3. IONIC EQUILIBRIA

Can you recall ?



- What is chemical equilibrium ?
- What are electrolytes ?

3.1 Introduction : The equilibrium between ions and unionized molecules in solution is called ionic equilibrium. The principles of chemical equilibrium we studied in standard XI will be applied to ionic equilibria. In this chapter with the help of these principles we determine equilibrium constants and concentrations of ions and unionized species. In particular examine the following ionic equilibria :

- $H^{\oplus}$ and $OH^{\ominus}$ ions and unionized water molecules.
- Ionization of weak acids and weak bases.
- Reactions between ions of salt and ions of water.
- Solid salt and its ions in water.

3.2 Types of electrolyte : The substances which give rise to ions when dissolved in water are electrolytes. The non electrolytes are those which do not ionize and exist as molecules in aqueous solutions.

The electrolytes are classified into strong and weak electrolytes. This classification is based on their extent of ionisation in dilute aqueous solutions.

3.2.1 Strong electrolyte : The electrolytes ionizing completely or almost completely are strong electrolytes. For example : strong acids, strong bases and salts.

3.2.2 Weak electrolyte : The electrolytes which dissociate to a smaller extent in aqueous solution are weak electrolytes. Weak acids and weak bases belong to this class.

The weak electrolytes dissociate only partially in dilute aqueous solutions. An equilibrium thus can be established between the ions and nonionized molecules. The ionization reaction therein is represented as double arrow($\rightleftharpoons$) between the ions and nonionized molecule.

Use your brain power



Which of the following is a strong electrolyte ?

HF, AgCl, $CuSO_4$, CH_3COONH_4, H_3PO_4.

3.2.3 Degree of dissociation ($\propto$) : The degree of dissociation of an electrolyte is defined as a fraction of total number of moles of the electrolyte that dissociates into its ions when the equilibrium is attained. It is denoted by symbol $\propto$ and given by

$$\propto = \frac{\text{number of moles dissociated}}{\text{total number of moles}} \quad \ldots\ldots(3.1)$$

$$\text{Percent dissociation} = \propto \times 100 \quad \ldots\ldots(3.2)$$

If 'c' is the molar concentration of an electrolyte the equilibrium concentration of cation or anion is ($\propto \times c$) mol dm^{-3}.

3.3 Acids and Bases : Acids and bases are familiar chemical compounds. Acetic acid is found in vinegar, citric acid in lemons, magnesium hydroxide in antacids, ammonia in household cleaning products. The tartaric acid is present in tamarind paste. These are some acids and bases we come across in everyday life.

3.3.1 Arrhenius theory of acids and bases

According to this theory acids and bases are defined as follows :

Acid : Acid is a substance which contains hydrogen and gives rise to $H^{\oplus}$ ions in aqueous solution. For example :

$$HCl\ (aq) \xrightarrow{water} H^{\oplus}(aq) + Cl^{\ominus}(aq)$$

$$CH_3COOH(aq) \xrightleftharpoons{water} CH_3COO^{\ominus}(aq) + H^{\oplus}(aq)$$

Arrhenius described $H^{\oplus}$ ions in water as bare ions; they hydrate in aqueous solutions and thus represented as hydronium ions $H_3O^{\oplus}$. We herewith conveniently represent them as $H^{\oplus}$.

Do you know ?

Hydrochloric acid, HCl present in the gastric juice is secreted by our stomach and is essential for digestion of food.

Base : Base is a substance that contains OH group and produces hydroxide ions ($OH^{\ominus}$) ions in aqueous solution. For example,

$$NaOH\ (aq) \longrightarrow Na^{\oplus}(aq) + OH^{\ominus}(aq)$$

$$NH_4OH(aq) \rightleftharpoons NH_4^{\oplus}(aq) + OH^{\ominus}(aq)$$

Arrhenius theory accounts for properties of different acids and bases and is applicable only to aqueous solutions. It does not account for the basicity of NH_3 and Na_2CO_3 which do not have OH group.

3.3.2 Bronsted - Lowry theory : J. N. Bronsted and T. M. Lowry (1923) proposed a more general theory known as the Bronsted-Lowry proton transfer theory. According to this theory acids and bases are defined as follows.

Acid : Acid is a substance that donates a proton ($H^{\oplus}$) to another substance.

Base : Base is a substance that accepts a proton ($H^{\oplus}$) from another substance.

For example :

$$\underset{Acid_1}{HCl} + \underset{Base_2}{NH_3} \rightleftharpoons \underset{Acid_2}{NH_4^{\oplus}} + \underset{Base_1}{Cl^{\ominus}}$$

In the above reaction HCl and $NH_4^{\oplus}$ are proton donors and act as acids. The NH_3 and $Cl^{\ominus}$ are proton acceptors and act as bases. Further it follows that the products of the Bronsted-Lowry acid-base reactions are acids bases.

The base produced by releasing the proton from an acid is the conjugate base of that acid. Likewise the acid produced when a base accepts a proton is called the conjugate acid of that base. A pair of an acid and a base differing by a proton is said to be a **conjugate acid-base pair**.

$$\underset{Acid_1}{HCl(aq)} + \underset{Base_2}{H_2O(l)} \rightleftharpoons \underset{Acid_2}{H_3O^{\oplus}(aq)} + \underset{Base_1}{Cl^{\ominus}(aq)}$$

conjugate acid-base pair$_2$

conjugate acid-base pair$_1$

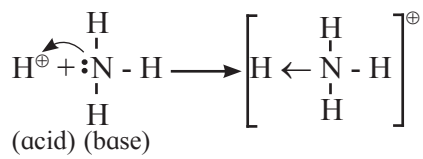
3.3.3 Lewis theory :

A more generalized acid-base concept was put forward by G.N. Lewis in 1923. According to this theory acids and bases are defined as follows.

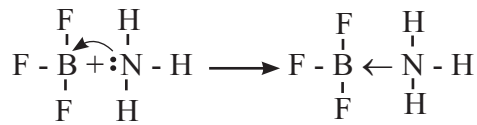
Acid : Any species that accepts a share in an electron pair is called Lewis acid.

Base : Any species that donates a share in an electron pair is called Lewis base.

For example :



(acid) (base)



(acid) (base)

Use your brain power



- All Bronsted bases are also Lewis bases, but all Bronsted acids are not Lewis acids. Explain.

Amphoteric nature of water : Water has the ability to act as an acid as well as a base. Such behaviour is known as amphoteric nature of water. For example :

$H_2O(l) + NH_3(aq) \rightleftharpoons OH^{\ominus}(aq) + NH_4^{\oplus}(aq)$

Acid

$H_2O(l) + HCl(aq) \rightleftharpoons H_3O^{\oplus}(aq) + Cl^{\ominus}(aq)$

Base

H_2O acts as an acid towards NH_3 and as a base towards HCl. Therefore H_2O is amphoteric.

3.4 Ionisation of acids and bases

Acids and bases are classified as strong acids and strong bases, weak acids and weak bases on the basis of their **extent of dissociation**. Strong acids and bases are almost completely dissociated in water. For example :

$HCl\ (aq) \longrightarrow H^{\oplus}(aq) + Cl^{\ominus}\ (aq)$

$NaOH\ (aq) \longrightarrow Na^{\oplus}(aq) + OH^{\ominus}(aq)$

Typical strong acids are HCl, HNO_3, H_2SO_4, HBr and HI while typical strong bases may include NaOH and KOH.

Weak acids and weak bases are partially dissociated in water. The solution of a weak acid or a weak base contains undissociated molecules along with a small number of ions at equilibrium. For example :

$CH_3COOH(aq) \rightleftharpoons CH_3COO^{\ominus}(aq) + H^{\oplus}(aq)$

$NH_4OH(aq) \rightleftharpoons NH_4^{\oplus}(aq) + OH^{\ominus}(aq)$

Note that HCOOH, HF, H_2S are examples of weak acids while $Fe(OH)_3$, $Cu(OH)_2$ are examples of weak bases.

3.4.1 Dissociation constant of weak acids and weak bases :

The dissociation of a weak acid HA in water is expressed as

$HA(aq) \rightleftharpoons H^{\oplus}(aq) + A^{\ominus}(aq)$

The equilibrium constant called acid-dissociation constant for this equilibrium is :

$$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]} \qquad \text{..... (3.3)}$$

Similarly the dissociation of weak base BOH in water is represented as :

$BOH(aq) \rightleftharpoons B^{\oplus}(aq) + OH^{\ominus}(aq)$

The equilibrium constant called base-dissociation constant for this equilibrium is,

$$K_b = \frac{[B^{\oplus}][OH^{\ominus}]}{[BOH]} \qquad \text{..... (3.4)}$$

Thus, the dissociation constant of a weak acid or a weak base is defined as **the equilibrium constant for dissociation equilibrium of weak acid or weak base, respectively**.

3.4.2 Ostwald's dilution law :

Arrhenius concept of acids and bases was expressed quantitatively by F. W. Ostwald in the form of the dilution law in 1888.

a. Weak acids : Consider an equilibrium of weak acid HA that exists in solution partly as the undissociated species HA and partly $H^{\oplus}$ and $A^{\ominus}$ ions. Then

$HA(aq) \rightleftharpoons H^{\oplus}(aq) + A^{\ominus}(aq)$

The acid dissociation constant is given by Eq. (3.3)

$$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]}$$

Suppose 1 mol of acid HA is initially present in volume V dm^3 of the solution. At equilibrium the fraction dissociated would be $\propto$, where $\propto$ is degree of dissociation of the acid. The fraction of an acid that remains undissociated would be $(1 - \propto)$.

$HA(aq) \rightleftharpoons H^{\oplus}(aq) + A^{\ominus}(aq)$			
Amount present at equilibrium/ mol	$(1-\alpha)$	α	α
concentration at equilibrium/ mol dm^{-3}	$\frac{1-\alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

Thus, at equilibrium $[HA] = \frac{1-\alpha}{V}$, mol dm^{-3},

$[H^{\oplus}] = [A^{\ominus}] = \frac{\alpha}{V}$ mol dm^{-3}.

Substituting these in Eq. (3.3)

$$K_a = \frac{(\alpha/V)(\alpha/V)}{(1-\alpha)/V} = \frac{\alpha^2}{(1-\alpha)V} \quad \ldots\ldots (3.5)$$

If c is the initial concentration of an acid in mol dm^{-3} and V is the volume in dm^3 mol^{-1} then $c = 1/V$. Replacing $1/V$ in Eq. (3.5) by c we get

$$K_a = \frac{\alpha^2 c}{1-\alpha} \quad \ldots\ldots (3.6)$$

For the weak acid HA, α is very small, or $(1 - \alpha) \cong 1$. With this Eq. (3.5) and (3.6) reduce.

$$K_a = \alpha^2/V \text{ and } K_a = \alpha^2 c \quad \ldots\ldots (3.7)$$

$$\alpha = \sqrt{\frac{K_a}{c}} \text{ or } \alpha = \sqrt{K_a . V} \quad \ldots\ldots (3.8)$$

The Eq. (3.8) implies that the degree of dissociation of a weak acid is inversely proportional to the square root of its concentration or directly proportional to the square root of volume of the solution containing 1 mol of the weak acid.

b. Weak base : Consider 1 mol of weak base BOH dissolved in V dm^3 of solution. The base dissociates partially as

$$BOH(aq) \rightleftharpoons B^{\oplus}(aq) + OH^{\ominus}(aq)$$

The base dissociation constant is

$$K_b = \frac{[B^{\oplus}][OH^{\ominus}]}{[BOH]}$$

Let the fraction dissociated at equilibrium is α and that remains undissociated is $(1 - \alpha)$.

$BOH(aq) \rightleftharpoons B^{\oplus}(aq) + OH^{\ominus}(aq)$			
Amount present at equilibrium	$(1-\alpha)$	α	α
concentration at equilibrium	$\frac{1-\alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

A equilibrium,

$[BOH] = \frac{1-\alpha}{V}$ mol dm^{-3},

$[B^{\oplus}] = [OH^{\ominus}] = \frac{\alpha}{V}$ mol dm^{-3}.

Substitution of these concentrations in Eq. (3.4), gives

$$K_b = \frac{(\alpha/V)(\alpha/V)}{(1-\alpha)/V} = \frac{\alpha^2}{(1-\alpha)V} \quad \ldots\ldots (3.9)$$

Similar arguments in the case of weak acid, led to

$$K_b = \frac{\alpha^2 c}{(1-\alpha)} \quad \ldots\ldots (3.10)$$

$$\alpha = \sqrt{K_b . V}\ , \alpha = \sqrt{\frac{K_b}{c}} \quad \ldots\ldots (3.11)$$

The degree of dissociation of a weak base is inversely proportional to square root of its concentration and is directly proportional to square root of volume of the solution containing 1 mol of weak base.

Problem 3.1 : A weak monobasic acid is 0.05% dissociated in 0.02 M solution. Calculate dissociation constant of the acid.

Solution : The dissociation constant of acid is given by $K_a = \alpha^2 c$. Here,

$$\alpha = \frac{\text{percent dissociation}}{100} = \frac{0.05}{100} = 5 \times 10^{-4}$$

$c = 0.02$ M $= 2 \times 10^{-2}$ M

Hence $K_a = (5 \times 10^{-4})^2 \times 2 \times 10^{-2}$

$= 25 \times 10^{-8} \times 2 \times 10^{-2}$

$= 50 \times 10^{-10} = 5 \times 10^{-9}$

Problem 3.2 : The dissociation constant of NH_4OH is 1.8×10^{-5}. Calculate its degree of dissociation in 0.01 M solution.

Solution : The degree of dissociation is given by $\alpha = \sqrt{K_b/c}$. Here,

$K_b = 1.8 \times 10^{-5}; c = 0.01 = 1 \times 10^{-2}$ M

Hence, $\alpha = \sqrt{\frac{1.8 \times 10^{-5}}{1 \times 10^{-2}}} = \sqrt{1.8 \times 10^{-3}}$

$= \sqrt{18 \times 10^{-4}} = 4.242 \times 10^{-2} = 0.04242$

Problem 3.3 : A weak monobasic acid is 12% dissociated in 0.05 M solution. What is percent dissociation in 0.15 M solution.

Solution : If α_1 and α_2 are the values of degree of dissociation at two different concentrations c_1 and c_2 respectively, then

$K_a = \alpha_1^2 c_1 = \alpha_2^2 c_2$ Therefore $\alpha_1^2 c_1 = \alpha_2^2 c_2$

$\alpha_1 = \frac{12}{100}$ $c_1 = 0.05$ M, $c_2 = 0.15$ M,

$\alpha_2 = ?$

Substituting these values in the equation gives

$(0.12)^2 \times 0.05 = \alpha_2^2 \times 0.15$

$\alpha_2^2 = \frac{(12)^2 \times 0.05}{0.15} = 0.0048$

Hence $\alpha_2 = 0.0693$ %

$\therefore$ percent dissociation = 6.93 %

Problem 3.4 : Calculate $[H_3O^{\oplus}]$ in 0.1 mol dm^3 solution of acetic acid.

Given : $K_a\,[CH_3COOH] = 1.8 \times 10^{-5}$

Solution : Let α_1 be the degree of dissociation. Concentrations of various species involved at equilibrium are as follows.

$$\underset{(1-\alpha)c}{CH_3COOH} + H_2O \rightleftharpoons \underset{\alpha c}{CH_3COO^{\ominus}} + \underset{\alpha c}{H_3O^{\oplus}}$$

$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.1}}$

$= 1.34 \times 10^{-2}$

$[H_3O^{\oplus}] = \alpha \times c = 1.34 \times 10^{-2} \times 0.1$

$= 1.34 \times 10^{-3}$ mol/L

3.5 Autoionization of water : Pure water ionizes to a very small extent. The ionization equilibrium of water is represented as,

$$H_2O\,(l) + H_2O\,(l) \rightleftharpoons H_3O^{\oplus}(aq) + OH^{\ominus}(aq)$$

The equilibrium constant (K) for the ionization of water is given by

$$K = \frac{[H_3O^{\oplus}][OH^{\ominus}]}{[H_2O]^2} \quad \ldots\ldots\ldots (3.12)$$

or $K[H_2O]^2 = [H_3O^{\oplus}][OH^{\ominus}]$ ..... (3.13)

A majority of H_2O molecules are undissociated, consequently concentration of water $[H_2O]$ can be treated as constant. Then

$[H_2O]^2 = K'$. Substituting this in Eq. (3.13) we get,

$$K \times K' = [H_3O^{\oplus}][OH^{\ominus}] \quad \ldots\ldots\ldots (3.14)$$

$$K_w = [H_3O^{\oplus}][OH^{\ominus}]$$

where $K_w = KK'$ is called ionic product of water. The product of molar concentrations of hydronium (or hydrogen) ions and hydroxyl ions at equilibrium in pure water at the given temperature is called ionic product of water.

In pure water $H_3O^{\oplus}$ ion concentration always equals the concentration of $OH^{\ominus}$ ion. Thus at 298 K this concentration is found to be 1.0×10^{-7} mol/L.

$K_w = (1.0 \times 10^{-7})\,(1.0 \times 10^{-7})$

$K_w = 1.0 \times 10^{-14}$ ..... (3.15)

Internet my friend

Find out the values of ionic product K_w of water at various temperatures.

273 K, 283K, 293K, 303K, 313K, 323 K

3.6 pH Scale : Instead of writing concentration of $H_3O^{\oplus}$ ions in mol dm^{-3}, sometimes it is convenient to express it on the logarithmic scale. This is known as pH scale.

Sorensen in 1909 defined the pH of a solution as the negative logarithm to the base 10, of the concentration of $H^{\oplus}$ ions in solution in mol dm^{-3}. Expressed mathematically as

$pH = -\log_{10}[H^{\oplus}]$

Similarly *pOH* of a solution can be defined as the negative logarithm to the base 10, of the molar concentration of $OH^{\ominus}$ ions in solution.

Thus, $pOH = -\log_{10}[OH^{\ominus}]$ ..... (3.16)

3.6.1 Relationship between pH and pOH

The ionic product of water is

$K_w = [H_3O^{\oplus}][OH^{\ominus}]$

Now, $K_w = 1 \times 10^{-14}$ at 298 K and thus

$[H_3O^{\oplus}][OH^{\ominus}] = 1.0 \times 10^{-14}$

Taking logarithm of both the sides, we write

$\log_{10}[H_3O^{\oplus}] + \log_{10}[OH^{\ominus}] = -14$

$-\log_{10}[H_3O^{\oplus}] + \{-\log_{10}[OH^{\ominus}]\} = 14$

From Eq. (3.16) and (3.17)

$pH + pOH = 14$ ..... (3.18)

3.6.2 Acidity, basicity and neutrality of aqueous solutions

1. Neutral solution : For pure water or any aqueous neutral solution at 298 K

$[H_3O^{\oplus}] = [OH^{\ominus}] = 1.0 \times 10^{-7}$ M

Hence, $pH = -\log_{10}[H^{\oplus}] = -\log_{10}[1 \times 10^{-7}] = 7$

2. Acidic solution : In acidic solution, there is excess of $H_3O^{\oplus}$ ions, or $[H_3O^{\oplus}] > [OH^{\ominus}]$ Hence, $[H_3O^{\oplus}] > 1 \times 10^{-7}$ and $pH < 7$

3. Basic solution : In basic solution, the excess of $OH^{\ominus}$ ions are present that is $[H_3O^{\oplus}] < [OH^{\ominus}]$ or $[H_3O^{\oplus}] < 1.0 \times 10^{-7}$ with $pH > 7$.

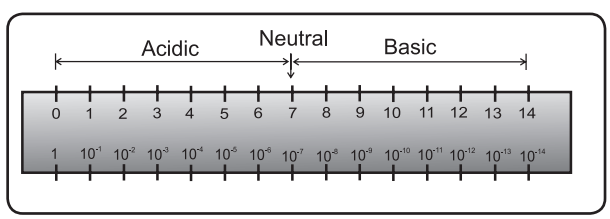


Fig. 3.1 : *pH* scale

Problem 3.5 : Calculate *pH* and *pOH* of 0.01 M HCl solution.

Solution : HCl is a strong acid. It dissociates almost completely in water as

$HCl\ (aq) + H_2O(l) \longrightarrow H_3O^{\oplus}(aq) + Cl^{\ominus}(aq)$

Hence, $[H_3O^{\oplus}] = c = 0.01M = 1 \times 10^{-2}$ M

$pH = -\log_{10}[H_3O^{+}] = -\log_{10}[1 \times 10^{-2}] = 2$

We know that $pH + pOH = 14$

$\therefore pOH = 14 - pH = 14 - 2 = 12$

Problem 3.6 : *pH* of a solution is 3.12. Calculate the concentration of $H_3O^{\oplus}$ ion.

Solution : *pH* is given by

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

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

$= -3.12$

$= -3 - 0.12 + 1 - 1$

$= (-3 - 1) + 1 - 0.12$

$= -4 + 0.88 = \bar{4}.88$

Thus $[H_3O^{\oplus}]$ = antilog $[\bar{4}.88]$

$= 7.586 \times 10^{-4}$ M

Problem 3.7 : A weak monobasic acid is 0.04 % dissociated in 0.025M solution. What is *pH* of the solution ?

Solution : A weak monobasic acid HA dissociates as :

$HA + H_2O(l) \rightleftharpoons H_3O^{\oplus}(aq) + A^{\ominus}(aq)$

Percent dissociation $= \alpha \times 100$

or $\alpha = \dfrac{\text{percent dissociation}}{100}$

$= \dfrac{0.04}{100} = 4 \times 10^{-4}$

Now $[H_3O^{\oplus}] = \alpha \times c$

$= 4 \times 10^{-4} \times 0.025$ M $= 10^{-5}$ M

$\therefore pH = -\log_{10}[H_3O^{\oplus}] = -\log_{10}[10^{-5}] = 5$

Use your brain power



- Suppose that *pH* of monobasic and dibasic acid is the same. Does this mean that the molar concentrations of both acids are identical ?
- How *pH* of pure water vary with temperature ? Explain.

Problem 3.8 : The *pH* of monoacidic weak base is 11.2. Calculate its percent dissociation in 0.02 M solution.

Solution : *pOH* of the solution is given as :

$$pOH = 14 - pH = 14 - 11.2 = 2.8$$

$$pOH = -\log_{10}[OH^{\ominus}]$$

$$\log_{10}[OH^{\ominus}] = -pOH$$

$$= -2.8 = -2 - 0.8 - 1 + 1$$

$$= -3 + 0.2 = \bar{3}.2$$

$$[OH^{\ominus}] = \text{antilog } \bar{3}.2 = 1.585 \times 10^{-3} \text{ mol/dm}^3$$

For monoacidic base,

$$BOH\ (aq) \rightleftharpoons B^{\oplus}(aq) + OH^{\ominus}(aq)$$

$$[OH^{\ominus}] = \propto c$$

$$\propto = \frac{[OH^{\ominus}]}{c} = \frac{1.585 \times 10^{-3}}{0.02} = 0.07925$$

$$\text{Percent dissociation} = \propto \times 100$$

$$= 0.07925 \times 100$$

$$= 7.925\ \%$$

Do you know ?



- *pH* is crucial for digestion of food and other biochemical reactions in our body.
- *pH* of gastric juice is about 2.
- *pH* of blood is maintained within range 7.36 to 7.42.
- Enzymes function effectively only at a certain *pH*. For example trypsin acts best for alkaline *pH*.

3.7 Hydrolysis of salts

3.7.1 Types of salts

These are of four types

I. Salts derived from **strong acid and strong base**. For example : NaCl, Na_2SO_4, $NaNO_3$, KCl, KNO_3.

II. Salts derived from **strong acids and weak bases**. For example : NH_4Cl, $CuSO_4$, NH_4NO_3, $CuCl_2$.

III. Salts derived from **weak acids and strong bases**. For example : CH_3COONa, KCN, Na_2CO_3.

IV. Salts derived from **weak acids and weak bases**. For example : CH_3COONH_4, NH_4CN.

3.7.2 Concept of hydrolysis : When a salt is dissociated in water, it dissociates completely into its constituent ions. The solvent water dissociates slightly as,

$$H_2O\ (l) + H_2O\ (l) \rightleftharpoons H_3O^{\oplus}(aq) + OH^{\ominus}(aq)$$

Pure water is neutral and $[H_3O^{\oplus}] = [OH^{\ominus}]$. If the ions of the salt do not interact with water, the hydronium and hydroxyl ion concentrations remain equal and the solution is neutral. When one or more of the salt ions react with water, the equality of concentrations of $H_3O^{\oplus}$ and $OH^{\ominus}$ ions is disturbed. The solution, does not remain neutral and becomes acidic or basic depending on the type of the salt. Such a reaction between the ions of salt and the ions of water is called hydrolysis of salt. **Hydrolysis of salt is defined as the reaction in which cations or anions or both ions of a salt react with ions of water to produce acidity or alkalinity (or sometimes even neutrality).**

3.7.3 Salts of strong acids and strong bases

NaCl is a salt of strong acid HCl and a strong base NaOH. When it is dissolved in water, it dissociates completely into its ions.

$$NaCl\ (aq) \longrightarrow Na^{\oplus}(aq) + Cl^{\ominus}(aq)$$

The ions $Na^{\oplus}$ and $Cl^{\ominus}$ have no tendency to react with water. This is because the possible products, NaOH and HCl of such reactions are

strong electrolytes and dissociate completely in aqueous solutions.

In other words,

$Na^{\oplus}(aq) + Cl^{\ominus}(aq) + H_2O \rightarrow HCl(aq) + NaOH(aq)$

(strong acid) (strong base)

[Possible products]

$HCl(aq) + NaOH(aq) + H_2O \rightarrow H_3O^{\oplus}(aq) + Cl^{\ominus}(aq) + Na^{\oplus}(aq) + OH^{\ominus}(aq)$

Thus the reactants and the products are the same. This implies that neither the cation nor anion of the salt reacts with water or there is no hydrolysis. Equality $H_3O^{\oplus} = OH^{\ominus}$ produced by ionization of water is not disturbed and solution is neutral. It may be concluded that salt of strong acid and strong base does not undergo hydrolysis.

3.7.4 Salts of strong acids and weak bases :

$CuSO_4$ is salt of strong acid H_2SO_4 and weak base $Cu(OH)_2$. When $CuSO_4$ is dissolved in water, it dissociates completely as,

$$CuSO_4(aq) \longrightarrow Cu^{2\oplus}(aq) + SO_4^{2\ominus}(aq)$$

$SO_4^{2\ominus}$ ions of salt have no tendency to react with water because the possible product H_2SO_4 is strong electrolyte. The reaction of $Cu^{2\oplus}$ ions with $OH^{\ominus}$ ions form unionized $Cu(OH)_2$. The hydrolytic equilibrium for $CuSO_4$ is then written as,

$$Cu^{2\oplus}(aq) + 4H_2O(l) \rightleftharpoons Cu(OH)_2(aq) + 2H_3O^{\oplus}(aq)$$

Due to the presence of excess of $H_3O^{\oplus}$ ions, the resulting solution of $CuSO_4$ becomes acidic and turns blue litmus red.

Formation of sparingly soluble $Cu(OH)_2$ by hydrolysis makes the aqueous solution of $CuSO_4$ turbid. If H_2SO_4, that is $H_3O^{\oplus}$ ions are added, the hydrolytic equilibrium shifts to the left. A turbidity of $Cu(OH)_2$ dissolves to give a clear solution. To get clear solution of $CuSO_4$, the addition of H_2SO_4 would be required.

3.7.5 Salts of weak acids and strong bases

CH_3COONa is a salt of weak acid CH_3COOH and strong base NaOH, when dissolved in water, it dissociates completely.

$$CH_3COONa(aq) \longrightarrow CH_3COO^{\ominus}(aq) + Na^{\oplus}(aq)$$

Water dissociates slightly as,

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^{\oplus}(aq) + OH^{\ominus}(aq)$$

Solution of CH_3COONa contains $Na^{\oplus}$, $H_3O^{\oplus}$, $CH_3COO^{\ominus}$, $OH^{\ominus}$. The $Na^{\oplus}$ ions of salt have no tendency to react with $OH^{\ominus}$ ions of water since the possible product of the reaction is NaOH, a strong electrolyte.

On the other hand the reaction of $CH_3COO^{\ominus}$ ions of salt with the $H_3O^{\oplus}$ ions from water produces unionized CH_3COOH.

$$CH_3COO^{\ominus}(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^{\ominus}(aq)$$

Thus, the hydrolytic equilibrium for CH_3COONa is,

$$CH_3COONa(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + Na^{\oplus}(aq) + OH^{\ominus}(aq)$$

As a result of excess $OH^{\ominus}$ ions produced the solution becomes basic. The solution of CH_3COONa is therefore basic.

Can you tell ?



Why an aqueous solution of NH_4Cl is acidic while that of HCOOK basic ?

Remember...



As a general rule the solutions of salts of strong acids and strong bases are neutral, the solutions of salts of strong acids and weak bases are acidic and the solutions of salts of strong bases and weak acids are basic.

3.7.6 Salts of weak acids and weak bases:

When salt BA of weak acid HA and weak base BOH is dissolved in water, it dissociates completely as

$$BA(aq) \longrightarrow B^{\oplus}(aq) + A^{\ominus}(aq)$$

The hydrolysis reaction involves the interaction of both the ions of the salt with water,

$B^{\oplus}(aq) + A^{\ominus}(aq) + H_2O \rightleftharpoons BOH + HA$

(weak base) (weak acid)

The solution may turn out acidic, basic or neutral depending on the relative strength of weak base and weak acid formed in the hydrolysis.

i. if, $K_a > K_b$, the solution will be acidic.

ii. if, $K_a < K_b$, the solution will be basic.

iii. if, $K_a = K_b$, the solution will be neutral.

i. Salt of weak acid and weak base for which $K_a > K_b$.

NH_4F is a salt of weak acid HF ($K_a = 7.2 \times 10^{-4}$) and weak base NH_4OH ($K_b = 1.8 \times 10^{-5}$). Here, K_a is greater than K_b. The salt hydrolyses as

$NH_4^{\oplus}(aq) + F^{\ominus}(aq) + H_2O \rightleftharpoons NH_4OH(aq) + HF(aq)$

(weak base) (weak acid)

The acid HF is slightly stronger than base NH_4OH. The two ions react with water as

$NH_4^{\oplus}(aq) + 2H_2O(l) \rightleftharpoons NH_4OH(aq) + H_3O^{\oplus}(aq)$

..... (3.19)

$F^{\ominus}(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^{\ominus}(aq)$

..... (3.20)

The $NH_4^{\oplus}$ ions hydrolyse to a slightly greater extent than the $F^{\ominus}$ ions. That means the reaction produces more $H_3O^{\oplus}$ ions than the $OH^{\ominus}$ ions produced in reaction (3.20). In other words, $NH_4^{\oplus}$ ions are slightly stronger as acid than $F^{\ominus}$ ions as base. The solution of NH_4F is thus only slightly acidic and turns blue litmus red.

ii. Salt of weak acid and weak base for which $K_a < K_b$: NH_4CN is the salt of weak acid HCN ($K_a = 4.0 \times 10^{-10}$) and weak base NH_4OH ($K_b = 1.8 \times 10^{-5}$) showing that $K_a < K_b$. When NH_4CN is dissolved in water, it hydrolyses as

$NH_4^{\oplus}(aq) + CN^{\ominus}(aq) + H_2O(l) \rightleftharpoons NH_4OH(aq) + HCN(aq)$

(weak base) (weak acid)

The base NH_4OH is stronger than the acid HCN. The ions of the salt react with water as,

$NH_4^{\oplus}(aq) + H_2O(l) \rightleftharpoons NH_4OH(aq) + H_3O^{\oplus}(aq)$

..... (3.21)

$CN^{\ominus}(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^{\ominus}(aq)$

..... (3.22)

The $CN^{\ominus}$ ions hydrolyse to a greater extent than $NH_4^{\oplus}$ ions, The reaction (3.22) produces more $OH^{\ominus}$ ions than the $H_3O^{\oplus}$ ions produced in reaction (3.21). The solution of NH_4CN is, basic and turns red litmus blue.

iii. Salt of weak acid and weak base for which $K_a = K_b$.

CH_3COONH_4 is a salt of weak acid, CH_3COOH ($K_a = 1.8 \times 10^{-5}$) and weak base, NH_4OH ($K_b = 1.8 \times 10^{-5}$).

When the salt CH_3COONH_4 is dissolved in water, it undergoes hydrolysis :

$CH_3COO^{\ominus}(aq) + NH_4^{\oplus}(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + NH_4OH(aq)$

(weak acid) (weak base)

The ions of the salt react with water as

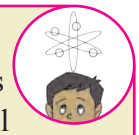
i. $CH_3COO^{\ominus}(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^{\ominus}(aq)$

ii. $NH_4^{\oplus}(aq) + 2H_2O(l) \rightleftharpoons NH_4OH(aq) + H_3O^{\oplus}(aq)$

As $K_a = K_b$, the relative strength of acid and base produced in hydrolysis is the same. Therefore, the solution is neutral. Hydrolysis of $NH_4^{\oplus}$ produces as many $H_3O^{\oplus}$ ions as that of $CH_3COO^{\ominus}$ produces $OH^{\ominus}$ ions.

3.8 Buffer solutions : Buffer solution is defined as a solution which resists drastic changes in pH when a small amount of strong acid or strong base or water is added to it.

Can you think ?



Home made jams and gellies without any added chemical preservative additives spoil in a few days whereas commercial jams and jellies have a long shelf life. Explain. What role does added sodium benzoate play?

3.8.1 Types of buffer solutions

There are two types of buffer solutions. Acidic buffer used to maintain an acidic pH, while basic buffer maintains alkaline pH.

a. Acidic buffer solution : A solution containing a weak acid and its salts with strong base is called an acidic buffer solution.

For example : A solution containing weak acid such as CH_3COOH and its salt such as CH_3COONa is an acidic buffer solution.

pH of acidic buffer is given by the equation

$$pH = pK_a + \log_{10}\frac{[salt]}{[acid]} \quad \ldots\ldots\ldots\ldots (3.23)$$

where $pK_a = -\log_{10}K_a$ $\ldots\ldots\ldots\ldots (3.24)$

and K_a is the dissociation constant of the acid.

b. Basic buffer solution : A solution containing a weak base and its salt with strong acid is the basic buffer solution.

For example : A solution containing a weak base such as NH_4OH and its salt such as NH_4Cl is a basic buffer solution.

The *pOH* of basic buffer is given by,

$$pOH = pK_b + \log_{10}\frac{[salt]}{[base]} \quad \ldots\ldots\ldots\ldots (3.25)$$

where $pK_b = -\log_{10}K_b$ $\ldots\ldots\ldots\ldots (3.26)$ and K_b is the dissociation constant for the base. Equations (3.23), (3.24), (3.25) and (3.26) are known to **Henderson Hasselbalch equation**.

3.8.2 Buffer action : Let us consider sodium acetate - acetic acid buffer. Here sodium acetate is a strong electrolyte which dissociates completely in water producing large concentration of $CH_3COO^{\ominus}$ as follows :

$$CH_3COONa(aq) \longrightarrow CH_3COO^{\ominus}(aq) + Na^{\oplus}(aq)$$

On the other hand since the acetic acid is a weak acid, the concentration of undissociated CH_3COOH molecules is usually high. If a strong acid is added to this solution the added $H^{\oplus}$ ions will be consumed by the conjugate base $CH_3COO^{\ominus}$ present in large concentration. Similarly, if small amount of base is added, the added $OH^{\ominus}$ ions will be neutralized by the large concentration of acetic acid as shown in the following reactions :

$$\underset{\text{(large concentraion)}}{CH_3COO^{\ominus}(aq)} + \underset{\text{(added acid)}}{H^{\oplus}(aq)} \longrightarrow CH_3COOH(aq)$$

$$\underset{\text{(large concentraion)}}{CH_3COOH(aq)} + \underset{\text{(added base)}}{OH^{\ominus}(aq)} \longrightarrow CH_3COO^{\ominus}(aq) + H_2O(l)$$

The acid or base added thus can not change the $[H^{\oplus}]$ or $[OH^{\ominus}]$ concentrations and, *pH* of the buffer remains unchanged. Dilution does not have any effect on *pH* of buffer. This is because the concentration ratio term in Eq. (3.23) and Eq. (3.25) remains the same. The dilution does not change this ratio.

3.8.3 Properties of buffer solution

The *pH* of a buffer solution does not change appereciably

i. by addition of small amount of either strong acid or strong base, ii. on dilution or iii. when it is kept for long time.

Can you tell ?



It is enough to add a few mL of a buffer solution to maintain its *pH*. Which property of buffer is used here?

3.8.4 Applications of buffer solution

Buffer solution finds extensive applications in a variety of fields. Some of its applications are given.

i. In biochemical system : *pH* of blood in our body is maintained at 7.36 - 7.42 due to $(HCO_3^{\ominus} + H_2CO_3)$ buffer. A mere change of 0.2 *pH* units can cause death. The saline solution used for intravenous injection must contain

buffer system to maintain the proper *pH* of the blood.

ii. Agriculture : The soils get buffered due to presence of salts such as carbonate, bicarbonate, phosphates and organic acids. The choice of fertilizers depends upon *pH* of soil.

iii. Industry : Buffers play an important role in paper, dye, ink, paint and drug industries.

iv. Medicine : Penicillin preparations are stabilized by addition of sodium citrate as buffer. When citric acid is added to milk of magnesia ($Mg(OH)_2$), magnesium citrate is formed, which is a buffer.

v. Analytical chemistry : In qualitative analysis, a *pH* of 8 to 10 is required for precipitation of cations IIIA group. It is maintained with the use of ($NH_4OH + NH_4Cl$) buffer.

Problem 3.9 : Calculate the *pH* of buffer solution containing 0.05 mol NaF per litre and 0.015 mol HF per litre. [$K_a = 7.2 \times 10^{-4}$ for HF]

Solution : The *pH* of acidic buffer is given by Henderson-Hasselbalch equation

$$pH = pK_a + \log_{10} \frac{[salt]}{[acid]}$$

$\therefore pK_a = -\log_{10} K_a = -\log_{10} 7.2 \times 10^{-4}$

$= 4 - \log_{10} 7.2 = 4 - 0.8573 = 3.1427$

[salt] = 0.05 M, [acid] = 0.015M

Substitution in the above equation gives

$$pH = 3.1427 + \log_{10} \frac{0.05}{0.015}$$

$= 3.1427 + \log 3.33$

$= 3.1427 + 0.5224 = 3.6651 \approx 3.67$

Problem 3.10 : Calculate the *pH* of buffer solution composed of 0.1 M weak base BOH and 0.2 M of its salt BA. [$K_b = 1.8 \times 10^{-5}$ for the weak base]

Solution : *pOH* of basic buffer is given by Henderson-Hasselbalch equation

$$pOH = pK_b + \log_{10} \frac{[salt]}{[base]}$$

$\therefore pK_b = -\log_{10} K_b$

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

$= 5 - 0.2553 = 4.7447$

[salt] = 0.02 M, [acid] = 0.1M

Substitution of these in the above equation gives

$pOH = 4.7447 + \log \frac{0.02}{0.1} = 4.7447 + \log 2$

$= 4.7447 + 0.3010 = 5.0457$

$pH = 14 - pOH = 14 - 5.0457$

$= 8.9543$

3.9 Solubility product

Can you recall ?



- What is solubility of a compound ?
- What is saturated solution ?
- What is meant by the sparingly soluble salt ?

Do you know ?



The process of dissolution and precipitation of sparingly soluble ionic compounds are of important in our everyday life, industry and medicine. Kidney stone is developed due to the precipitation of insoluble calcium oxalate, CaC_2O_4. The process of tooth decay occurs due to dissolution of enamel composed of hydroxyapatite, $Ca_5(PO_4)_3OH$ in acidic medium.

3.9.1 Solubility equilibria : Hereafter we confine our attention to sparingly soluble compounds that is, compounds those dissolve only slightly in water.

Suppose some powdered sparingly soluble salt such as AgCl is put into water and stirred vigorously. A very small amount of AgCl dissolves in water to form its saturated solution. Most of the salt remains undissolved. Thus, solid AgCl is in contact with its saturated solution. AgCl is a strong electrolyte. Hence the quantity of AgCl that dissolves in water dissociates completely into its constituent ions, $Ag^{\oplus}$ and $Cl^{\ominus}$. A dynamic equilibrium exists between undissolved solid AgCl and the dissolved ions, $Ag^{\oplus}$ and $Cl^{\ominus}$, in the saturated solution. This equilibrium, called solubility equilibrium, is represented as :

$$AgCl(s) \rightleftharpoons Ag^{\oplus}(aq) + Cl^{\ominus}(aq)$$

The expression for its equilibrium constant is :

$$K = \frac{[Ag^{\oplus}][Cl^{\ominus}]}{[AgCl]} \quad \ldots\ldots\ldots\ldots (3.27)$$

The concentration of undissolved solid AgCl is constant we may write

$$[AgCl] = \text{constant} = K'$$

Substituting in Eq. (3.27) we write

$$K = \frac{[Ag^{\oplus}][Cl^{\ominus}]}{K'}$$

$$K \times K' = [Ag^{\oplus}][Cl^{\ominus}]$$

The product of $K \times K'$ is another constant and is called **solubility product**, that is the product of concentrations of ions in a saturated solution. It is denoted by K_{sp}.

$$K_{sp} = [Ag^{\oplus}][Cl^{\ominus}]$$

For the general salt solubility equilibrium

$$B_xA_y(s) \rightleftharpoons xB^{y\oplus}(aq) + yA^{x\ominus}(aq)$$

The solubility product is

$$K_{sp} = [B^{y\oplus}]^x[A^{x\ominus}]^y \quad \ldots\ldots\ldots\ldots (3.28)$$

Thus, in the saturated solution of sparingly soluble salt the product of equilibrium concentrations of the constituent ions raised to the power equal to their respective coefficients in the balanced equilibrium expression at a given temperature is called solubility product.

Consider following examples.

i. $BaSO_4(s) \rightleftharpoons Ba^{2\oplus}(aq) + SO_4^{2\ominus}(aq)$

$K_{sp} = [Ba^{2\oplus}][SO_4^{2\ominus}]$

ii. $CaF_2(s) \rightleftharpoons Ca^{2\oplus}(aq) + 2F^{\ominus}(aq)$

$K_{sp} = [Ca^{2\oplus}][F^{\ominus}]^2$

iii. $Bi_2S_3(s) \rightleftharpoons 2Bi^{3\oplus}(aq) + 3S^{2\ominus}(aq)$

$K_{sp} = [Bi^{3\oplus}]^2[S^{2\ominus}]^3$

iv. $Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2\oplus}(aq) + 2PO_4^{3\ominus}(aq)$

$K_{sp} = [Ca^{2\oplus}]^3[PO_4^{3\ominus}]^2$

3.9.2 Relationship between solubility and solubility product : The solubility of a compound is the amount in grams that dissolves per unit volume (which may be 100 mL or 1L of its saturated solution).

Molar solubility : The number of moles of a compound that dissolve to give one litre of saturated solution is called its molar solubility.

$$\text{molar solubility (mol/L)} = \frac{\text{solubility in g/L}}{\text{molar mass in g/mol}}$$

Consider once again the solubility equilibrium for B_xA_y,

$$B_xA_y(s) \rightleftharpoons xB^{y\oplus}(aq) + yA^{x\ominus}(aq)$$

The solubility product is given by Eq. (3.28) :

$$K_{sp} = [B^{y\oplus}]^x[A^{x\ominus}]^y$$

If S is the molar solubility of the compound, the equilibrium concentrations of the ions in the saturated solution will be

$$[B^{y\oplus}] = xS \text{ mol/L}$$

$$[A^{x\ominus}] = xS \text{ mol/L}$$

From Eq. (3.28)

$$K_{sp} = [xS]^x[yS]^y = x^xy^yS^{x+y} \quad \ldots\ldots\ldots\ldots (3.29)$$

For example :

i. For AgBr,

$$AgBr(s) \rightleftharpoons Ag^{\oplus}(aq) + Br^{\ominus}(aq)$$

Here, $x = 1, y = 1$

$\therefore K_{sp} = S \times S = S^2$

ii. For PbI_2,

$PbI_2(s) \rightleftharpoons Pb^{2\oplus}(aq) + 2I^{\ominus}(aq)$

x = 1, y = 2

Therefore, $K_{sp} = (1)^1(2)^2S^{1+2} = 4S^3$

iii. $Al(OH)_3$,

$Al(OH)_3(s) \rightleftharpoons Al^{3\oplus}(aq) + 3OH^{\ominus}(aq)$

x = 1, y = 3

$K_{sp} = (1)^1(3)^3S^{1+3} = 27S^4$

Use your brain power



What is the relationship between molar solubility and solubility product for salts given below

i. Ag_2CrO_4 ii. $Ca_3(PO_4)_2$ iii. $Cr(OH)_3$.

3.9.3 Condition of precipitation : Ionic product (*IP*) of an electrolyte is defined in the same way as solubility product (K_{sp}). The only difference is that the ionic product expression contains concentration of ions under any condition whereas expression of K_{sp} contains only equilibrium concentrations. If,

a. $IP = K_{sp}$; the solution is saturated and solubility equilibrium exists.

b. $IP > K_{sp}$; the solution is supersaturated and hence precipitation of the compound will occur.

c. *If* $IP < K_{sp}$, the solution is unsaturated and precipitation will not occur.

Problem 3.11 : A solution is prepared by mixing equal volumes of 0.1M $MgCl_2$ and 0.3M $Na_2C_2O_4$ at 293 K. Would MgC_2O_4 precipitate out ? K_{sp} of MgC_2O_4 at 293 K is 8.56×10^{-5}.

Solution : When solution is prepared by mixing equal volumes, volume gets doubled and hence effective concentration of ions would be half of initial concentration,

$[Mg^{2+}] = \frac{0.1}{2} = 0.05$ mol/L

$[C_2O_4^{2-}] = \frac{0.3}{2}$ M = 0.15 mol/L

These ions would react to form sparingly soluble salt MgC_2O_4 in accordance with reaction

$Mg^{2\oplus}(aq) + C_2O_4^{2\ominus}(aq) \rightleftharpoons MgC_2O_4(s)$

Ionic product in the solution is given by

$[Mg^{2+}][C_2O_4^{2-}(aq)] = 0.05 \times 0.15$

$= 0.0075 = 7.5 \times 10^{-3}$

the K_{sp} value for MgC_2O_4 at 293 K is 8.56×10^{-5}. As ionic product is greater than K_{sp} precipitation will take place.

Problem 3.12 : The solubility product of AgBr is 5.2×10^{-13}. Calculate its solubility in mol dm^{-3} and g dm^{-3}(Molar mass of AgBr = 187.8 g mol^{-1})

Solution : The solubility equilibrium of AgBr is :

$AgBr(s) \rightleftharpoons Ag^{\oplus}(aq) + Br^{\ominus}(aq)$

x = 1, y = 1

$K_{sp} = [Ag^{\oplus}][Br^{\ominus}] = S^2$

$S = \sqrt{K_{sp}} = \sqrt{5.2 \times 10^{-13}}$

$= 7.2 \times 10^{-7}$ mol dm^{-3}

The solubility in g dm^{-3} = molar solubility in mol dm^{-3} × molar mass g mol^{-1}

$S = 7.2 \times 10^{-7}$ mol $dm^{-3} \times 187.8$ g mol^{-1}

$= 1.35 \times 10^{-4}$ g dm^{-3}

Problem 3.13 : If 20.0 cm^3 of 0.050 M $Ba(NO_3)_2$ are mixed with 20.0 cm^3 of 0.020 M NaF, will BaF_2 precipitate ? K_{sp} of BaF_2 is 1.7×10^{-6} at 298 K.

Solution : Final volume of solution is

20 + 20 = 40 cm^3,

$[Ba(NO_3)_2] = \frac{0.050 \times 20}{40} = 0.025$ M

$[NaF] = \frac{0.020 \times 20}{40} = 0.010$M

Therefore $[Ba^{2\oplus}] = 0.025$ M and

$[F^{\ominus}] = 0.010$M

Hence ionic product of BaF_2 is

$IP = [Ba^{2\oplus}][F^{\ominus}]^2$

$= 0.025 \times (0.01)^2$

$= 2.5 \times 10^{-6}$

$K_{sp}(BaF_2) = 1.7 \times 10^{-6}$ Thus, $K_{sp} < IP$

Ionic product in the solution is greater than K_{sp}. Hence BaF_2 will precipitate from the solution.

3.10 Common ion effect :

Can you recall ?



Which reagents are used to precipitate (i) group II, (ii) group III B, (iii) group III A of basic radicals/ cations ?

Consider a solution of weak acid CH_3COOH and its soluble ionic salt CH_3COONa.

CH_3COOH is weak acid, dissociates only slightly in solution

$$CH_3COOH \rightleftharpoons CH_3COO^{\ominus}(aq) + H^{\oplus}(aq)$$

CH_3COONa being a strong electrolyte dissociates almost completely in solution.

$$CH_3COONa(aq) \longrightarrow CH_3COO^{\ominus} + Na^{\oplus}$$

Both the acid and the salt produce $CH_3COO^{\ominus}$ ions in solution. CH_3COONa dissociates completely. Therefore it provides high concentration of $CH_3COO^{\ominus}$ ions. According to Le-Chatelier principle, the addition of $CH_3COO^{\ominus}$ from CH_3COONa to the solution of CH_3COOH, shifts equilibrium of dissociation of CH_3COOH to left. Thus reverse reaction is favoured in which $CH_3COO^{\ominus}$ combines with $H^{\oplus}$ to form unionised CH_3COOH. Hence dissociation of CH_3COOH is supressed due to presence of CH_3COONa containing a common $CH_3COO^{\ominus}$ ion.

The common ion effect states that the ionisation of a weak electrolyte is supressed in presence of a strong electrolyte containing an ion common to the weak electrolyte.

Remember...



Common ion effect is a special case of Le-Chatelier's principle in which the stress applied to an equilibrium system is an increase in the concentration of one of the product (ions). The effect of this stress is reduced by shifting the equilibrium to the reactant side.

Can you tell ?



How does the ionization of NH_4OH suppressed by addition of NH_4Cl to the solution of NH_4OH ?

3.10.1 Common ion effect and solubility

Do you know ?



The hardness of water is due to presence of $Ca^{2\oplus}$ ions. It is surprising to know that $Ca^{2\oplus}$ ions can be removed by adding more $Ca^{2\oplus}$ ions in the form of lime $Ca(OH)_2$, to the hard water. The $OH^{\ominus}$ ions of lime react with $HCO_3^{\ominus}$ ions present in the hard water to form $CO_3^{2\ominus}$ ions.

$$OH^{\ominus}(aq) + HCO_3^{\ominus}(aq) \longrightarrow CO_3^{2\ominus}(aq) + H_2O(l)$$

Solubility product of $CaCO_3$ is very low ($K_{sp} = 4.5 \times 10^{-9}$). Addition of lime makes $IP >> Ksp$ which results in the precipitation of $CaCO_3$ and thereby removal of hardness.

The presence of a common ion also affects the solubility of a sparingly soluble salt. Consider, the solubility equilibrium of AgCl,

$$AgCl(s) \rightleftharpoons Ag^{\oplus}(aq) + Cl^{\ominus}(aq)$$

The solubility product of AgCl is

$$K_{sp} = [Ag^{\oplus}][Cl^{\ominus}]$$

Suppose $AgNO_3$ is added to the saturated solution of AgCl. The salt $AgNO_3$ being a strong electrolyte dissociates completely in the solution.

$$AgNO_3(aq) \longrightarrow Ag^{\oplus}(aq) + NO_3^{\ominus}(aq)$$

The dissociation of AgCl and $AgNO_3$ produce a common $Ag^{\oplus}$ ion. The concentration of $Ag^{\oplus}$ ion in the solution increases owing to complete dissociation of $AgNO_3$. According to Le-chatelier's principle the addition of $Ag^{\oplus}$ ions from $AgNO_3$ to the solution of AgCl shifts the solubility equilibrium of AgCl from right to left. The reverse reaction in which AgCl precipitates, is favoured until the solubility equilibrium is re-established. The value of K_{sp} however, remains the same since it is an equilibrium constant. The solubility of a sparingly soluble compound, thus decreases with the presence of a common ion in solution.

Exercises

1. Choose the most correct answer :

i. The *pH* of 10^{-8} M of HCl is
   a. 8 b. 7
   c. less than 7 d. greater than 7

ii. Which of the following solution will have pH value equal to 1.0 ?
   a. 50 mL of 0.1M HCl + 50mL of 0.1M NaOH
   b. 60 mL of 0.1M HCl + 40mL of 0.1M NaOH
   c. 20 mL of 0.1M HCl + 80mL of 0.1M NaOH
   d. 75 mL of 0.2M HCl + 25mLof 0.2M NaOH

iii. Which of the following is a buffer solution ?
   a. $CH_3COONa + NaCl$ in water
   b. $CH_3COOH + HCl$ in water
   c. $CH_3COOH + CH_3COONa$ in water
   d. $HCl + NH_4Cl$ in water

iv. The solubility product of a sparingly soluble salt AX is 5.2×10^{-13}. Its solubility in mol dm^{-3} is
   a. 7.2×10^{-7} b. 1.35×10^{-4}
   c. 7.2×10^{-8} d. 13.5×10^{-8}

v. Blood in human body is highly buffered at *pH* of
   a. 7.4 b. 7.0
   c. 6.9 d. 8.1

vi. The conjugate base of $[Zn(H_2O)_4]^{2\oplus}$ is
   a. $[Zn(H_2O)_4]^{2\ominus}NH_3$
   b. $[Zn(H_2O)_3]^{2\ominus}$
   c. $[Zn(H_2O)_3OH]^{\oplus}$
   d. $[Zn(H_2O)H]^{3\oplus}$

vii. For *pH* > 7 the hydronium ion concentration would be
   a. 10^{-7}M b. $< 10^{-7}$M
   c. $> 10^{-7}$M d. $\geq 10^{-7}$M

2. Answer the following in one sentence :

i. Why cations are Lewis acids ?

ii. Why is KCl solution neutral to litmus?

iii. How are basic buffer solutions prepared?

iv. Dissociation constant of acetic acid is 1.8×10^{-5}. Calculate percent dissociation of acetic acid in 0.01 M solution.

v. Write one property of a buffer solution.

vi. The *pH* of a solution is 6.06. Calculate its $H^{\oplus}$ ion concentration.

vii. Calculate the *pH* of 0.01 M sulphuric acid.

viii. The dissociation of H_2S is suppressed in the presence of HCl. Name the phenomenon.

ix. Why is it necessary to add H_2SO_4 while preparing the solution of $CuSO_4$?

x. Classify the following buffers into different types :

a. $CH_3COOH + CH_3COONa$

b. $NH_4OH + NH_4Cl$

c. Sodium benzoate + benzoic acid

d. $Cu(OH)_2 + CuCl_2$

3. Answer the following in brief :

i. What are acids and bases according to Arrhenius theory ?

ii. What is meant by conjugate acid-base pair?

iii. Label the conjugate acid-base pair in the following reactions

a. $HCl + H_2O \rightleftharpoons H_3O^{\oplus} + Cl^{\ominus}$

b. $CO_3^{2\ominus} + H_2O \rightleftharpoons OH^{\ominus} + HCO_3^{\ominus}$

iv. Write a reaction in which water acts as a base.

v. Ammonia serves as a Lewis base whereas $AlCl_3$ is Lewis acid. Explain.

vi. Acetic acid is 5% ionised in its decimolar solution. Calculate the dissociation constant of acid

(Ans : 2.63×10^{-4})

vii. Derive the relation $pH + pOH = 14$.

viii. Aqueous solution of sodium carbonate is alkaline whereas aqueous solution of ammonium chloride is acidic. Explain.

ix. pH of a weak monobasic acid is 3.2 in its 0.02 M solution. Calculate its dissociation constant.

x. In NaOH solution $[OH^{\ominus}]$ is 2.87×10^{-4}. Calculate the *pH* of solution.

4. Answer the following :

i. Define degree of dissociation. Derive Ostwald's dilution law for the CH_3COOH.

ii. Define *pH* and *pOH*. Derive relationship between *pH* and *pOH*.

iii. What is meant by hydrolysis ? A solution of CH_3COONH_4 is neutral. why ?

iv. Dissociation of HCN is suppressed by the addition of HCl. Explain.

vi. Derive the relationship between degree of dissociation and dissociation constant in weak electrolytes.

vii. Sulfides of cation of group II are precipitated in acidic solution (H_2S + HCl) whereas sulfides of cations of group IIIB are precipitated in ammoniacal solution of H_2S. Comment on the relative values of solubility product of sulfides of these.

viii. Solubility of a sparingly soluble salt get affected in presence of a soluble salt having one common ion. Explain.

ix. The *pH* of rain water collected in a certain region of Maharashtra on particular day was 5.1. Calculate the $H^{\oplus}$ ion concentration of the rain water and its percent dissociation.

x. Explain the relation between ionic product and solubility product to predict whether a precipitate will form when two solutions are mixed?

Activity :



Take two test tubes and label them as A and B. Add Zinc filings in both the test tubes. In the test tube labelled A add 5 mL of 1M HCl and in test B 5 mL of acetic acid. Keep the test tubes on the stand. Note down your observations.

a. Do you see any effervescence coming from the two test tubes ?

b. Which gas is evolved ?

c. How do you identify the gas ?

d. What is the relative rate at which the gas is evolved in the two test tubes

e. Based on your observations comment on the strength of acids used.