Ionic Equilibrium

1 Introduction

In simple terms, ionic equilibrium can be defined as ions in equilibrium. However, to be more accurate, ionic equilibrium may be defined as equilibrium that involves ions along with molecule(s). Electrolytic substances or electrolytes conduct electricity in their molten states or in aqueous solutions. Common examples of electrolytes are acids, bases and salts. When an electrolyte is dissolved in water, it dissociates into cations and anions. For example, when sodium chloride is dissolved in water, it gets dissociated into sodium ion (Na^+) and chloride ion (Cl^-). It is found that sodium chloride is completely dissociated leaving no undissociated unit. However, all electrolytes do not ionize to the same extent.

Depending upon the extent of ionization, electrolytes are divided into three classes:

- *Strong Electrolytes*: These are electrolytic substances which ionize almost completely in water. Examples include HCl, H_2SO_4, HNO_3. $NaOH$, $NaCl$, etc. Aqueous solutions of strong electrolytes are good conductors of electricity. Their ionizations are represented by single headed arrow:

$$NaCl \rightarrow Na^+ + Cl^-$$

- *Weak Electrolytes*: These are electrolytic substances which ionize to a very small extent in water. Examples include CH_3COOH, NH_4OH, HCN, etc. Aqueous solutions of weak electrolytes are poor conductors of electricity.
- *Moderate Electrolyte*: These are substances whose behaviour is intermediate between strong and weak electrolytes. $BaCl_2$, trichloroacetic acid (Cl_3CCOOH) are examples of this type.

When a weak electrolyte is added in water, it gets partially ionized and a dynamic equilibrium is established between the ions formed and unionized molecules. Such Ionic equilibria are represented as:

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

$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$$

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

In this unit, we will be restricted to ionic equilibria of acids and bases in water only. In the next unit, we will take hydrolysis equilibria of salts and solubility equilibria of sparingly soluble salts in water for discussion.

2 Degree of Ionization

A quantitative measure of extent of ionization or dissociation is expressed in terms of degree of ionization (α). It is defined as the fraction of total number of molecules of an electrolyte which ionizes into ions. Mathematically, degree of ionization is equal to the ratio of number of molecules dissociated or ionized to the total number of molecules of the electrolyte. Thus,

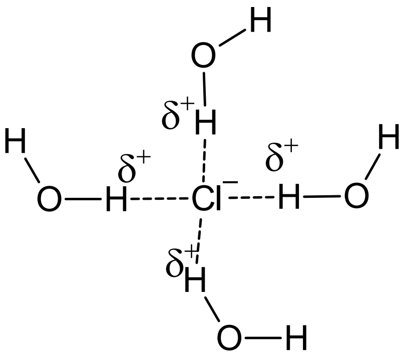
$$\alpha = \frac{number\ of\ molecules\ ionized}{total\ number\ of\ molecules}$$

2.1 Factors Affecting Degree of Ionization

Why some electrolytes ionize to a large extent while some ionize to a small extent? There are several factors which influences to what extent an electrolyte dissociates:

(i) *Nature of the solvent*: Nature of the solvent play an important part in the process of ionization of an electrolyte. Ions of an electrolyte are strongly bound together in the lattice of the solid. A solvent with high dielectric constant weakens the force of electrostatic attraction between the ions and thereby facilitates the process of dissociation. Whenever the ions become free, solvent molecules coordinate with them (Figure 6.1). This is known as solvation of ions. Solvation is a stabilising process. This stabilisation process ultimately makes the dissolution of the electrolyte easier. Thus, solvents with high dielectric constant and with high solvating power are best at ionizing electrolytes to a great extent.

(ii) *Concentration of the electrolyte:* Lower the concentration of the electrolyte higher is the dissociation.



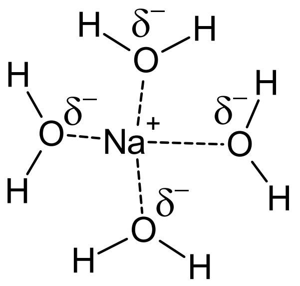


Figure 1.1: Water molecules coordinate with Na^+ and Cl^- ions through positive and negative dipoles

(iii) *Temperature*: Dissociation is an endothermic process. According to Le Chatelier's principle, if heat is supplied to the system, the system will absorb the heat by driving the dissociation process to a greater extent. So, dissociation increases with increase in temperature.

CHECK YOUR PROGRESS

1. State whether the following statement is true or false:

   Strong electrolytes are completely ionized in water due to which ionic equilibrium is not of any significance.

2. Fill in the blanks:

   (i) Barium chloride is an example of a ....Electrolyte.

   (ii) Extent of ionization of an electrolyte........... ......with increase in temperature.

   (iii) Solvents with ....dielectric constants are best at ionizing electrolytes.

3 Ionization Constant and Ionic Product of Water

Water is amphiprotic in the sense that it can act both as an acid and a base. Two molecules of water, therefore, can exchange a proton leading to an equilibrium known as autoprotolysis or self-ionization equilibrium which is represented as:

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

The corresponding equilibrium constant is:

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

Degree of ionization of water is very small, which means only a negligible number of water molecules gets ionized leaving the concentration of undissociated water molecules practically constant. Thus,

$$K \times [H_2O]^2 = [H_3O^+][OH^-]$$

$$\Rightarrow K \times constant = [H_3O^+][OH^-]$$

$$\Rightarrow K_W = [H_3O^+][OH^-]$$

The constant $K_W = [H_3O^+][OH^-]$ is called the ionic product of water or autoprotolysis constant of water. It varies with T. The value of K_W increases with increase in temperature. This can be justified by applying Le Chatelier's principle to the self-ionization equilibrium of water:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq); \Delta H = +57.3\ kJ\ mol^{-1}$$

Since, the forward reaction is endothermic, an increase in temperature will shift the equilibrium in the forward direction favouring self-ionization of water. As a result, concentration of H_3O^+ and OH^- increases. Hence, K_W increases with rise in temperature.

$$\text{At 298 } K,\ K_W = [H_3O^+][OH^-] = 1.008 \times 10^{-14}$$

So long as no ions are present in water (pure water), $[H_3O^+] = [OH^-]$. So,

$$[H_3O^+]^2 = 1.008 \times 10^{-14}$$

$$\Rightarrow [H_3O^+] = 1.0 \times 10^{-7}$$

Thus, in pure water at 298 K, $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} mol\ L^{-1}$

The autoprotolysis equilibrium is always present in any aqueous solution. At 298 K, the relation $K_W = [H_3O^+][OH^-] = 1.008 \times 10^{-14}$ must always be satisfied regardless of any other equilibria present in the aqueous solution. When an acid or base is added to pure water, concentrations of H_3O^+ and OH^- change and becomes unequal unlike pure water. However, as stated above, K_W remains constant.

If we add a little amount of an acid to water at 298 K, concentration of H_3O^+ ion in water becomes higher than $1.0 \times 10^{-7} mol\ L^{-1}$. According to Le Chatelier's principle, as a response autoprotolysis equilibrium will shift in the reverse direction, i. e., H_3O^+ and OH^- ions would combine to form water molecules to keep K_W constant. In such a situation, $[OH^-]$ can be calculated as

$$[OH^-] = \frac{K_W}{[H_3O^+]}$$

Concentration of H_3O^+ ion will be more than that of OH^- ions in acidic solution.

If we add a little amount of a base to water at 298 K, concentration of OH^-ion in water becomes higher than $1.0 \times 10^{-7} mol\ L^{-1}$. As a response, to keep K_W constant autoprotolysis equilibrium will shift in the reverse direction, i. e., H_3O^+ and OH^- ions would combine to form water molecules. In such a situation, $[OH^-]$ can be calculated as

$$[H_3O^+] = \frac{K_W}{[OH^-]}$$

In a basic solution, concentration of OH^- ions will be more that that of H_3O^+ ions.

3.1 Numerical Examples

Example 1. Calculate $[H_3O^+]$ and $[OH^-]$ in $0.01M\ HCl$ solution at 298 K.

Solution: HCl is a strong electrolyte, so it ionizes completely as

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

Here, concentration of hydronium ion is equal to the concentration of HCl

$$\therefore [H_3O^+] = [HCl] = 0.01M = 1 \times 10^{-2} mol\ L^{-1}$$

$$and \quad [OH^-] = \frac{K_W}{[H_3O^+]} = \frac{1 \times 10^{-14}}{1 \times 10^{-2}} = 1 \times 10^{-12} mol\ L^{-1}$$

Example 2. Calculate $[H_3O^+]$ and $[OH^-]$ in $0.005M\ NaOH$ solution at 298 K.

Solution: $NaOH$ is a strong electrolyte, so it completely ionizes as

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$$

Here, concentration of hydroxide ion is equal to the concentration of $NaOH$

$$\therefore [OH^-] = [NaOH] = 0.005\ M = 5 \times 10^{-3}\ mol\ L^{-1}$$

$$and\ [H_3O^+] = \frac{K_W}{[OH^-]} = \frac{1 \times 10^{-14}}{5 \times 10^{-3}} = 2 \times 10^{-12}\ mol\ L^{-1}$$

Example 3. Find the ratio of dissociated water molecules to undissociated water molecules in pure water at 298 K.

Solution: Density of pure water = $1000\ gL^{-1}$

Molar mass of water = $18\ g\ mol^{-1}$

∴ molarity of pure water,

$$[H_2O] = \frac{1000\ gL^{-1}}{18\ g\ mol^{-1}} = 55.55\ M$$

Molarity of dissociated water = 1×10^{-7}

∴ the ratio of dissociated water molecules to undissociated water molecules is

$$\frac{1 \times 10^{-7}}{55.} = 1.8 \times 10^{-9}$$

CHECK YOUR PROGRESS

3. What is the effect of temperature on ionic product of water?
4. What will be the effect of addition of some acid to water on its ionic product?
5. Write the autoprotolysis equilibrium of water.
6. What is the concentration of H_3O^+ and OH^- ions in water at 298 K?

4 Ionization of Weak Acids and Bases

At moderate concentration, weak electrolytes undergo incomplete ionization in water and the unionized molecules exists in equilibrium with the ions in solution. This equilibrium is called ionic equilibrium. In this section, we are going to discuss ionization equilibria of weak acids and bases.

4.1 Ionization of Weak Acids

In the case of a weak acid like HA, the equilibrium may be expressed as

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

Applying the law of chemical equilibrium, the equilibrium constant K_C is represented by

$$K_C = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

$$\Rightarrow K_C[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

Concentration of water remains almost constant; so, K_C and $[H_2O]$ can be combined to produce another constant K_a.

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

Here, K_a is called the ionization constant or the acidity constant of the acid. Larger the value of K_a, higher is the concentration of H_3O^+, stronger is the acid. So, K_a is a measure of the strength of an acid.

Let c be the number of moles of HA and α be its degree of dissociation.

	HA	$+$	H_2O	$\rightleftharpoons$	H_3O^+	$+$	A^-
Initial concentration	c				0		0
Equilibrium concentration	$c - c\alpha$				$c\alpha$		$c\alpha$

$$\therefore K_a = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

For a weak acid, $\alpha \ll 1$,

$$\therefore K_a = c\alpha^2$$

$$or\ \alpha = \sqrt{\frac{K_a}{c}}$$

Thus,

$$\alpha \propto \frac{1}{\sqrt{c}} \propto \sqrt{V}$$

For weak electrolytes, degree of dissociation at a particular temperature is directly proportional to dilution. This is known as Ostwald's dilution law.

Now, concentration of H_3O^+ can be calculated using

$$[H_3O^+] = c\alpha = c\sqrt{\frac{K_a}{c}} = \sqrt{K_a c}$$

Values of K_a falls over a wide range. For example, for NH_4^+ $K_a = 5.6 \times 10^{-10}$ and for HIO_3 $K_a = 0.16$ at 298 K. It is convenient to list them as their logarithms. Therefore,

$$pK_a = -logK_a$$

The higher the pK_a of an acid, the smaller its K_a and hence weaker is the acid. For weak acids, in general $K_a < 1$ and hence pK_a is positive. For strong acids, in general, $K_a > 1$ and pK_a is negative.

4.2 Ionization of Weak Bases

Ionisation equilibrium of a weak base is represented as

$$BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$$

Ionization constant of a weak base is given by

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

Here, K_b is called the ionization constant or the basicity constant of the base. Larger the value of K_b, higher is the concentration of OH^- stronger is the base. So, K_b is a measure of the strength of a base.

Let c be the number of moles of BOH and α be its degree of dissociation.

	BOH	$\rightleftharpoons OH^-$	$+$	A^-
Initial concentration	c	0		0
Equilibrium concentration	$c - c\alpha$	$c\alpha$		$c\alpha$

$$\therefore K_b = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

For a weak base, $\alpha \ll 1$, so,

$$K_b = c\alpha^2$$

$$\text{or } \alpha = \sqrt{\frac{K_b}{C}}$$

Thus, degree of dissociation of a weak base

$$\alpha \propto \frac{1}{\sqrt{c}} \propto \sqrt{V}$$

For weak bases, degree of dissociation at a particular temperature is directly proportional to dilution.

4.3 Ionization equilibria of Polyprotic Acids

Some polybasic and polyprotic acids ionize in a stepwise manner. Ionization constants are determined for each step. Following examples may be cited:

(i) Ionization of sulphuric acid

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \qquad K_{A1} = \frac{[H^+][HSO_4^-]}{[H_2SO_4]}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^- \qquad K_{A2} = \frac{[H^+][SO_4^-]}{[HSO_4^-]}$$

(ii) Ionization of oxalic acid

$$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^- \qquad K_{A1} = \frac{[H^+][HC_2O_4^-]}{[H_2C_2O_4]}$$

$$HC_2O_4^- \rightleftharpoons H^+ + C_2O_4^- \qquad K_{A2} = \frac{[H^+][C_2O_4^-]}{[HC_2O_4^-]}$$

(iii) Ionization of phosphoric acid

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad K_{A1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^- \qquad K_{A2} = \frac{[H^+][HPO_4^-]}{[H_2PO_4^-]}$$

$$HPO_4^- \rightleftharpoons H^+ + PO_4^- \qquad K_{A3} = \frac{[H^+][PO_4^-]}{[\mathrm{HPO}_4^-]}$$

Here, K_{A1}, K_{A2}, ….. are called first ionization constant, second ionization constant, etc.

It can be shown that overall equilibrium constant is the product of the equilibrium constants of the successive equilibrium steps. Let us take the case of H_3PO_4. Overall equilibrium constant K for the equilibrium

$$H_3PO_4 \rightleftharpoons H^+ + PO_4^-$$

is given by

$$\mathrm{K} = \frac{[H^+][PO_4^-]}{[H_3PO_4]} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \times \frac{[H^+][HPO_4^-]}{[H_2PO_4^-]} \times \frac{[H^+][PO_4^-]}{[\mathrm{H}PO_4^-]}$$

$$= K_{A1} \times K_{A2} \times K_{A3}$$

Thus, overall equilibrium constant of a polyprotic acid is the product of the equilibrium constants for each contributing successive equilibrium.

Another important point to note here is that first ionization is stronger than the second ionization, second ionization is stronger than the third ionization and so on. In general,

$$K_{A1} > K_{A2} > K_{A3}$$

This is so because a proton from a neutral acid molecule is released more easily than from a negative ion. Similarly, a proton is released by a uni-negative ion more easily than by a di-negative ion.

4.4 Numerical Examples

Example 4. Value of K_b for 0.1 M ammonium hydroxide solution is 1.8×10^{-5}. Calculate the concentration of hydroxide ion.

Solution: $NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

Here, $[NH_4^+] = [OH^-]$ and $[NH_4OH] = 0.1M$, so

$$K_b = \frac{[OH^-]^2}{[NH_4OH]}$$

$$\Rightarrow 1.8 \times 10^{-5} = \frac{[OH^-]^2}{0.1}$$

$$\Rightarrow [OH^-]^2 = 0.1 \times 1.8 \times 10^{-5}$$

$$\Rightarrow [OH^-] = (1.8 \times 10^{-5})^{\frac{1}{2}} = 1.34 \times 10^{-3}$$

Example 5. Value of K_a for 0.20 M hydrocyanic acid solution is 4.9×10^{-10}. Calculate the degree of dissociation.

Solution: Let α be the degree of dissociation.

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

Initial concentration	0.2	0	0
Equilibrium concentration	$0.2(1-\alpha)$	0.2α	0.2α

$$K_a = \frac{[H_3O^+][CN^-]}{[HCN]}$$

$$\Rightarrow 4.9 \times 10^{-10} = \frac{(0.2\alpha)(0.2\alpha)}{0.2(1-\alpha)}$$

$$\Rightarrow 4.9 \times 10^{-10} = 0.2\alpha^2 \qquad (\therefore 1-\alpha \approx 1)$$

$$\Rightarrow \alpha = \sqrt{\frac{4.9 \times 10^{-10}}{0.2}} = 4.95 \times 10^{-5}$$

Example 6. A $0.001M$ acetic acid solution is 12.7% ionized at 298 K. Find pK_a of acetic acid.

Solution: Given, $\alpha = 12.7\% = 0.127$

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

Initial concentration	0.001	0	0
Equilibrium concentration	$0.001(1-\alpha)$	0.001α	0.001α

$$\therefore K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(0.001\alpha)(0.001\alpha)}{0.001(1-\alpha)} = \frac{0.001\alpha^2}{1-\alpha}$$

$$\Rightarrow K_a = \frac{0.001 \times (0.127)^2}{1-0.127} = 1.85 \times 10^{-5}$$

$$\therefore pK_a = -logK_a = -\log(1.85 \times 10^{-5}) = 4.73$$

CHECK YOUR PROGRESS

7. Say true or false:

(i) If the pK_a of an acid is large, it is a strong acid.

(ii) Degree of dissociation of a weak acid is directly proportional to the volume of the solution.

5 pH Scale

Concentration of hydronium ion in aqueous solution determines the acidic or basic nature of a solution. So, a convenient way of expression of hydronium ion concentration in a solution is desirable. Hydronium ion concentration can vary over a wide range, e. g., in 1 $M\ HCl(aq)$ solution, $[H_3O^+] = 0.81$, in pure water, $[H_3O^+] = 10^{-7}$, and in 1 $M\ NaOH(aq)$ solution, $[H_3O^+] \approx 10^{-14}$. The pH scale was introduced by Sorenson to express hydronium ion concentration in a more compact and convenient way without having negative exponents. The pH of any solution is defined as

$$pH = -log_{10}[H_3O^+]$$

For a neutral solution at 298 K, $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} mol\ L^{-1}$

$$\therefore pH = \log(1.0 \times 10^{-7}) = 7$$

It can be shown that at 298 K,

for acidic solution, $pH < 7$

for basic solution, $pH > 7$

for neutral solution, $pH = 7$

The higher the pH of a solution, the lower is the hydronium ion concentration and hence, lower is the acidic strength. When $[H_3O^+] = 1, pH = 0$. When $[H_3O^+] < 1, pH > 0$ and when $[H_3O^+] > 1, pH < 0$, i. e., pH can be negative.

Like pH, we can define pOH as

$$pOH = -\log [OH^-]$$

Now,

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

$$\Rightarrow logK_W = log[H_3O^+] + log[OH^-]$$

$$\Rightarrow -logK_W = -log[H_3O^+] - log[OH^-]$$

$$\Rightarrow pK_w = pH + pOH$$

At 298 K, $K_W = 10^{-14}$, so $pK_w = -logK_W = -\log(10^{-14}) = 14$

$$\therefore pH + pOH = 14$$

5.1 Calculation of pH of Strong Acids and Bases

- Self-ionization or autoprotolysis of water always contributes to the $[H_3O^+]$ and $[OH^-]$. But, in calculating $[H_3O^+]$ in an aqueous solution of strong acid, the strong acid is regarded as the only significant source of H_3O^+ unless the solution is extremely dilute (e. g. $[H_3O^+] < 10^{-6}M$).
- Similarly, in calculating $[OH^-]$ in an aqueous solution of strong base, the strong base is regarded as the only significant source of OH^- unless the solution is extremely dilute (e. g. $[OH^-] < 10^{-6}M$).
- When H_3O^+ and OH^- furnished by the added acid or base is comparable to those produced by autoprotolysis of water, then the autoprotolysis contribution should be taken into account in addition to those contributed by the added acid or base.

Example 6. Calculate the pH of $0.01\ M\ HCl(aq)$.

Solution: $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

$0.01M$ $\quad\quad\quad\quad$ $0.01M$

$$\therefore [H_3O^+] = 0.01M$$

$$\therefore pH = -log[H_3O^+] = -\log(0.01) = -\log(10^{-2}) = 2$$

Example 7. Calculate the pH of $0.1\ M\ H_2SO_4(aq)$.

Solution: $H_2SO_4(aq) + 2H_2O(l) \rightarrow 2H_3O^+(aq) + SO_4{}^-(aq)$

$$0.1M \qquad\qquad\qquad 2 \times 0.1M$$

$$\therefore [H_3O^+] = 2 \times 0.1M = 0.2M$$

$$\therefore pH = -log[H_3O^+] = -\log(0.2) = -\log(2 \times 10^{-1}) = 1 - \log 2 = 0.699$$

Example 8. Calculate the pH of $0.001\ M\ NaOH(aq)$.

Solution:

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$$

$$0.001M \qquad\qquad\qquad 0.001M$$

$$\therefore [OH^-] = 0.001M$$

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

$$At\ 298\ K, \qquad pH + pOH = 14$$

$$\Rightarrow pH = 14 - pOH$$

$$\Rightarrow pH = 14 - 3 = 11$$

Example 9. Calculate $[H_3O^+]$ of a solution whose pH is 4.5.

Solution: $pH = 4.5$

$$\Rightarrow -log[H_3O^+] = 4.5$$

$$\Rightarrow log[H_3O^+] = -4.5$$

$$\Rightarrow [H_3O^+] = antilog(-4.5) = 3.16 \times 10^{-5}M$$

Example 10. Calculate the pH of $10^{-8}M\ HCl(aq)$ solution at 298 K.

Solution: Since H_3O^+ ion contribution from HCl is small and are comparable to those contributed by autoprotolysis of water, therefore, H_3O^+ ions contributed by autoprotolysis of water must be considered.

Let the contribution from autoprotolysis of water be $[H_3O^+] = [OH^-] = x$

$\therefore$ Total $[H_3O^+] = x + 10^{-8}$ and $[OH^-] = x$

At 298 $K, K_W = [H_3O^+][OH^-] = 10^{-14}$

,

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

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

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

$$\therefore x = \frac{-10^{-8} + \sqrt{10^{-16} + 4 \times 10^{-14}}}{2} = 9.51 \times 10^{-8}$$

$\therefore [H_3O^+] = 9.51 \times 10^{-8} + 10^{-8} = 10.51 \times 10^{-8}$

$$\therefore pH = -\log(10.51 \times 10^{-8}) = -\log(10.51) + 8 = 6.98$$

5.2 Calculation of pH of Weak Acids and Bases

Example 10. Calculate the pH of 0.01 M solution of $CH_3COOH(aq)$. At 298 K, K_a for acetic acid is 1.8×10^{-5}.

Solution: The dissociation equilibrium is

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

Applying law of mass action, equilibrium constant is given by

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Here, $[H_3O^+] = [CH_3COO^-]$

$$\therefore K_a = \frac{[H_3O^+]^2}{[CH_3COOH]}$$

Putting $[CH_3COOH] = 0.01M = 1 \times 10^{-2}M$,

$$1.8 \times 10^{-5} = \frac{[H_3O^+]^2}{1 \times 10^{-2}}$$

$$\Rightarrow [H_3O^+]^2 = 1.8 \times 10^{-5} \times 1 \times 10^{-2}$$

$$\Rightarrow [H_3O^+] = (1.8 \times 10^{-7})^{\frac{1}{2}} = 4.242 \times 10^{-4}\, mol\, L^{-1}$$

$\therefore pH = -\log(4.242 \times 10^{-4}) = 4 - log4.242 = 4 - 0.6276 = 3.37$

Example 11. K_a for an acid HA is 4.9×10^{-8}. After making necessary approximation, calculate the following for its 0.1 M solution at 298 K:

(i) % dissociation

(ii) pH

(iii) $[OH^-]$

Solution: The dissociation equilibrium is

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

Let c be the number of moles of HA and α be its degree of dissociation.

$$HA(aq) \quad + \quad H_2O(l) \rightleftharpoons \quad H_3O^+(aq) \quad + \quad A^-(aq)$$

Initial concentration	c	0	0
Equilibrium concentration	$c - c\alpha$	$c\alpha$	$c\alpha$

$$\therefore K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

Since the acid is weak, $\alpha \ll 1$,

$$\therefore K_a = c\alpha^2$$

(i)

$$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{4.9 \times 10^{-8}}{0.1}} = 7 \times 10^{-4}$$

$$\therefore \%\ dissociation = 0.07\%$$

(ii) $[H_3O^+] = c\alpha = 0.1 \times 7 \times 10^{-4} = 7 \times 10^{-5}\ mol\ L^{-1}$

$$\therefore pH = -\log(7 \times 10^{-5}) = 5 - log7 = 5 - 0.8451 = 4.15$$

(iii) Ionic product is given by

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

$$\therefore\ [OH^-] = \frac{K_W}{[H_3O^+]}$$

$$= \frac{1 \times 10^{-14}}{7 \times 10^{-5}} = 1.43 \times 10^{-10}\ \ mol\ L^{-1}$$

CHECK YOUR PROGRESS

8. How the pH of a neutral solution changes with increase in temperature?

9. Assuming complete dissociation, calculate the pH of the following solutions:

(i) $0.003\ M\ HCl(aq)$

(ii) $0.005M\ NaOH(aq)$

(iii) $0.002\ M\ HBr(aq)$

(iv) $0.002\ M\ KOH(aq)$

10. pH of a $10^{-8}M$ solution of HCl is

(a) 8

(b) 6

(c) Between 6 and 7

(d) Between 7 and 8

(Select the correct answer)

6 Common Ion Effect

The degree of dissociation of a weak electrolyte is suppressed by the addition of a strong electrolyte which has an ion in common with the weak electrolyte. This is referred to as common ion effect. Acetic acid is a weak electrolyte; its equilibrium can be expressed as:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

When sodium acetate (having common ion CH_3COO^-) or a strong acid (having common ion H_3O^+) is added to a solution of acetic acid, ionization of acetic acid is suppressed. Similarly, when ammonium chloride is added to a solution of ammonium hydroxide (both have NH_4^+ ion in common), dissociation of ammonium hydroxide is suppressed:

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

Let us consider the dissociation of a weak electrolyte AB:

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

Its equilibrium constant K is given by

$$K = \frac{[A^+][B^-]}{[AB]}$$

The equilibrium constant K has a definite value at a given temperature. If another electrolyte containing A^+ or B^- ions is added to the above solution, it will increase the concentration of A^+ or B^- in solution. In order that K may remain constant, the concentration of AB must increase. So, the equilibrium will shift towards left, thereby suppressing the dissociation of AB.

7 Answers to Check Your Progress

Ans to Q No 1: True

Ans to Q No 2: (i) moderate
(ii) increases
(iii) high

Ans to Q No 3: Ionic product increases with increase in temperature.

Ans to Q No 4: Ionic product is constant as long as the temperature is constant, addition of an acid will have no effect upon it.

Ans to Q No 5: $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

Ans to Q No 6: In pure water at 298 K, $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} mol\, L^{-1}$

Ans to Q No 7: (i) False
(ii) True

Ans to Q No 8: pH of a neutral solution decreases with increase in temperature because $[H_3O^+]$ ion concentration increases with increase in the extent of dissociation with temperature.

Ans to Q No 9: (i) $[H_3O^+] = [HCl] = 0.003M = 3 \times 10^{-3}M$

$$pH = -\log(3 \times 10^{-3}) = 3 - log3 = 3 - 0.477 = 2.523$$

(ii) $[OH^-] = [NaOH] = 0.005\ M = 5 \times 10^{-3}M$

$$[H_3O^+] = \frac{K_W}{[OH^-]} = \frac{1 \times 10^{-14}}{5 \times 10^{-3}} = 2 \times 10^{-12}$$

$$pH = -log(2 \times 10^{-12}) = 12 - log2 = 12 - 0.301 = 11.699$$

(iii) $[H_3O^+] = [HBr] = 0.002M = 2 \times 10^{-3}M$

$$pH = -\log(2 \times 10^{-3}) = 3 - log2 = 3 - 0.301 = 2.699$$

(iv) $[OH^-] = [KOH] = 0.002\ M = 2 \times 10^{-3}M$

$$[H_3O^+] = \frac{K_W}{[OH^-]} = \frac{1 \times 10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12}$$

$$pH = -log(5 \times 10^{-12}) = 12 - log\ 5 = 12 - 0.669 = 11.301$$

Ans to Q No 10: (c) Between 6 and 7

8 Model Questions

1. What is meant by ionic equilibrium?
2. Describe the three classes of electrolytes with examples.
3. Define degree of ionisation of an electrolyte. Discuss the factors that influence the degree of ionization.
4. What is autoprotolysis?
5. Define ionic product of water. Explain with the help of Le Chatelier's principle how does it change with temperature?
6. At 298 K, show that $pH + pOH = 14$
7. Derive a relation between ionization constant and degree of ionization of acetic acid.
8. State and explain Ostwald's law of dilution.
9. Explain common ion effect with example.
10. Dissociation of acetic acid is supressed by the addition of sodium acetate. Explain.
11. pH of $10^{-7}M\ HCl$ is not 7. Explain.
12. Calculate the degree of ionization and pH of a $0.05M$ ammonia solution. The value of K_b for ammonia is 1.77×10^{-5}.
13. Calculate the $[H_3O^+]\ and\ [OH^-]$ in $0.01M\ NaOH$ solution.

9 Hydrolysis of Salts

For convenience of treatment, we study the hydrolysis of different categories of salt separately.

9.1 Salts of Strong Acids and Strong Bases

Salt of a strong acid and a strong base does not undergo hydrolysis. Hence, aqueous solutions of such salts are neutral. Let us consider the example of sodium chloride. When $NaCl$ is dissolved in water, Na^+ and Cl^- ions are produced. Neither of these ions have any tendency to interact with the H_3O^+ ions *or* OH^- ions produced by water because the resulting products $NaOH$ and $NaCl$ get completely dissociated. Consequently, concentration of H_3O^+ and OH^- *ions* remain static.

9.2 Salts of Weak Acids and Strong Bases

Whenever a salt of this category is dissolved in water, an alkaline solution results. Examples of such salts include CH_3COONa, Na_2CO_3, Na_3PO_4, etc. Let us consider the aqueous solution of CH_3COONa. It dissociates completely to form CH_3COO^- and Na^+ ions. CH_3COO^- ion interacts with H_3O^+ from water to produce a weak electrolyte CH_3COOH. To maintain constancy of K_W, more water molecules undergo dissociation, thereby increasing the concentration of OH^- ions. The overall equilibrium can be represented as

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

Hydrolysis Constant:

In general, the hydrolysis equilibrium of a salt BA formed by a weak acid HA and a strong base BOH is given by

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

Assuming a constant concentration of water, the equilibrium constant for the hydrolysis equilibrium (hydrolysis constant) is expressed as

$$K_h = \frac{[HA][OH^-]}{[A^-]} \dots\dots\dots\dots\dots\dots\dots\dots\dots (i)$$

In addition to the hydrolysis equilibrium, the ionisation equilibrium of the weak acid and the autoprotolysis equilibrium must also be established in the system:

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

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

Therefore, following laws of equilibria must also hold good simultaneously:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \dots\dots\dots\dots\dots\dots\dots\dots . (ii)$$

$$K_W = [H_3O^+][OH^-] \dots\dots\dots\dots\dots\dots .. (iii)$$

$$\frac{(iii)}{(ii)} \Rightarrow \frac{K_W}{K_a} = \frac{[H_3O^+][OH^-][HA]}{[H_3O^+][A^-]} = \frac{[HA][OH^-]}{[A^-]} = K_h$$

Thus,

$$K_h = \frac{K_W}{K_a} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots ... (iv)$$

It is evident that the hydrolysis constant K_h is inversely proportional to the dissociation constant K_a of the weak acid. So, the weaker the acid, the higher will be the hydrolysis constant of the salt.

Degree of hydrolysis: Let $c\ mol\ L^{-1}$ be the initial concentration of the salt and h be the degree of hydrolysis at equilibrium.

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

Initial concentration	c	0	0
Equilibrium concentration	$c - ch$	ch	ch

The hydrolysis constant

$$K_h = \frac{[HA][OH^-]}{[A^-]} = \frac{(ch)(ch)}{c(1-h)} = \frac{ch^2}{1-h}$$

When h is very small, we can assume $1 - h \approx 1$. In such a case,

$$K_h = ch^2$$

$$\Rightarrow h = \sqrt{\frac{K_h}{c}}$$

Using (iv),

$$h = \sqrt{\frac{K_W}{K_a c}} \dots\dots\dots\dots\dots\dots\dots\dots\dots (v)$$

From (v), it is clear that weaker the acid, greater is the degree of hydrolysis.

pH of the solution:

At equilibrium, $[OH^-] = ch$

$$\therefore [H_3O^+] = \frac{K_W}{[OH^-]} = \frac{K_W}{ch}$$

Substituting the value of h from (v),

$$[H_3O^+] = \frac{K_W}{c}\sqrt{\frac{K_a c}{K_W}} = \sqrt{\frac{K_W K_a}{c}}$$

Now,

$$pH = -\log[H_3O^+] = -\log\left(\frac{K_W K_a}{c}\right)^{\frac{1}{2}}$$

$$\Rightarrow pH = \frac{1}{2}[-logK_W - logK_a + logc]$$

$$\Rightarrow pH = \frac{1}{2}pK_W + \frac{1}{2}pK_a + \frac{1}{2}logc \dots\dots\dots\dots (vi)$$

At 298 K, $pK_W = 14$, so the equation becomes

$$pH = 7 + \frac{1}{2}(pK_a + logc) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.. (vii)$$

9.3 Salts of Strong Acids and Weak Bases

When a salt of a strong acid and a weak base is dissolved in water, the resulting solution becomes acidic due to hydrolysis of the salt. Some examples of such salts are NH_4Cl, $CuSO_4$, $AlCl_3$, etc. Let us consider the case of NH_4Cl. Ammonium chloride produces ${NH_4}^+$and Cl^- on complete dissociation. ${NH_4}^+$ ion accepts OH^- ion produced by autoprotolysis of water; resulting NH_4OH is a weak electrolyte which gets dissociated to a very little extent. More water molecules will be dissociated to make up for the loss of OH^- ion, so that K_W remains constant. As a result, concentration of H_3O^+ ion increases and the solution becomes acidic. Hydrolysis equilibrium of ${NH_4}^+$ ion is expressed as:

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

Hydrolysis Constant:

In general, the hydrolysis equilibrium of a salt BA formed by a strong acid HA and a weak base BOH is given by

$$B^+ + H_2O \rightleftharpoons BOH + H_3O^+$$

Assuming a constant concentration of water, the equilibrium constant for the hydrolysis equilibrium (hydrolysis constant) is expressed as

$$K_h = \frac{[BOH][H_3O^+]}{[B^+]} \dots\dots\dots\dots\dots\dots\dots\dots\dots (viii)$$

In addition to the hydrolysis equilibrium, the ionisation equilibrium of the weak base and the autoprotolysis equilibrium must also be established in the system:

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

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

Therefore, following laws of equilibria must also hold good simultaneously:

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \dots\dots\dots\dots\dots\dots\dots\dots. (ix)$$

$$K_W = [H_3O^+][OH^-] \dots\dots\dots\dots\dots.. (x)$$

$$\frac{(x)}{(ix)} \Rightarrow \frac{K_W}{K_b} = \frac{[H_3O^+][OH^-][BOH]}{[B^+][OH^-]} = \frac{[BOH][H_3O^+]}{[B^+]} = K_h$$

Thus,

$$K_h = \frac{K_W}{K_b} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots... (xi)$$

It is evident that the hydrolysis constant K_h is inversely proportional to the dissociation constant K_b of the weak base. So, the weaker the base, the higher will be the hydrolysis constant of the salt.

Degree of hydrolysis: Let $c\ mol\ L^{-1}$ be the initial concentration of the salt and h be the degree of hydrolysis at equilibrium.

$$B^+ + H_2O \rightleftharpoons BOH + H_3O^+$$

Initial concentration	c	0	0
Equilibrium concentration	$c - ch$	ch	ch

The hydrolysis constant

$$K_h = \frac{[BOH][H_3O^+]}{[B^+]} = \frac{(ch)(ch)}{c(1-h)} = \frac{ch^2}{1-h}$$

When h is very small, we can assume $1 - h \approx 1$. In such a case,

$$K_h = ch^2$$

$$\Rightarrow h = \sqrt{\frac{K_h}{c}}$$

Using (xi),

$$h = \sqrt{\frac{K_W}{K_b c}} \dots\dots\dots\dots\dots\dots\dots\dots\dots (xii)$$

From (v), it is clear that weaker the base, the higher is the degree of hydrolysis.

pH *of the solution*:

At equilibrium, $[H_3O^+] = ch$

Substituting the value of h from (xii),

$$[H_3O^+] = c\sqrt{\frac{K_W}{K_b c}} = \sqrt{\frac{K_W c}{K_b}}$$

Now,

$$pH = -\log[H_3O^+] = -\log\left(\frac{K_W c}{K_b}\right)^{\frac{1}{2}}$$

$$\Rightarrow pH = \frac{1}{2}[-logK_W - logc - (-\log K_b)]$$

$$\Rightarrow pH = \frac{1}{2}pK_W - \frac{1}{2}pK_b - \frac{1}{2}logc \dots\dots\dots\dots (xiii)$$

At 298 K, $pK_W = 14$, so the equation becomes

$$pH = 7 - \frac{1}{2}(pK_b + logc) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.. (xiv)$$

9.4 Salts of Weak Acids and Weak Bases

For this category of salts, both the cation and the anion undergo hydrolysis. Extent of hydrolysis undergone by the cation and the anion may be same or different depending upon the strengths of the corresponding acid and the base contributing them. Accordingly, the resulting solution may be neutral, acidic or basic. Example of this category of salt are CH_3COONH_4, $(NH_4)_2CO_3$, $AlPO_4$, etc. Let us consider the case of CH_3COONH_4. It produces ${NH_4}^+$and CH_3COO^- ions in equal amounts. The ${NH_4}^+$ ions combine with OH^- ions furnished by water to produce NH_4OH which is feebly dissociated. Similarly, the CH_3COO^- ions combine with H_3O^+ to produce feebly dissociated CH_3COOH. The equilibrium is represented by

$$CH_3COO^- + NH_4{}^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH.$$

In this case, both the H_3O^+ and OH^- ions are taken up by the two ions of the salt in equal amounts leading to a neutral solution.

Hydrolysis Constant:

In general, the hydrolysis equilibrium of a salt BA formed by a weak acid HA and a weak base BOH is given by

$$B^+ + A^- + H_2O \rightleftharpoons BOH + HA$$

Assuming a constant concentration of water, the equilibrium constant for the hydrolysis equilibrium (hydrolysis constant) is expressed as

$$K_h = \frac{[BOH][HA]}{[B^+][A^-]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (xv)$$

In addition to the hydrolysis equilibrium, the ionisation equilibrium of the weak base, ionisation equilibrium of the weak acid and the autoprotolysis equilibrium must also be established individually in the system:

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

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

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

Therefore, following laws of equilibria must also hold good simultaneously:

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots. (xvi)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \ldots\ldots\ldots\ldots\ldots\ldots.. (xvii)$$

$$K_W = [H_3O^+][OH^-] \ldots\ldots\ldots\ldots\ldots.. (xix)$$

K_h can be rearranged as

$$K_h = \frac{[HA][BOH]}{[H_3O^+][A^-]}\frac{[H_3O^+][OH^-]}{[B^+][OH^-]} = \frac{[H_3O^+][OH^-]}{\frac{[H_3O^+][A^-]}{[HA]} \times \frac{[B^+][OH^-]}{[BOH]}} = \frac{K_W}{K_a \times K_b}$$

Thus,

$$K_h = \frac{K_W}{K_a \times K_b} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots... (xx)$$

Degree of hydrolysis: Let $c\ mol\, L^{-1}$ be the initial concentration of the salt and h be the degree of hydrolysis at equilibrium.

	$B^+ \quad +$	$A^- + H_2O \rightleftharpoons$	$BOH \quad +$	HA
Initial concentration	c	c	0	0
Equilibrium concentration	$c - ch$	$c - ch$	ch	ch

The hydrolysis constant

$$K_h = \frac{[BOH][HA]}{[B^+][A^-]} = \frac{(ch)(ch)}{c(1-h)\times c(1-h)} = \frac{h^2}{(1-h)^2}$$

When h is very small, we can assume $1 - h \approx 1$. In such a case,

$$K_h = h^2$$

$$\Rightarrow h = \sqrt{K_h}$$

Using (xx),

$$h = \sqrt{\frac{K_W}{K_a \times K_b}} \dots\dots\dots\dots\dots\dots\dots\dots\dots (xxi)$$

From (xxi), it is clear that weaker the acid and the base, the greater is the degree of hydrolysis of the salt. Also, the degree of hydrolysis is independent of the concentration of the salt solution. As K_W increases with increase in temperature, much more than either of K_a and K_b does, the degree of hydrolysis also increases with increase in temperature.

pH of the solution:

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

$$\Rightarrow [H_3O^+] = K_a\frac{[HA]}{[A^-]} = K_a\frac{ch}{c(1-h)} = K_a\frac{h}{(1-h)} = K_a \times h \quad [\because 1 - h \approx 1]$$

Thus,

$$[H_3O^+] = K_a \times h$$

Using (xxi),

$$[H_3O^+] = K_a\sqrt{\frac{K_W}{K_a \times K_b}} = \sqrt{\frac{K_W \times K_a}{K_b}}$$

Now,

$$pH = -\log[H_3O^+] = -\log\left(\frac{K_W K_a}{K_b}\right)^{\frac{1}{2}}$$

$$\Rightarrow pH = \frac{1}{2}[-logK_W - \log K_a - (-\log K_b)]$$

$$\Rightarrow pH = \frac{1}{2}pK_W + \frac{1}{2}pK_a - \frac{1}{2}pK_b \dots\dots\dots\dots (xxii)$$

At 298 K, $pK_W = 14$, so the equation becomes

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

Following conclusions may be drawn:

(i) If $pK_a = pK_b$, $pH = 7$. So, the resulting solution is neutral.
(ii) If $pK_a < pK_b$, $pH < 7$. So, the solution is acidic.
(iii) If $pK_a > pK_b$, $pH > 7$. So, the solution is basic.

9.5 Numerical Examples

Example 1. Calculate hydrolysis constant, degree of hydrolysis and pH of an aqueous solution of KCN of $0.01\ M$ concentration. K_a for HCN is 6.2×10^{-10}.

Solution: The hydrolysis constant is given by

$$K_h = \frac{K_W}{K_a}$$

$$= \frac{10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5}$$

Degree of hydrolysis is given by

$$h = \sqrt{\frac{K_h}{c}} = \left(\frac{1.6 \times 10^{-5}}{10^{-2}}\right)^{\frac{1}{2}} = 4 \times 10^{-4}$$

Given $K_a = 6.2 \times 10^{-10}$

$$\therefore pK_a = -logK_a = -\log(6.2 \times 10^{-10}) = 10 - log6.2 = 10 - 0.7924 = 9.2$$

$$pH = \frac{1}{2}pK_W + \frac{1}{2}pK_a + \frac{1}{2}logc$$

$$= \frac{1}{2} \times 14 + \frac{1}{2} \times 9.2 + \frac{1}{2} \times \log(10^{-2}) = 7 + 4.6 - 1 = 10.6$$

Example 2. Calculate

(i) hydrolysis constant,
(ii) degree of hydrolysis, and
(iii) pH of an aqueous solution of NH_4Cl of $0.01\ M$ concentration at 25^0C.
K_b for NH_4OH is 1.81×10^{-5}.

Solution:

(i) NH_4Cl is a salt of a strong acid and weak base. Its hydrolysis constant is given by

$$K_h = \frac{K_W}{K_b} = \frac{10^{-14}}{1.81 \times 10^{-5}} = 5.52 \times 10^{-10}$$

(ii) Degree of hydrolysis is given by

$$h = \sqrt{\frac{K_h}{c}} = \left(\frac{5.52 \times 10^{-10}}{10^{-2}}\right)^{\frac{1}{2}} = 2.35 \times 10^{-4}$$

(iii) Given $K_b = 1.81 \times 10^{-5}$

$\therefore pK_b = -logK_b = -\log(1.81 \times 10^{-5}) = 5 - log1.81 = 5 - 0.2577 = 4.74$

$$pH = \frac{1}{2}pK_W - \frac{1}{2}pK_b - \frac{1}{2}logc$$

$$= \frac{1}{2} \times 14 - \frac{1}{2} \times 4.74 - \log(10^{-2})$$

$$= 7 - 2.37 + 2$$

$$= 6.63$$

CHECK YOUR PROGRESS

1. Predict the acidic, basic or neutral character of the aqueous solution of the following salts:

$$NaCl, KBr, NaCN, NH_4NO_3, NaNO_2, KF$$

2. Say true or false:

pH of aqueous solution of $CuSO_4$ is less than 7.

3. If $pK_a = pK_b = 4.74$, what will be the pH of $0.1\ M$ ammonium acetate solution?

4. For aqueous solution of which of the following salts, degree of hydrolysis is independent of the concentration of the salt:

(a) KCl

(b) CH_3COONa

(c) NH_4Cl

(d) CH_3COONH_4

5.When a salt of strong acid and weak base is hydrolysed, the resulting solution has

(a) $pH = 7$ (b) $pH = 0$ (c) $pH < 7$ (d) $pH > 7$

10 Buffer Solutions

Buffer solutions are solutions which resist changes in its pH on addition of a small amount of an acid or a base. Generally, two types of buffer solutions are found:

(i) Acidic buffer: An equimolar mixture of weak acid and its salt formed with a strong base gives an acidic buffer. An equimolar mixture of acetic acid and sodium acetate forms an acidic buffer.

(ii) Basic buffer: An equimolar mixture of weak base and its salt formed with a strong acid gives a basic buffer. An equimolar mixture of ammonium hydroxide and ammonium chloride forms a basic buffer.

In addition to these, an aqueous solution of a salt formed by a weak acid and a weak base also forms a buffer solution. Examples of this category of salt include CH_3COONH_4, $(NH_4)_2CO_3$, $(NH_4)_3PO_4$, etc.

10.1 Mechanism of Buffer Action

To understand the mechanism of buffer action, let us address the following questions:

Why does an aqueous solution of ammonium acetate act as a buffer?

Why cannot an aqueous solution of sodium chloride act as a buffer?

Being a strong electrolyte ammonium acetate ionizes completely to produce ${NH_4}^+$ and CH_3COO^- ions. Whenever an acid is added to the solution, H_3O^+ ions produced by the acid combine with the acetate ions producing almost unionized acetic acid:

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

Thus, concentration of H_3O^+ions almost remain constant. Whenever a base is added to the solution of ammonium acetate, OH^- ions provided by the base is captured by the ${NH_4}^+$ions to produce NH_4OH. Being a weak electrolyte, NH_4OH remains almost unionized. With no change in OH^- ion concentration, pH of the solution remains constant.

In aqueous solution, $NaCl$ ionizes completely to produce $Na^+$and Cl^-. If an acid is added, H_3O^+ ion concentration increases. Because, the HCl formed on the addition of the acid is completely dissociated. On the other hand, the $NaOH$ formed on addition of a base (OH^-) gets completely dissociated. Consequently, concentration of OH^- increases. So, *pH* increases.

Now let us consider the buffers formed by an equimolar mixture of acetic acid and sodium acetate. The solution contains a large number of Na^+ and CH_3COO^- ions due to complete ionization of the strong electrolyte

CH_3COONa. It also contains a large number of undissociated acetic acid molecules. Whenever an acid is added to the buffer, the H_3O^+ would be trapped by the CH_3COO^- ions present in large number. It results in undissociated acetic acid molecules leading to no change in pH of the mixture:

$$CH_3COO^-(aq) + H_3O^+(aq) \rightleftharpoons CH_3COOH + H_2O(l)$$

Due to the H_3O^+ neutralisation by the CH_3COO^- ions, buffer mixture is said to possess reserve alkalinity.

Whenever a strong base is added to the mixture, undissociated CH_3COOH molecules present in the mixture neutralises the OH^- ions:

$$CH_3COOH + OH^-(aq) \rightleftharpoons CH_3COO^-(aq) + H_2O(l)$$

Thus, acetic acid molecules do not allow the pH to increase. In this case, the buffer mixture is said to possess reserve acidity due to the presence of CH_3COOH.

Finally, let us take an equimolar mixture of a weak base NH_4OH and its salt NH_4Cl which acts as a basic buffer. The buffer mixture contains large number of ${NH_4}^+$ ions, Cl^- ions and undissociated NH_4OH molecules. When a little amount of a strong acid is added, NH_4OH neutralise the added H_3O^+ ions.

$$H_3O^+ + NH_4OH \rightleftharpoons H_2O + {NH_4}^+$$

Thus, the undissociated NH_4OH molecules offer reserve basicity to the mixture. Whenever a strong base is added, the ${NH_4}^+$ ions capture the OH^- ions forming the feebly dissociated NH_4OH. Thus, the ${NH_4}^+$ ions offer reserve acidity to the buffer.

10.2 pH of a Buffer Solution

Let us consider a buffer mixture of a weak acid HA and its salt M^+A^-. Let c_a and c_s be the initial concentrations of the acid and the salt, respectively.

Ionization equilibria of HA is represented by

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

$$\therefore [HA] = c_a - [H_3O^+]$$

Ionization constant is given by

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

$$\Rightarrow [H_3O^+] = K_a \frac{[HA]}{[A^-]} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (xxiv)$$

Applying electro-neutrality principle, and considering that the salt is completely ionized:

$$[A^-] = c_s + [H_3O^+]$$

So, expression $(xxiv)$ becomes

$$[H_3O^+] = K_a \frac{c_a - [H_3O^+]}{c_s + [H_3O^+]} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.. (xxv)$$

Instead of solving this quadratic equation for $[H_3O^+]$, we can simplify it through approximations. Ionization of the weak acid is suppressed by the addition of common ion A^- through the salt, so concentration of H_3O^+ is negligible compared to c_a and c_s. Therefore, expression (xxv) may be simplified as

$$[H_3O^+] = K_a \frac{c_a}{c_s} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.. (xxvi)$$

Taking negative logarithm on both sides of $(xxvi)$,

$$-log[H_3O^+] = -logK_a - log\left(\frac{c_a}{c_s}\right)$$

$$\Rightarrow pH = pK_a - \ log\left(\frac{c_a}{c_s}\right)$$

$$\Rightarrow pH = pK_a + \ log\left(\frac{c_s}{c_a}\right)$$

or

$$pH = pK_a + \ log\frac{[salt]}{[acid]} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. (xxvii)$$

This is known as Henderson-Hasselbach equation.

Following similar considerations, Henderson-Hasselbach equation for the buffer mixture of a weak base and its salt is given by

$$pOH = pK_b + \ log\frac{[salt]}{[base]} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. (xxviii)$$

Now, at 298 K, $pH + pOH = 14$, so

$$pH = 14 - pK_b - \ log\frac{[salt]}{[base]} \dots\dots\dots\dots\dots\dots\dots. (xxix)$$

10.3 Buffer Capacity and Buffer Index

Buffer capacity of a buffer mixture is its capacity to resist change in pH value. Buffer capacity of a buffer mixture is quantitively measured by a parameter called *buffer index* introduced by van Slyke. Buffer index is defined as number of moles of a strong acid or strong base required to be added in per litre of the buffer solution to effect unit pH change. Mathematically,

$$\beta = \frac{\Delta n}{\Delta pH}$$

where Δn is the number of moles of a strong acid or base added per litre of the buffer, and ΔpH is the change in pH on addition of the acid or base.

Thus, larger is the amount of buffer required to effect unit change in pH, higher is the buffer capacity.

10.4 Numerical Examples

Example 1. Calculate the pH of a buffer solution containing $0.2\ M$ acetic acid and $0.02\ M$ sodium acetate. K_a for acetic acid is 1.8×10^{-5}.

Solution: Given $K_a = 1.8 \times 10^{-5}$

$$pK_a = -logK_a$$

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

$$= 5 - log1.8$$

$$= 4.74$$

Applying Henderson-Hasselbach equation

$$pH = pK_a + \ log\frac{[salt]}{[acid]}$$

$$= 4.74 + log\left(\frac{0.02}{0.2}\right) = 4.74 + log(10^{-1}) = 4.74 - 1 = 3.73$$

Example 2. Calculate the pH of a buffer solution containing $0.2\ mol$ of NH_4Cl and $0.1\ mol$ NH_4OH per litre of the solution. K_b for NH_4OH is 1.85×10^{-5}.

Solution: Given $K_b = 1.85 \times 10^{-5}$

$$\therefore pK_b = -logK_b = -\log(1.85 \times 10^{-5}) = 5 - log1.85 = 4.73$$

Using Henderson-Hasselbach equation

$$pOH = pK_b + \ log\frac{[salt]}{[base]} = 4.733 + log\left(\frac{0.2}{0.1}\right) = 4.733 + 0.301 = 5.034$$

$$\therefore pH = 14 - pOH = 14 - 5.034 = 8.966$$

CHECK YOUR PROGRESS

6. Choose from the following pairs the combinations that would act as buffer solution:

(a) $NH_4Cl + \ NH_3$ (b) $CH_3COOH + HCl$ (c) $CH_3COONa + CH_3COOH$ (d) $HCl + NaOH$

7. Fill in the blanks:

(a) An equimolar mixture of weak acid and its salt formed with a strong base give ……buffer.

(b) An equimolar mixture of ammonium hydroxide and ammonium chloride forms a …. Buffer.

8. Say true or false: The larger is the amount of buffer required to effect unit change in pH, the higher is the buffer capacity.

9. An equimolar mixture of a weak base NH_4OH and its salt NH_4Cl acts as a basic buffer. Which of the following species offers reserve acidity to the buffer mixture:

(a) NH_4OH (b) Cl^- (c) ${NH_4}^+$ (d) OH^-

10. Define buffer index.

11 Theory of Acid–Base Indicators

In acid–alkali titrations, the equivalence point is detected using substances called acid–base indicators, which change colour at or near the equivalence point. An acid–base indicator is a weak organic acid or base that exhibits one colour in acidic solutions and an entirely different colour in alkaline solutions. The actual colour produced depends on the pH of the solution. The colour change of an indicator is not sudden or abrupt; rather, it occurs over a small pH range known as the colour change interval of the indicator.

11.1 Ostwald Theory acid-base indicator:

According to this theory, acid–base indicators are regarded as weak organic acids or bases. The unionized form of an acid indicator (HIn) or a basic indicator (InOH) has one colour, while the corresponding ionized form has a different colour. The ionization equilibria in aqueous solutions may be represented as:

$$\text{Hin} + H_2O \rightleftharpoons H_3O^+ + In^-$$

and

$$InOH \rightleftharpoons In^+ + OH^-$$

Applying the law of mass action to the ionization equilibrium of an acid indicator (HIn), the ionization constant is:

$$K_{Ind} = \frac{[H_3O^+][In^-]}{[HIn]} \quad \dots\dots\dots(1)$$

or

$$[H_3O^+] = K_{Ind}\frac{[HIn]}{[In^-]}\dots\dots\dots\dots(2)$$

or

$$[H_3O^+] = K_{Ind}\frac{[Unionized\ form]}{[Ionized\ form]}$$

In acidic solutions, the presence of excess H_3O^+ ions suppress the ionization of the acid indicator, so $[In^-]$ remains small. Therefore, the observed colour is mainly due to the unionized form (HIn).

In alkaline solutions, the equilibrium shifts to the right, increasing the concentration of the ionized form (In^-). Hence, in alkaline medium, the indicator exists predominantly in the ionized form, and its colour becomes apparent.

The actual colour of the indicator depends on the ratio of the concentrations of the ionized and unionized forms and is therefore directly related to the hydrogen ion concentration of the medium. Equation (2) may be rewritten as:

$$-log[H_3O^+] = -log\ K_{Ind} - log\ \frac{[HIn]}{[In^-]}$$

Or

$$pH = pK_{Ind} + log\frac{[In^-]}{[HIn]} \dots\dots\dots(3)$$

At any given pH, both forms of the indicator are present. It is important to note that the human eye has a limited ability to detect either colour when one form predominates significantly. In general, when:

$$\frac{[HIn]}{[In^-]} = 10$$

equation (3) becomes

$$pH = pK_{Ind} - 1$$

and the observed colour corresponds mainly to the unionized form.

When:

$$\frac{[In^-]}{[HIn]} = 10$$

equation (3) becomes

$$pH = pK_{Ind} + 1$$

and the colour is due to the ionized form. Thus, the colour change interval is given by:

$$pH = pK_{Ind} \pm 1$$

This interval spans approximately two pH units—one unit above and one unit below the pK_{Ind} value of the indicator. Within this range, the indicator gradually changes colour, as the change depends on the logarithm of the ratio of the concentrations of the two coloured forms.

When pH = pK_{Ind} , the ratio $[HIn]/[In^-]$ becomes unity, and the indicator exhibits a colour corresponding to an equimolar mixture of the two forms. This is known as the middle tint of the indicator, provided both colours have equal intensity.

11.2 Universal indicator

By suitably mixing certain indicators, the colour change can be extended over a wide pH range. Such a mixture is called a universal indicator. These are commonly used to determine the approximate pH of solutions. One example is a mixture of methyl red, methyl orange, bromothymol blue, and phenolphthalein, covering a pH range of 3–11.

11.3 Action of Phenolphthalein

Phenolphthalein is a colourless weak acid. It dissolves in water and dissociates slightly to produce colourless hydrogen ions and pink-coloured anions:

$$HPh + H_2O \rightleftharpoons H_3O^+ + Ph^- \qquad \text{........(1)}$$

In reality, the situation is more complex. Phenolphthalein first undergoes a reversible tautomeric transformation into a differently coloured form, which then dissociates almost completely:

$$\underset{\text{(Colourless)}}{HPh} \rightleftharpoons \underset{\text{(Coloured tautomeric form)}}{HPh^*} \rightleftharpoons H_3O^+ + \underset{\text{(Pink)}}{Ph^-} \quad \text{.......(2)}$$

However, since the concentration of the undissociated tautomeric form is very small, the simplified equation (1) is generally adequate. In acidic solutions, the H_3O^+ ions suppress the dissociation of phenolphthalein (common ion effect), shifting the equilibrium to the left, and the solution remains colourless. In alkaline solutions, OH^- ions combine with H_3O^+ ions to form water, shifting the equilibrium to the right and increasing the concentration of the pink-coloured anions. Thus, the solution turns pink.

Phenolphthalein is not suitable for titrating a weak base (e.g., ammonium hydroxide) against a strong acid because the OH^- ions present at the end point are insufficient to shift the equilibrium enough to produce the pink colour at pH ≈ 8.3. Hence, excess weak base is required to observe the end point.

11.4 Action of Methyl Orange

Methyl orange is a weak base, often represented as MeOH. It dissolves in water and dissociates slightly:

$$\underset{\text{Yellow}}{MeOH} + H_2O \rightleftharpoons \underset{\text{Red}}{Me^+} + \underset{\text{Colourless}}{OH^-} \quad \text{........(3)}$$

The undissociated form (MeOH) is yellow, while the ionized form (Me^+) is red.

In acidic solutions, H^+ ions combine with OH^- ions to form water, shifting the equilibrium to the right and increasing the concentration of red Me^+ ions. Thus, the solution appears red.

In alkaline solutions, the presence of OH^- ions suppresses the dissociation of methyl orange, and the solution remains yellow.

Methyl orange is not suitable for titrating a weak acid (e.g., acetic acid) against a strong base because the H^+ ions from the weak acid at the end point are insufficient to shift the equilibrium toward the red Me^+ form. Therefore, excess weak acid is required to observe the end point.

12 Solubility Product and Solubility

When a sparingly soluble salt is added to water, a dynamic equilibrium is established between the undissociated solid salt and the dissociated ions. For example, $AgCl$ is sparingly soluble in water. When we add $AgCl$ to water, the equilibrium established in a saturated solution between undissolved $AgCl(s)$ and the Ag^+ and the Cl^- ions:

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

We express the law of chemical equilibrium for this solubility equilibrium as

$$K = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

$$\Rightarrow K[AgCl] = [Ag^+][Cl^-]$$

Concentration of the pure solid $AgCl$ remains almost constant, so $K[AgCl]$ is taken as another constant K_{sp} known as solubility product.

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

Solubility product varies with temperature because solubility of a salt is a temperature dependent quantity.

Now, let us take a salt such as CaF_2 whose stoichiometric coefficients in the dissociation equilibrium are not equal to unity.

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

Equilibrium constant is given by

$$K = \frac{[Ca^{2+}][F^-]^2}{[CaF_2]}$$

$$\Rightarrow K[CaF_2] = [Ca^{2+}][F^-]^2$$

$$\Rightarrow K_{sp} = [Ca^{2+}][F^-]^2$$

Now, let us consider a salt of type A_xB_y, the dissociation equilibrium of which can be represented by

$$A_xB_y(s) \rightleftharpoons xA^{y+} + yB^{x-}$$

and the solubility product is given by

$$K_{sp} = [A^{y+}]^x[B^{x-}]^y$$

Thus, solubility product of a salt at a particular temperature is defined as the product of the concentration terms of the ions in the saturated solution with each term being raised to the power equal to the stoichiometric coefficient of the ion in the dissociation equilibrium of one mole of the salt.

12.1 Applications of Solubility Product

(i) Determination of solubility of sparingly soluble salts

From the knowledge of solubility product, it is possible to calculate solubility of a sparingly soluble salt. Let us consider the example of $AgCl$ which dissociates as

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

Let $s\,mol\,L^{-1}$ be the solubility of the salt, then

$$[Ag^+] = s\,mol\,L^{-1} \text{ and } [Cl^-] = s\,mol\,L^{-1}$$

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

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

For a salt like $Zr_3(PO_4)_4$, where stoichiometric coefficients of the ions in the dissociation equilibrium are not equal to unity, let the solubility be $s\,mol\,L^{-1}$. From its dissociation equilibrium,

$$Zr_3(PO_4)_4(s) \rightleftharpoons 3Zr^{4+}(aq) + 4PO_4^{3-}(aq)$$

we get,

$$[Zr^{4+}] = 3s\,molL^{-1} \text{ and } [PO_4^{3-}] = 4s\,molL^{-1}$$

$$\therefore K_{sp} = [Zr^{4+}]^3[PO_4^{3-}]^4$$

$$\Rightarrow K_{sp} = (3s)^3(4s)^4 = 6912\,s^7$$

$$\therefore Solubility, s = \left(\frac{K_{sp}}{6912}\right)^{1/7}$$

Finally, let us take a general salt A_xB_y. Its dissociation equilibrium in a saturated solution may be expressed as

$$A_xB_y(s) \rightleftharpoons xA^{y+} + yB^{x-}$$

Let the solubility of the salt be $s\,mol\,L^{-1}$, then

$$[A^{y+}] = xs\,mol\,L^{-1} \text{ and } [B^{x-}] = ys\,mol\,L^{-1}$$

$$\therefore K_{sp} = [A^{y+}]^x[B^{x-}]^y$$

$$= (xs)^x(ys)^y$$

$$= x^xy^ys^{x+y}$$

$$or\ s^{x+y} = \frac{K_{sp}}{x^xy^y}$$

$$or\ s = \left(\frac{K_{sp}}{x^xy^y}\right)^{1/x+y}$$

(ii) Prediction of precipitation reaction

Using solubility product data, we can predict whether a salt will be precipitated or not under a given set of conditions. A salt gets precipitated when product of the concentrations of its ion in the solution (ionic product) at a particular temperature exceeds the solubility product of the salt at that temperature.

(iii) In qualitative analysis

During qualitative analysis of inorganic salts, the metal ions are precipitated out from the solution on the basis of solubility product principle and common ion effect. Metal ions are precipitated out from solutions as chlorides, sulphides, hydroxide etc. Let us discuss some examples.

(a) Group II cations ($Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, As^{3+}, Sb^{3+}, Sn^{2+}$) are preferentially precipitated out as their sulphides by passing H_2S gas in presence of $HCl(aq)$. Other metal ions such as $Fe^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}$, etc are not precipitated in this way. H_2S is a weak acid which ionizes as

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

On addition of hydrochloric acid, ionization of H_2S is suppressed due to common ion effect of H^+. As a consequence, an already low concentration of S^{2-} ions in the solution becomes even more smaller. Even at this low concentration of S^{2-} ions, solubility products of the group II metal sulphides are exceeded. Solubility products of the metal sulphides of cobalt, nickel, manganese, zinc, etc are comparatively high. So, at this low concentration of S^{2-} ions, solubility products of these metal sulphides are not exceeded and hence remain in solution.

(b) Metal ions $Mn^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}$ are precipitated as their sulphides from their ammoniacal solutions by passing H_2S gas. Dissociation of H_2S is enhanced by the addition of NH_4OH. The relevant equilibria in this case are

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

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

The OH^- ions furnished by NH_4OH abstracts the H^+ ions produced by H_2S. As a consequence, dissociation of H_2S increases resulting in a higher concentration of S^{2-} ions. At this level of concentration of S^{2-} ions, ionic products of the metal ions $Mn^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}$ with S^{2-} ion exceed the solubility products of the corresponding metal sulphides. So, Sulphides of these metals are precipitated.

(c) In qualitative analysis, metal ions Fe^{3+}, Al^{3+} and Cr^{3+} are precipitated from their solution as hydroxides by the addition of ammonium hydroxides in presence of excess of ammonium chloride. In absence of ammonium chloride, hydroxides of metals such as zinc, magnesium etc also get precipitated along with the hydroxides of iron, aluminium and chromium.

Ammonium hydroxide, being a weak base, ionizes as

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

Addition of ammonium chloride increases the concentration of NH_4^+ ion (common ion) in the solution. Due to common ion effect, ionization of ammonium hydroxide is suppressed. Concentration of OH^- ions become so low that ionic products of only Fe^{3+}, Al^{3+} and Cr^{3+} with the OH^- exceed the solubility products of the corresponding metal hydroxides. Hydroxides of iron, aluminium and chromium are, thus precipitated. Solubility products of the hydroxides of magnesium, zinc, etc are comparatively much higher, so they do not get precipitated.

12.2 Numerical Examples

Example 1. Solubility of silver chromate, Ag_2CrO_4 is $8.0 \times 10^{-5}\, mol\, L^{-1}$. Calculate solubility product.

Solution: Solubility equilibrium of Ag_2CrO_4 is

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$

$$s \qquad\qquad 2s \qquad\qquad s$$

Given $s = 8.0 \times 10^{-5}\, mol\, L^{-1}$

$$\therefore [Ag^+] = 2 \times 8.0 \times 10^{-5}\, mol\, L^{-1} = 1.6 \times 10^{-4} mol\, L^{-1}$$

$$[CrO_4^{2-}] = 8.0 \times 10^{-5}\, mol\, L^{-1}$$

$$\therefore K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (1.6 \times 10^{-4})^2(8.0 \times 10^{-5}) = 2.048 \times 10^{-12}$$

Example 2. Solubility product of calcium fluoride, CaF_2 at $298\, K$ is 1.7×10^{-10}. Calculate its solubility in $mol\, L^{-1}$.

Solution: Let the solubility of calcium fluoride be $s\, mol\, L^{-1}$

Solubility equilibrium is expressed as

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

$$s \qquad\qquad s \qquad\qquad 2s$$

Solubility product is given by

$$K_{sp} = [Ca^{2+}][F^-]^2 = s \times (2s)^2 = 4s^3$$

$$\therefore s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}} = \left(\frac{1.7 \times 10^{-10}}{4}\right)^{\frac{1}{3}} = (42.5 \times 10^{-12})^{1/3} = 3.49 \times 10^{-4}\, mol\, L^{-1}$$

Example 3. Calculate the solubility of $Mg(OH)_2$ in $0.01\, M\ NaOH(aq)$ solution. K_{sp} for $Mg(OH)_2$ is 1.2×10^{-11}.

Solution: Let $x\, mol\, L^{-1}$ be the solubility of $Mg(OH)_2$ in $0.01\, M\ NaOH$, then

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

$$x \qquad\qquad x \qquad\qquad 2x$$

$$[Mg^{2+}] = x\, mol\, L^{-1}$$

Considering complete ionization of $NaOH$, $[OH^-] = 2x + 0.01$

$$\therefore K_{sp} = [Mg^{2+}][OH^-]^2 = x(2x + 0.01)^2 = 1.2 \times 10^{-11}$$

$$\Rightarrow x \times 10^{-4} = 1.2 \times 10^{-11} \ \ (neglecting\ 2x\ in\ comparison\ to\ 0.01)$$

$$\Rightarrow x = 1.2 \times 10^{-7}$$

Example 4. Predict whether precipitation of $Ba(SO_4)_2$ will occur or not when $100\, mL$ of $0.004\, M\ \ Ba(NO_2)_2$ solution is mixed with $400\, mL$ of $0.05\, M$ $Na_2(SO_4)_2$ solution. K_{sp} for $Ba(SO_4)_2$ is 1.5×10^{-9}.

Solution: Final volume of the mixture is $500\, mL$. Concentration of Ba^{2+} and SO_4^{2-} ion after mixing:

$$[Ba^{2+}] = \frac{(0.004\, mol\, L^{-1})(100\, mL)}{(500\, mL)} = 8.0 \times 10^{-4} mol\, L^{-1}$$

$$[SO_4^{2-}] = \frac{(0.005\, mol\, L^{-1})(400\, mL)}{(500\, mL)} = 4.0 \times 10^{-2} mol\, L^{-1}$$

Ionic product, $[Ba^{2+}][SO_4^{2-}] = (8.0 \times 10^{-4})(4.0 \times 10^{-2}) = 3.2 \times 10^{-5}$

Here, Ionic product, $3.2 \times 10^{-5} >$ solubility product, 1.5×10^{-9}. So, $Ba(SO_4)_2$ will precipitate out.

CHECK YOUR PROGRESS

11. Write the solubility equilibria of the following salts in water and express their solubility product:
    (i) $Ba(SO_4)_2$
    (ii) $Zr_3(PO_4)_4$
    (iii) $PbCl_2$
12. Say true or false:
    Precipitation occurs only when solubility product is greater than the ionic product.
13. If solubility of $PbCl_2$ is y then what will be its solubility product?

12.3 ANSWERS TO CHECK YOUR PROGRESS

Ans to Q No 1: Aqueous solutions of $NaCN, NaNO_2, KF$ are basic, of $NaCl, KBr$ are neutral and of NH_4NO_3 is acidic.

Ans to Q No 2: True, it is a salt of strong acid and weak base.

Ans to Q No 3: $pH = \frac{1}{2}pK_W + \frac{1}{2}pK_a - \frac{1}{2}pK_b = \frac{1}{2} \times 14 + \frac{1}{2} \times 4.74 - \frac{1}{2} \times 4.74 = 7$

Ans to Q No 4: (d) CH_3COONH_4

Ans to Q No 5: (c) $pH < 7$

Ans to Q No 6: (a) $NH_4Cl + NH_3$ (c) $CH_3COONa + CH_3COOH$

Ans to Q No 7: (a) acidic

(b) basic

Ans to Q No 8: True

Ans to Q No 9: (c) ${NH_4}^+$

Ans to Q No 10: Buffer index is defined as number of moles of a strong acid or strong base required to be added in per litre of the buffer solution to effect unit pH change.

Ans to Q No 11: $Ba(SO_4)_2(s) \rightleftharpoons Ba^{2+}(aq) + 2\,SO_4^{2-}(aq), K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]^2$

$$Zr_3(PO_4)_4(s) \rightleftharpoons 3Zr^{4+}(aq) + 4PO_4^{3-}(aq), K_{sp} = [Zr^{4+}]^3[PO_4^{3-}]^4$$

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq), K_{sp} = [Pb^{2+}][Cl^-]^2$$

Ans to Q No 12: False

Ans to Q No 13: $4s^3$

Ans to Q No 14: (d) $108\,y^5$

Ans to Q No 15: (b) MnS

12.4 MODEL QUESTIONS

14. What is meant by hydrolysis of a salt?
15. Why cannot NaCl undergo hydrolysis?
16. If $pK_a > pK_b$, then what would be the nature of aqueous solution of a salt of weak acid and weak base?
17. Calculate the hydrolysis constant for $0.1\,M$ sodium acetate solution. ($K_a = 1.8 \times 10^{-5}$).
18. Define solubility product. Express the solubility of a salt of the type A_xB_y in terms of its solubility product.
19. Show that the degree of hydrolysis of a salt of weak acid and weak base is independent of concentration of the salt.
20. Discuss the application of solubility product and common ion effect in qualitative analysis.
21. Explain the following:
    (i) The aqueous solution of ammonium chloride is acidic.
    (ii) A mixture of sodium acetate and acetic acid acts as buffer.
    (iii) Aqueous solution of CH_3COONH_4 is neutral.
    (iv) Aqueous solution of sodium carbonate is alkaline in nature.
22. Derive an expression for the degree of hydrolysis, hydrolysis constant and pH of an aqueous salt of
    (i) Weak acid and strong base
    (ii) Strong acid and weak base
23. What are buffer solutions. Discuss the mechanism of buffer action of
    (i) an acidic buffer
    (ii) a basic buffer
24. Write a short note on buffer capacity.
25. Derive Henderson-Hasselbach equation for the pH of a buffer mixture of a weak acid and its salt.