [BaSO_4]$$

For a pure solid substance the concentration remains constant and we can write

$$K_{sp} = K[BaSO_4] = [Ba^{2+}][SO_4^{2-}] \qquad (6.43)$$

We call K_{sp} the *solubility product constant* or simply *solubility product*. The experimental value of K_{sp} in above equation at 298K is 1.1×10^{-10}. This means that for solid barium sulphate in equilibrium with its saturated solution, the product of the concentrations of barium and sulphate ions is equal to its solubility product constant. The concentrations of the two ions will be equal to the molar solubility of the barium sulphate. If molar solubility is S, then

$$1.1 \times 10^{-10} = (S)(S) = S^2$$
$$\text{or} \qquad S = 1.05 \times 10^{-5}.$$

Thus, molar solubility of barium sulphate will be equal to 1.05×10^{-5} mol L^{-1}.

A salt may give on dissociation two or more than two anions and cations carrying different charges. For example, consider a salt like *zirconium phosphate* of molecular formula $(Zr^{4+})_3(PO_4^{3-})_4$. It dissociates into 3 zirconium cations of charge +4 and 4 phosphate anions of charge –3. If the molar solubility of zirconium phosphate is S, then it can be seen from the stoichiometry of the compound that

$$[Zr^{4+}] = 3S \text{ and } [PO_4^{3-}] = 4S$$

and $K_{sp} = (3S)^3 (4S)^4 = 6912 (S)^7$

or $S = \{K_{sp} / (3^3 \times 4^4)\}^{1/7} = (K_{sp} / 6912)^{1/7}$

A solid salt of the general formula $M_x^{p+} X_y^{q-}$ with molar solubility S in equilibrium with its saturated solution may be represented by the equation:

$M_xX_y(s) \rightleftharpoons xM^{p+}(aq) + yX^{q-}(aq)$

(where x × p$^+$ = y × q$^-$)
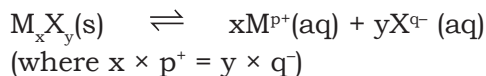
And its solubility product constant is given by:

$K_{sp} = [M^{p+}]^x[X^{q-}]^y = (xS)^x(yS)^y$ (6.44)

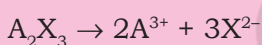$= x^x \cdot y^y \cdot S^{(x+y)}$

$S^{(x+y)} = K_{sp} / x^x \cdot y^y$

$S = (K_{sp} / x^x \cdot y^y)^{1/x+y}$ (6.45)

The term K_{sp} in equation is given by Q_{sp} (section 6.6.2) when the concentration of one or more species is not the concentration under equilibrium. Obviously under equilibrium conditions $K_{sp} = Q_{sp}$ but otherwise it gives the direction of the processes of precipitation or dissolution. The solubility product constants of a number of common salts at 298K are given in Table 6.9.

Table 6.9 The Solubility Product Constants, K_{sp} of Some Common Ionic Salts at 298K.

Name of the Salt	Formula	K_{sp}
Silver Bromide	AgBr	5.0×10^{-13}
Silver Carbonate	Ag$_2$CO$_3$	8.1×10^{-12}
Silver Chromate	Ag$_2$CrO$_4$	1.1×10^{-12}
Silver Chloride	AgCl	1.8×10^{-10}
Silver Iodide	AgI	8.3×10^{-17}
Silver Sulphate	Ag$_2$SO$_4$	1.4×10^{-5}
Aluminium Hydroxide	Al(OH)$_3$	1.3×10^{-33}
Barium Chromate	BaCrO$_4$	1.2×10^{-10}
Barium Fluoride	BaF$_2$	1.0×10^{-6}
Barium Sulphate	BaSO$_4$	1.1×10^{-10}
Calcium Carbonate	CaCO$_3$	2.8×10^{-9}
Calcium Fluoride	CaF$_2$	5.3×10^{-9}
Calcium Hydroxide	Ca(OH)$_2$	5.5×10^{-6}
Calcium Oxalate	CaC$_2$O$_4$	4.0×10^{-9}
Calcium Sulphate	CaSO$_4$	9.1×10^{-6}
Cadmium Hydroxide	Cd(OH)$_2$	2.5×10^{-14}
Cadmium Sulphide	CdS	8.0×10^{-27}
Chromic Hydroxide	Cr(OH)$_3$	6.3×10^{-31}
Cuprous Bromide	CuBr	5.3×10^{-9}
Cupric Carbonate	CuCO$_3$	1.4×10^{-10}
Cuprous Chloride	CuCl	1.7×10^{-6}
Cupric Hydroxide	Cu(OH)$_2$	2.2×10^{-20}
Cuprous Iodide	CuI	1.1×10^{-12}
Cupric Sulphide	CuS	6.3×10^{-36}
Ferrous Carbonate	FeCO$_3$	3.2×10^{-11}
Ferrous Hydroxide	Fe(OH)$_2$	8.0×10^{-16}
Ferric Hydroxide	Fe(OH)$_3$	1.0×10^{-38}
Ferrous Sulphide	FeS	6.3×10^{-18}
Mercurous Bromide	Hg$_2$Br$_2$	5.6×10^{-23}
Mercurous Chloride	Hg$_2$Cl$_2$	1.3×10^{-18}
Mercurous Iodide	Hg$_2$I$_2$	4.5×10^{-29}
Mercurous Sulphate	Hg$_2$SO$_4$	7.4×10^{-7}
Mercuric Sulphide	HgS	4.0×10^{-53}
Magnesium Carbonate	MgCO$_3$	3.5×10^{-8}
Magnesium Fluoride	MgF$_2$	6.5×10^{-9}
Magnesium Hydroxide	Mg(OH)$_2$	1.8×10^{-11}
Magnesium Oxalate	MgC$_2$O$_4$	7.0×10^{-7}
Manganese Carbonate	MnCO$_3$	1.8×10^{-11}
Manganese Sulphide	MnS	2.5×10^{-13}
Nickel Hydroxide	Ni(OH)$_2$	2.0×10^{-15}
Nickel Sulphide	NiS	4.7×10^{-5}
Lead Bromide	PbBr$_2$	4.0×10^{-5}
Lead Carbonate	PbCO$_3$	7.4×10^{-14}
Lead Chloride	PbCl$_2$	1.6×10^{-5}
Lead Fluoride	PbF$_2$	7.7×10^{-8}
Lead Hydroxide	Pb(OH)$_2$	1.2×10^{-15}
Lead Iodide	PbI$_2$	7.1×10^{-9}
Lead Sulphate	PbSO$_4$	1.6×10^{-8}
Lead Sulphide	PbS	8.0×10^{-28}
Stannous Hydroxide	Sn(OH)$_2$	1.4×10^{-28}
Stannous Sulphide	SnS	1.0×10^{-25}
Strontium Carbonate	SrCO$_3$	1.1×10^{-10}
Strontium Fluoride	SrF$_2$	2.5×10^{-9}
Strontium Sulphate	SrSO$_4$	3.2×10^{-7}
Thallous Bromide	TlBr	3.4×10^{-6}
Thallous Chloride	TlCl	1.7×10^{-4}
Thallous Iodide	TlI	6.5×10^{-8}
Zinc Carbonate	ZnCO$_3$	1.4×10^{-11}
Zinc Hydroxide	Zn(OH)$_2$	1.0×10^{-15}
Zinc Sulphide	ZnS	1.6×10^{-24}

Problem 6.26

Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with water. The solubility product of A_2X_3, $K_{sp} = 1.1 \times 10^{-23}$.

Solution

$A_2X_3 \rightarrow 2A^{3+} + 3X^{2-}$

$K_{sp} = [A^{3+}]^2 [X^{2-}]^3 = 1.1 \times 10^{-23}$

If S = solubility of A_2X_3, then

$[A^{3+}] = 2S;\ [X^{2-}] = 3S$

therefore, $K_{sp} = (2S)^2(3S)^3 = 108S^5$

$= 1.1 \times 10^{-23}$

thus, $S^5 = 1 \times 10^{-25}$

$S = 1.0 \times 10^{-5}$ mol/L.

Problem 6.27

The values of K_{sp} of two sparingly soluble salts Ni(OH)$_2$ and AgCN are 2.0×10^{-15} and 6×0^{-17} respectively. Which salt is more soluble? Explain.
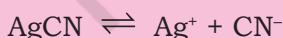
Solution

$AgCN \rightleftharpoons Ag^+ + CN^-$

K_{sp} = [Ag$^+$][CN$^-$] = 6 × 10^{-17}

Ni(OH)$_2$ ⇌ Ni^{2+} + 2OH$^-$

K_{sp} = [Ni^{2+}][OH$^-$]^2 = 2 × 10^{-15}

Let [Ag$^+$] = S$_1$, then [CN$^-$] = S$_1$

Let [Ni^{2+}] = S$_2$, then [OH$^-$] = 2S$_2$

S$_1^2$ = 6 × 10^{-17} , S$_1$ = 7.8 × 10^{-9}

(S$_2$)(2S$_2$)^2 = 2 × 10^{-15}, S$_2$ = 0.58 × 10^{-4}

Ni(OH)$_2$ is more soluble than AgCN.

6.13.2 Common Ion Effect on Solubility of Ionic Salts

It is expected from Le Chatelier's principle that if we increase the concentration of any one of the ions, it should combine with the ion of its opposite charge and some of the salt will be precipitated till once again K_{sp} = Q_{sp}. Similarly, if the concentration of one of the ions is decreased, more salt will dissolve to increase the concentration of both the ions till once again K_{sp} = Q_{sp}. This is applicable even to soluble salts like sodium chloride except that due to higher concentrations of the ions, we use their activities instead of their molarities in the expression for Q_{sp}. Thus if we take a saturated solution of sodium chloride and pass HCl gas through it, then sodium chloride is precipitated due to increased concentration (activity) of chloride ion available from the dissociation of HCl. Sodium chloride thus obtained is of very high purity and we can get rid of impurities like sodium and magnesium sulphates. The common ion effect is also used for almost complete precipitation of a particular ion as its sparingly soluble salt, with very low value of solubility product for gravimetric estimation. Thus we can precipitate silver ion as silver chloride, ferric ion as its hydroxide (or hydrated ferric oxide) and barium ion as its sulphate for quantitative estimations.

Problem 6.28

Calculate the molar solubility of Ni(OH)$_2$ in 0.10 M NaOH. The ionic product of Ni(OH)$_2$ is 2.0 × 10^{-15}.

Solution

Let the solubility of Ni(OH)$_2$ be equal to S.

Dissolution of S mol/L of Ni(OH)$_2$ provides S mol/L of Ni^{2+} and 2S mol/L of OH$^-$, but the total concentration of OH$^-$ = (0.10 + 2S) mol/L because the solution already contains 0.10 mol/L of OH$^-$ from NaOH.

K_{sp} = 2.0 × 10^{-15} = [Ni^{2+}] [OH$^-$]^2

= (S) (0.10 + 2S)^2

As K_{sp} is small, 2S << 0.10,

thus, (0.10 + 2S) ≈ 0.10

Hence,

2.0 × 10^{-15} = S (0.10)^2

S = 2.0 × 10^{-13} M = [Ni^{2+}]

The solubility of salts of weak acids like phosphates increases at lower pH. This is because at lower pH the concentration of the anion decreases due to its protonation. This in turn increase the solubility of the salt so that K_{sp} = Q_{sp}. We have to satisfy two equilibria simultaneously i.e.,

K_{sp} = [M$^+$] [X$^-$],

$$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq);$$

$$K_a = \frac{\left[H^+(aq)\right]\left[X^-(aq)\right]}{\left[HX(aq)\right]}$$

[X$^-$] / [HX] = K_a/[H$^+$]

Taking inverse of both side and adding 1 we get

$$\frac{[HX]}{[X^-]} + 1 = \frac{[H^+]}{K_a} + 1$$

$$\frac{[HX] + [H^-]}{[X^-]} = \frac{[H^+] + K_a}{K_a}$$

Now, again taking inverse, we get

[X$^-$] / {[X$^-$] + [HX]} = f = K_a/(K_a + [H$^+$]) and it can be seen that 'f' decreases as pH decreases. If S is the solubility of the salt at a given pH then

K_{sp} = [S] [f S] = S^2 {K_a/(K_a + [H$^+$])} and

S = {K_{sp} ([H$^+$] + K_a)/K_a}$^{1/2}$ (6.46)

Thus solubility S increases with increase in [H$^+$] or decrease in pH.

SUMMARY

When the number of molecules leaving the liquid to vapour equals the number of molecules returning to the liquid from vapour, equilibrium is said to be attained and is dynamic in nature. Equilibrium can be established for both physical and chemical processes and at this stage rate of forward and reverse reactions are equal. **Equilibrium constant, K_c** is expressed as the concentration of products divided by reactants, each term raised to the stoichiometric coefficient.

$$\text{For reaction, a A + b B} \rightleftharpoons \text{c C + d D}$$
$$K_c = [C]^c[D]^d/[A]^a[B]^b$$

Equilibrium constant has constant value at a fixed temperature and at this stage all the macroscopic properties such as concentration, pressure, etc. become constant. For a gaseous reaction equilibrium constant is expressed as K_p and is written by replacing concentration terms by partial pressures in K_c expression. The direction of reaction can be predicted by reaction quotient Q_c which is equal to K_c at equilibrium. **Le Chatelier's principle** states that the change in any factor such as temperature, pressure, concentration, etc. will cause the equilibrium to shift in such a direction so as to reduce or counteract the effect of the change. It can be used to study the effect of various factors such as temperature, concentration, pressure, catalyst and inert gases on the direction of equilibrium and to control the yield of products by controlling these factors. **Catalyst** does not effect the equilibrium composition of a reaction mixture but increases the rate of chemical reaction by making available a new lower energy pathway for conversion of reactants to products and vice-versa.

All substances that conduct electricity in aqueous solutions are called **electrolytes**. Acids, bases and salts are electrolytes and the conduction of electricity by their aqueous solutions is due to anions and cations produced by the **dissociation or ionization of electrolytes** in aqueous solution. The strong electrolytes are completely dissociated. In weak electrolytes there is equilibrium between the ions and the unionized electrolyte molecules. According to **Arrhenius, acids** give hydrogen ions while bases produce hydroxyl ions in their aqueous solutions. **Brönsted-Lowry** on the other hand, defined an acid as a proton donor and a base as a proton acceptor. When a Brönsted-Lowry acid reacts with a base, it produces its conjugate base and a conjugate acid corresponding to the base with which it reacts. Thus a **conjugate pair of acid-base** differs only by one proton. **Lewis** further generalised the definition of an acid as an electron pair acceptor and a base as an electron pair donor. The expressions for ionization (equilibrium) constants of weak acids (K_a) and weak bases (K_b) are developed using Arrhenius definition. The degree of ionization and its dependence on concentration and common ion are discussed. The **pH scale** (pH = –log[H$^+$]) for the hydrogen ion concentration (activity) has been introduced and extended to other quantities (pOH = – log[OH$^–$]); pK_a = –log[K_a]; pK_b = –log[K_b]; and pK_w = –log[K_w] etc.). The ionization of water has been considered and we note that the equation: pH + pOH = pK_w is always satisfied. The salts of strong acid and weak base, weak acid and strong base, and weak acid and weak base undergo hydrolysis in aqueous solution. The definition of **buffer solutions**, and their importance are discussed briefly. The solubility equilibrium of sparingly soluble salts is discussed and the equilibrium constant is introduced as **solubility product constant** (K_{sp}). Its relationship with solubility of the salt is established. The conditions of precipitation of the salt from their solutions or their dissolution in water are worked out. The role of common ion and the solubility of sparingly soluble salts is also discussed.

SUGGESTED ACTIVITIES FOR STUDENTS REGARDING THIS UNIT

(a) The student may use pH paper in determining the pH of fresh juices of various vegetables and fruits, soft drinks, body fluids and also that of water samples available.

(b) The pH paper may also be used to determine the pH of different salt solutions and from that he/she may determine if these are formed from strong/weak acids and bases.

(c) They may prepare some buffer solutions by mixing the solutions of sodium acetate and acetic acid and determine their pH using pH paper.

(d) They may be provided with different indicators to observe their colours in solutions of varying pH.

(e) They may perform some acid-base titrations using indicators.

(f) They may observe common ion effect on the solubility of sparingly soluble salts.

(g) If pH meter is available in their school, they may measure the pH with it and compare the results obtained with that of the pH paper.

EXERCISES

6.1   A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.

a)   What is the initial effect of the change on vapour pressure?

b)   How do rates of evaporation and condensation change initially?

c)   What happens when equilibrium is restored finally and what will be the final vapour pressure?

6.2   What is K_c for the following equilibrium when the equilibrium concentration of each substance is: $[SO_2]= 0.60M$, $[O_2] = 0.82M$ and $[SO_3] = 1.90M$?

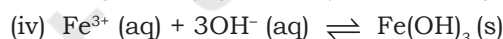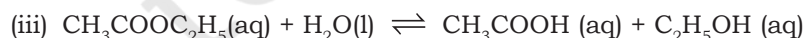$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

6.3   At a certain temperature and total pressure of 10^5Pa, iodine vapour contains 40% by volume of I atoms
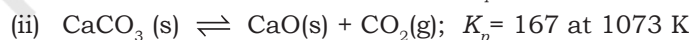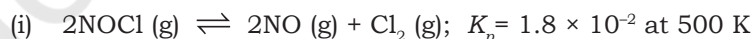
$$I_2 (g) \rightleftharpoons 2I (g)$$
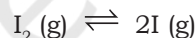
Calculate K_p for the equilibrium.

6.4   Write the expression for the equilibrium constant, K_c for each of the following reactions:

(i) $2NOCl (g) \rightleftharpoons 2NO (g) + Cl_2 (g)$

(ii) $2Cu(NO_3)_2 (s) \rightleftharpoons 2CuO (s) + 4NO_2 (g) + O_2 (g)$

(iii) $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH (aq) + C_2H_5OH (aq)$

(iv) $Fe^{3+} (aq) + 3OH^- (aq) \rightleftharpoons Fe(OH)_3 (s)$

(v) $I_2 (s) + 5F_2 \rightleftharpoons 2IF_5$
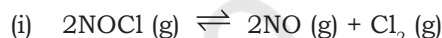
6.5   Find out the value of K_c for each of the following equilibria from the value of K_p:

(i) $2NOCl (g) \rightleftharpoons 2NO (g) + Cl_2 (g)$; $K_p= 1.8 \times 10^{-2}$ at 500 K

(ii) $CaCO_3 (s) \rightleftharpoons CaO(s) + CO_2(g)$; $K_p= 167$ at 1073 K

6.6 For the following equilibrium, K_c = 6.3 × 10^{14} at 1000 K

NO (g) + O$_3$ (g) $\rightleftharpoons$ NO$_2$ (g) + O$_2$ (g)
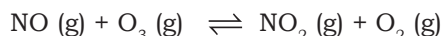
Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is K_c, for the reverse reaction?

6.7 Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression?

6.8 Reaction between N$_2$ and O$_{2-}$ takes place as follows:

$$2N_2 \text{ (g)} + O_2 \text{ (g)} \rightleftharpoons 2N_2O \text{ (g)}$$
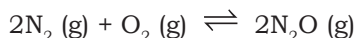
If a mixture of 0.482 mol N$_2$ and 0.933 mol of O$_2$ is placed in a 10 L reaction vessel and allowed to form N$_2$O at a temperature for which K_c= 2.0 × 10^{-37}, determine the composition of equilibrium mixture.

6.9 Nitric oxide reacts with Br$_2$ and gives nitrosyl bromide as per reaction given below:

$$2NO \text{ (g)} + Br_2 \text{ (g)} \rightleftharpoons 2NOBr \text{ (g)}$$
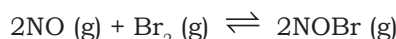
When 0.087 mol of NO and 0.0437 mol of Br$_2$ are mixed in a closed container at constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of NO and Br$_2$.

6.10 At 450K, K_p= 2.0 × 10^{10}/bar for the given reaction at equilibrium.

$$2SO_2\text{(g)} + O_2\text{(g)} \rightleftharpoons 2SO_3 \text{ (g)}$$
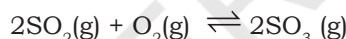
What is K_c at this temperature ?

6.11 A sample of HI(g) is placed in flask at a pressure of 0.2 atm. At equilibrium the partial pressure of HI(g) is 0.04 atm. What is K_p for the given equilibrium ?

$$2HI \text{ (g)} \rightleftharpoons H_2 \text{ (g)} + I_2 \text{ (g)}$$
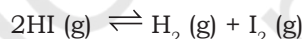
6.12 A mixture of 1.57 mol of N$_2$, 1.92 mol of H$_2$ and 8.13 mol of NH$_3$ is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction N$_2$ (g) + 3H$_2$ (g) $\rightleftharpoons$ 2NH$_3$ (g) is 1.7 × 10^2. Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

6.13 The equilibrium constant expression for a gas reaction is,

$$K_c = \frac{\left[NH_3\right]^4 \left[O_2\right]^5}{\left[NO\right]^4 \left[H_2O\right]^6}$$
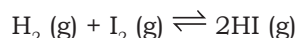
Write the balanced chemical equation corresponding to this expression.

6.14 One mole of H$_2$O and one mole of CO are taken in 10 L vessel and heated to 725 K. At equilibrium 40% of water (by mass) reacts with CO according to the equation,

$$H_2O \text{ (g)} + CO \text{ (g)} \rightleftharpoons H_2 \text{ (g)} + CO_2 \text{ (g)}$$
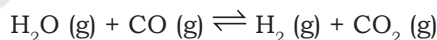
Calculate the equilibrium constant for the reaction.

6.15 At 700 K, equilibrium constant for the reaction:

$$H_2 \text{ (g)} + I_2 \text{ (g)} \rightleftharpoons 2HI \text{ (g)}$$

is 54.8. If 0.5 mol L^{-1} of HI(g) is present at equilibrium at 700 K, what are the concentration of H$_2$(g) and I$_2$(g) assuming that we initially started with HI(g) and allowed it to reach equilibrium at 700 K?

6.16 What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M ?

$2ICl$ (g) $\rightleftharpoons$ I_2 (g) + Cl_2 (g); K_c = 0.14
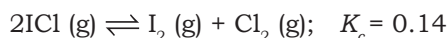
6.17 K_p = 0.04 atm at 899 K for the equilibrium shown below. What is the equilibrium concentration of C_2H_6 when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium?

$$C_2H_6 \text{ (g)} \rightleftharpoons C_2H_4 \text{ (g)} + H_2 \text{ (g)}$$

6.18 Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as:

$$CH_3COOH \text{ (l)} + C_2H_5OH \text{ (l)} \rightleftharpoons CH_3COOC_2H_5 \text{ (l)} + H_2O \text{ (l)}$$
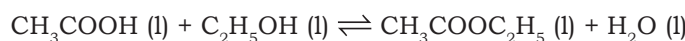
(i) Write the concentration ratio (reaction quotient), Q_c, for this reaction (note: water is not in excess and is not a solvent in this reaction)

(ii) At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after sometime. Has equilibrium been reached?

6.19 A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be 0.5×10^{-1} mol L^{-1}. If value of K_c is 8.3×10^{-3}, what are the concentrations of PCl_3 and Cl_2 at equilibrium?

$$PCl_5 \text{ (g)} \rightleftharpoons PCl_3 \text{ (g)} + Cl_2\text{(g)}$$

6.20 One of the reaction that takes place in producing steel from iron ore is the reduction of iron(II) oxide by carbon monoxide to give iron metal and CO_2.

FeO (s) + CO (g) $\rightleftharpoons$ Fe (s) + CO_2 (g); K_p = 0.265 atm at 1050K

What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are: p_{CO}= 1.4 atm and p_{CO_2} = 0.80 atm?
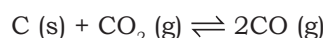
6.21 Equilibrium constant, K_c for the reaction

$$N_2 \text{ (g)} + 3H_2 \text{ (g)} \rightleftharpoons 2NH_3 \text{ (g) at 500 K is 0.061}$$

At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L^{-1} N_2, 2.0 mol L^{-1} H_2 and 0.5 mol L^{-1} NH_3. Is the reaction at equilibrium? If not in which direction does the reaction tend to proceed to reach equilibrium?

6.22 Bromine monochloride, BrCl decomposes into bromine and chlorine and reaches the equilibrium:

$$2BrCl \text{ (g)} \rightleftharpoons Br_2 \text{ (g)} + Cl_2 \text{ (g)}$$

for which K_c= 32 at 500 K. If initially pure BrCl is present at a concentration of 3.3×10^{-3} mol L^{-1}, what is its molar concentration in the mixture at equilibrium?

6.23 At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with soild carbon has 90.55% CO by mass

$$C \text{ (s)} + CO_2 \text{ (g)} \rightleftharpoons 2CO \text{ (g)}$$

Calculate K_c for this reaction at the above temperature.

6.24   Calculate a) $\Delta G^{\ominus}$ and b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298K
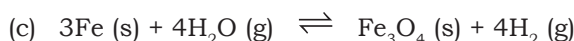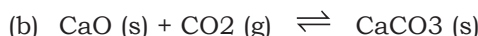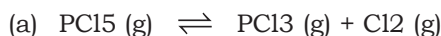
$$NO\ (g) + ½\ O_2\ (g) \rightleftharpoons NO_2\ (g)$$
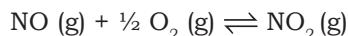
where

$\Delta_f G^{\ominus}\ (NO_2)$ = 52.0 kJ/mol

$\Delta_f G^{\ominus}\ (NO)$ = 87.0 kJ/mol

$\Delta_f G^{\ominus}\ (O_2)$ = 0 kJ/mol

6.25   Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?

(a)   PCl5 (g) $\rightleftharpoons$ PCl3 (g) + Cl2 (g)

(b)   CaO (s) + CO2 (g) $\rightleftharpoons$ CaCO3 (s)

(c)   3Fe (s) + 4H_2O (g) $\rightleftharpoons$ Fe_3O_4 (s) + 4H_2 (g)

6.26   Which of the following reactions will get affected by increasing the pressure? Also, mention whether change will cause the reaction to go into forward or backward direction.
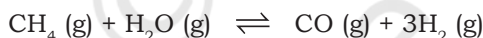
(i) $COCl_2$ (g) $\rightleftharpoons$ CO (g) + Cl_2 (g)

(ii)   CH4 (g) + 2S2 (g) $\rightleftharpoons$ CS2 (g) + 2H2S (g)

(iii)   CO2 (g) + C (s) $\rightleftharpoons$ 2CO (g)

(iv)   2H2 (g) + CO (g) $\rightleftharpoons$ CH3OH (g)

(v)   CaCO3 (s) $\rightleftharpoons$ CaO (s) + CO2 (g)

(vi)   4 NH_3 (g) + 5O_2 (g) $\rightleftharpoons$ 4NO (g) + 6H_2O(g)
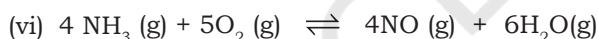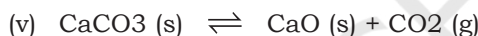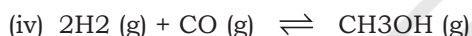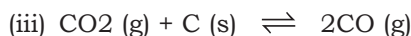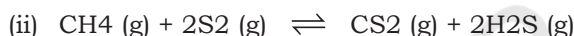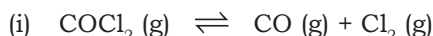
6.27   The equilibrium constant for the following reaction is 1.6×10^5 at 1024K

H_2(g) + Br_2(g) $\rightleftharpoons$ 2HBr(g)
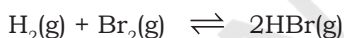
Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024K.

6.28   Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:

CH_4 (g) + H_2O (g) $\rightleftharpoons$ CO (g) + 3H_2 (g)

(a)   Write as expression for Kp for the above reaction.

(b)   How will the values of Kp and composition of equilibrium mixture be affected by

(i)   increasing the pressure

(ii)   increasing the temperature

(iii)   using a catalyst?

6.29   Describe the effect of:
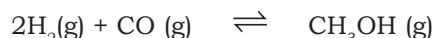
a)   addition of H2

b)   addition of CH3OH

c)   removal of CO

d)   removal of CH_3OH

on the equilibrium of the reaction:

2H_2(g) + CO (g) $\rightleftharpoons$ CH_3OH (g)

6.30   At 473 K, equilibrium constant K_c for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3}. If decomposition is depicted as,

PCl_5 (g) $\rightleftharpoons$ PCl_3 (g) + Cl_2 (g) $\Delta_r H^\ominus$ = 124.0 kJ mol^{-1}
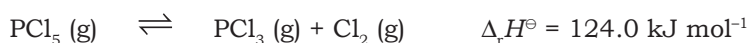
a)   write an expression for Kc for the reaction.

b)   what is the value of Kc for the reverse reaction at the same temperature?

c)   what would be the effect on K_c if (i) more PCl_5 is added (ii) pressure is increased (iii) the temperature is increased ?

6.31   Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and H_2. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction,

CO (g) + H_2O (g) $\rightleftharpoons$ CO_2 (g) + H_2 (g)

If a reaction vessel at 400 °C is charged with an equimolar mixture of CO and steam such that p_{co} = p_{H_2O} = 4.0 bar, what will be the partial pressure of H_2 at equilibrium? K_p= 10.1 at 400°C

6.32   Predict which of the following reaction will have appreciable concentration of reactants and products:

a)   Cl2 (g) $\rightleftharpoons$ 2Cl (g) Kc = 5 ×10–39

b)   Cl2 (g) + 2NO (g) $\rightleftharpoons$ 2NOCl (g)   Kc = 3.7 × 108

c)   Cl2 (g) + 2NO$_2$ (g) $\rightleftharpoons$ 2NO$_2$Cl (g) K_c = 1.8

6.33   The value of K_c for the reaction $3O_2$ (g) $\rightleftharpoons$ $2O_3$ (g) is 2.0 ×10^{-50} at 25°C. If the equilibrium concentration of O_2 in air at 25°C is 1.6 ×10^{-2}, what is the concentration of O_3?

6.34   The reaction, CO(g) + 3H$_2$(g) $\rightleftharpoons$ CH$_4$(g) + H$_2$O(g)

is at equilibrium at 1300 K in a 1L flask. It also contain 0.30 mol of CO, 0.10 mol of H$_2$ and 0.02 mol of H$_2$O and an unknown amount of CH$_4$ in the flask. Determine the concentration of CH$_4$ in the mixture. The equilibrium constant, K_c for the reaction at the given temperature is 3.90.

6.35   What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species:

HNO$_2$, CN$^-$, HClO$_4$, F$^-$, OH$^-$, CO$_3^{2-}$, and S^{2-}

6.36   Which of the followings are Lewis acids? H$_2$O, BF$_3$, H$^+$, and NH$_4^+$

6.37   What will be the conjugate bases for the Brönsted acids: HF, H$_2$SO$_4$ and HCO$^-_3$?

6.38   Write the conjugate acids for the following Brönsted bases: NH$_2^-$, NH$_3$ and HCOO$^-$.

6.39   The species: H$_2$O, HCO$_3^-$, HSO$_4^-$ and NH$_3$ can act both as Brönsted acids and bases. For each case give the corresponding conjugate acid and base.

6.40   Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base: (a) OH$^-$ (b) F$^-$ (c) H$^+$ (d) BCl$_3$.

6.41   The concentration of hydrogen ion in a sample of soft drink is 3.8 × 10^{-3} M. What is its pH?

6.42   The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.

6.43   The ionization constant of HF, HCOOH and HCN at 298K are 6.8 × 10^{-4}, 1.8 × 10^{-4} and 4.8 × 10^{-9} respectively. Calculate the ionization constants of the corresponding conjugate base.

6.44   The ionization constant of phenol is 1.0×10^{-10}. What is the concentration of phenolate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01M in sodium phenolate?

6.45   The first ionization constant of H_2S is 9.1×10^{-8}. Calculate the concentration of HS^- ion in its 0.1M solution. How will this concentration be affected if the solution is 0.1M in HCl also? If the second dissociation constant of H_2S is 1.2×10^{-13}, calculate the concentration of S^{2-} under both conditions.

6.46   The ionization constant of acetic acid is 1.74×10^{-5}. Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.

6.47   It has been found that the pH of a 0.01M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its pK_a.

6.48   Assuming complete dissociation, calculate the pH of the following solutions:

(a) 0.003 M HCl (b) 0.005 M NaOH (c) 0.002 M HBr (d) 0.002 M KOH

6.49   Calculate the pH of the following solutions:

a)   2 g of TlOH dissolved in water to give 2 litre of solution.

b)   0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution.

c)   0.3 g of NaOH dissolved in water to give 200 mL of solution.

d)   1mL of 13.6 M HCl is diluted with water to give 1 litre of solution.

6.50   The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK_a of bromoacetic acid.

6.51   The pH of 0.005M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate its ionization constant and pK_b.

6.52   What is the pH of 0.001M aniline solution? The ionization constant of aniline can be taken from Table 6.7. Calculate the degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline.

6.53   Calculate the degree of ionization of 0.05M acetic acid if its pK_a value is 4.74. How is the degree of dissociation affected when its solution also contains (a) 0.01M (b) 0.1M in HCl ?

6.54   The ionization constant of dimethylamine is 5.4×10^{-4}. Calculate its degree of ionization in its 0.02M solution. What percentage of dimethylamine is ionized if the solution is also 0.1M in NaOH?

6.55   Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below:

(a)   Human muscle-fluid, 6.83   (b)   Human stomach fluid, 1.2

(c)   Human blood, 7.38   (d)   Human saliva, 6.4.

6.56   The pH of milk, black coffee, tomato juice, lemon juice and egg white are 6.8, 5.0, 4.2, 2.2 and 7.8 respectively. Calculate corresponding hydrogen ion concentration in each.

6.57   If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH?

6.58   The solubility of $Sr(OH)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.