03 Ionic equilibria

Syllabus

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+Q.1 Can you recall?

i. What is chemical equilibrium?

Ans: Chemical equilibrium is the state of a system in which the concentration of the reactant and the concentration of the products do not change with time.

ii. What are electrolytes?

Ans: Electrolytes are the substance that conducts electric current as a result of a dissociation into positively and negatively charged particles.

3.1 Introduction

Q.2 What is ionic equilibrium? Give some examples of ionic equilibrium.

Ans:

i. The equilibrium between ions and unionized molecules in solution is called ionic equilibrium.

ii. H^+ and OH^- ions and unionized water molecules.

iii. Ionization of weak acids and weak bases.

iv. Reactions between ions of salt and ions of water.

v. Solid salt and its ions in water.

3.2 Types of electrolytes

Q.3 Water are electrolytes?

Ans: The substances which give rise to ions when dissolved in water are electrolytes.

Q.4 What are nonelectrolytes?

Ans: The non electrolytes are those which do not ionize and exist as molecules in aqueous solutions.

Q.5 Give the classification of electrolytes?

Ans:

i. The electrolytes are classified into strong and weak electrolytes.

ii. This classification is based on their extent of ionisation in dilute aqueous solutions.

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

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

Q.6 Explain the dissociation of weak electrolytes in water.

Ans:

i. The weak electrolytes dissociate only partially in dilute aqueous solutions. An equilibrium thus can be established between the ions and nonionized molecules.

ii. The ionization reaction therein is represented as double arrow ($\rightleftharpoons$) between the ions and nonionized molecule.

Q.7 Which of the following is a strong electrolyte?

HF, AgCl, $CuSO_4$, CH_3COONH_4, H_3PO_4

Ans:

Strong electrolyte	Weak electrolyte
AgCl, $CuSo_4$	HF
CH_3COONH_4	
H_3PO_4	

★Q.8 Define degree of dissociation.

Ans: 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.

Q.9 Give the formula for degree of dissociation and percent dissociation.

Ans:

i. $\propto = \dfrac{\text{number of moles dissociated}}{\text{total number of moles}}$

ii. Percent dissociation = $\propto \times 100$

iii. 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

Q.10 Give some examples of acids and bases we come across in life.

Ans:

i. Acids and bases are familiar chemical compounds.

ii. Acetic acid is found in vinegar, citric acid in lemons, magnesium hydroxide in antacids, ammonia in household cleaning products.

iii. The tartaric acid is present in tamarind paste. These are some acids and bases we come across in everyday life.

★Q.11 What are acids and bases according to Arrhenius theory?

Ans:

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

ii. **Acid:** Acid is a substance which contains hydrogen and gives rise to H^+ ions in aqueous solution. For example :

$$HCL_{(aq)} \xrightarrow{\text{water}} H^+_{(aq)} + Cl^-_{(aq)}$$

$$CH_3COOH_{(aq)} \underset{}{\overset{\text{water}}{\rightleftharpoons}} CH_3COO^-_{(aq)} + H^+_{(aq)}$$

Note-

i. Arrhenius described H^+ ions in water as bare ions; they hydrate in aqueous solutions and thus represented as hydronium ions H_3O^+. We herewith conveniently represent them as H^+.

ii. 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.

\+ **Do you know?**

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

Q.12 Write a short note on Bronsted – Lowry theory.

Ans:

i. J.N. Bronsted and T.M. Lowry (1923) proposed a more general theory known as the Bronsted Lowry proton transfer theory.

ii. According to this theory acids and bases are defined as follows.

iii. Acid is a substance that donates a proton (H^+) to another substance.

iv. Base is a substance that accepts a proton (H^+) from another substance.

v. For example :

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

vi. In the above reaction HCl and NH_4^+ are proton donors and act as acids. The NH_3 and Cl are proton acceptors and act as bases.

vii. Further it follows that the products of the Bronsted-Lowry acid-base reactions are acids bases.

Q.13 What is meant by conjugate acid-base pair?

Ans:

i. The base produced by accepting the proton from an acid is the conjugate base of that acid.

ii. Likewise the acid produced when a base accepts a proton is called the conjugate acid of that base.

iii. A pair of an acid and a base differing by a proton is said to be a **conjugate acid-base pair**.

$$\underset{\text{Acid}_1}{HCl_{(aq)}} + \underset{\text{Base}_2}{H_2O_{(l)}} \rightleftharpoons \underset{\text{Acid}_2}{H_3O^+_{(aq)}} + \underset{\text{Base}_1}{Cl^-_{(aq)}}$$

conjugate acid-base pair $_2$

conjugate acid-base pair $_1$

Q.14 Label the conjugate acid-base pair in the

following reactions:

i. $\mathbf{HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-}$

ii. $\mathbf{CO_3^{2-} + H_2O \rightleftharpoons OH^- + HCO_3^-}$

Ans :

i. $\underset{Acid_1}{HCl} + \underset{Base_2}{H_2O} \rightleftharpoons \underset{Acid_2}{H^3O^+} + \underset{Base_1}{Cl^-}$

ii. $\underset{Base_1}{CO_3^{2-}} + \underset{Acid_2}{H_2O} \rightleftharpoons \underset{Base_2}{OH^-} + \underset{Acid_1}{HCO_3^-}$

Q.15 Explain the Lewis acid-base theory and give suitable examples.

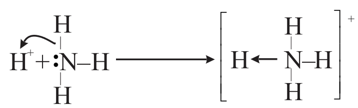
Ans :

i. A more generalized acid base concept was put forward by G.N. Lewis in 1923.

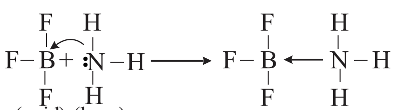
ii. According to this theory acids and bases are defined as follows.

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

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



(acid) (base)



(acid) (base)

Q.16 Why cations are Lewis acids?

Ans: Cations are electron deficient species and it can accept an electron pair. Hence, cations are Lewis acids.

Q.17 Ammonia serves as a Lewis base whereas $\mathbf{AlCl_3}$ is lewis acid. Explain.

Ans:

i. According to Lewis thoery, any species that accepts a share in an electron pair is called Lewis acid.

ii. The species that donates a share in an electron pair is called Lewis base.

iii. In ammonia (NH_3) molecule, nitrogen (N) has a lone pair of electrons to donate. Therefore, NH_3 acts as a Lewis acids.

iv. In aluminium chloride ($AlCl_3$) molecule. The octet of Al is incomplete. Therefore it can accept a lone pairs of electron to complete its octet. Hence $AlCl_3$ acts as a Lewis acids.

Q.18 All Bronsted bases are also Lewis bases, but all Bronsted acids are not Lewis acids. Explain

Ans :

i. According to Bronsted theory, an acid is a "proton donor" and a base is a "proton acceptor.

ii. According to Lewis concept, an acid is acceptor of lone pairs of electron while base is a donor of lone pair of electrons.

iii. So if Bronsted base is acceptor of proton means it is donating its lone pair to the proton that is same as lewis base.

iv. But to behave as Bronsted acid the species must contain proton, then only it will be proton donor.

v. But any of the chemical species can be lewis acid if it accepts the lone pair of electron (here no role of proton).

vi. Example is $AlCl_3$. $AlCl_3$ cannot donate proton hence not a Bronsted acid but it can accept lone pair of electrons hence it is lewis acid.

Q.19 Explain the amphoteric nature of water.

Ans :

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

ii. For example :

$$H_2O_{(l)} + NH_{3(aq)} \rightleftharpoons OH^-_{(aq)} + NH^+_{4(aq)}$$

Acid

$$H_2O_{(l)} + HCl_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$$

base

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

Q.20 Write a reaction in which water acts as a base.

Ans : $H_2O_{(l)} + HCl_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$

base

3.4 Ionisation of acids and bases

Q.21 How are acids and bases classified on the basis of their extent of dissociation?

Ans :

i. Acids and bases are classified as strong acids and strong bases, weak acids and weak bases on the basis of their **extent of dissociation**.

ii. Strong acids and bases are almost completely dissociated in water.

iii. For example :

$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

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

v. 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.

vi. For example:

$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$

$NH_4\ OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$

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

Q.22 Activity:

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

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

ii. Which gas is evolved?

iii. How do you identify the gas?

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

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

Ans :

i. Yes, there is effervescence coming from both the test tubes.

ii. Hydrogen gas is evolved in both the cases.

iii. We can identify the gas (hydrogen) by bringing a lighted candle is brought near the mouth of the test tube. The gas burns with a pop sound.

iv. The gas is evolved fast in test tube A (containing HCl) as compared to test tube B (containing acetic acid).

v. Since gas is evolved faster in test tube A, we can say that HCl is stronger acid as compared to acetic acid.

Q.23 Write a short note on dissociation constant of weak acids and bases.

Ans :

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

$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$

ii. The equilibrium constant called acid dissociation constant for this equilibrium is :

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

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

$BOH_{(aq)} \rightleftharpoons B^+_{(aq)} + OH^-_{(aq)}$

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

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

v. 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.

Q.24 Derive Ostwald's dilution law for weak acid HA.

Ans :

i. Consider an equilibrium of weak acid HA that exists in solution partly as the undissociated species HA and partly H^+ and A^- ions. Then

$HA_{(aq)}$ - $H^+_{(aq)} + A^-_{(aq)}$

The acid dissociation constant is given as

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

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

	$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$		
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},

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

Substituting these in Eq. ...(i)

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

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

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

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

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

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

The Eq. (v) 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.

★ Q.25 Derive Ostwald's dilution law for CH_3COOH.

Ans :

i. Consider an equilibrium of weak acid CH_3COOH that exists in solution partly as the undissociated species CH_3COOH and partly H^+ and CH_3COOH^- ions. Then

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COOH^-_{(aq)}$$

ii. The acid dissociation constant is given as:

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

iii. Suppose 1 mol of acid CH_3COOH is initially present in volume V dm^3 of the solution. At equilibrium, the fraction dissociated would be α, where α is degree of dissociation of the acid. The fraction of an acid that remains undissociated would be $(1 - \alpha)$.

	$CH_3OOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3OOH^-_{(aq)}$		
Amount present at equilibrium/ (mol)	$(1 - \alpha)$	α	α
concentration at equilibrium/ (mol dm^{-3})	$\frac{1-\alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

iv. Thus, at equilibrium $[CH_3COOH]$

$$= \frac{1-\alpha}{V} \text{ mol dm}^{-3}.$$

$[H^+] = [CH_3COO^-] = \frac{\alpha}{V}$ mol dm^{-3}.

v. Substituting these in equation (i),

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

vi. If c is the initial concentration of CH_3COOH in mol dm^{-3} and V is the volume in dm^3 mol^{-1} then c = 1/V. Replacing 1/V in equation (ii) by c, we get

$$K_a = \frac{\alpha / V \ \alpha / V}{1-\alpha / V} = \frac{\alpha^2}{1-\alpha V}$$

vii. For the weak acid CH_3COOH, α is very small, or $(1 - \alpha) = 1$.

With this equation (ii) and (iii) becomes:

$K_a = \alpha^2/V$ and $K_a = \alpha^2 c$ ...(iv)

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

The equation (v) implies that the degree of dissociation of a weak acid (CH_3COOH) 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.

Q.26 Derive Ostwald's dilution law for weak base BOH.

Ans :

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

$$BOH_{(aq)} \rightleftharpoons B^+_{(aq)} + OH^-_{(aq)}$$

The base dissociation constant is

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

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

	$BOH_{(aq)} \rightleftharpoons$	$B^+_{(aq)}$ +	$OH^-_{(aq)}$
Amount present at equilibrium/ mol	$(1-\alpha)$	α	α
concentration at equilibrium/ mol dm^{-3}	$\frac{1-\alpha}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

A equilibrium,

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

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

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

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

Similar arguments in the case of weak acid, led to

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

$$\alpha = \sqrt{K_b . V} \text{ or } \alpha = \sqrt{\frac{K_b}{c}} \quad ...(iv)$$

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.

Type-1

Numericals based on dissociation constant

+Q.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,

$$\alpha = \frac{\text{percent dissociation}}{100}$$

$$= \frac{0.05}{100} = 5\times10^{-4}$$

c = 0.02 M = 2×10^{-2} M

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

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

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

+Q.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, $\alpha = \sqrt{\frac{1.8\times10^{-5}}{1\times10^{-2}}} = \sqrt{1.8\times10^{-3}}$

$= \sqrt{18\times10^{-4}} = 4.242\times10^{-2} = 0.04242$

+Q.3 A weak monobasic acid is 12% dissociated in 0.05 M solution. What is percent dissociation in 0.15 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 of 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 $\alpha_2^2 = 0.0693$ %

percent dissociation = 6.93%

★ **Q.4 Acetic acid is 5% ionised in its decimolar solution. Calculate the dissociation constant of acid.**

Solution:

Percent dissociation = 5%,

Concentration (c) = 1 decimolar

Dissociation constant of acid (K_a)

Formulae:

i. Percent dissociation = $\alpha \times 100$

ii. $K_a = \alpha^2 c$

Calculation:

Using formula (i),

$$\alpha = \frac{\text{percent dissociation}}{100} = \frac{5}{100} = 0.05$$

c = 1 decimolar = 0.1 M

Using formula (ii),

$K_a = (0.05)^2 \times (0.1) = 2.5 \times 10^{-4}$

Ans: Dissociation constant of acid is 2.5×10^{-4}.

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

Solution:

Given: Dissociation constant (K_a) = 1.8×10^{-5},

Concentration (c) = 0.01 M

To find: Percent dissociation

Formulae:

i. $K_a = \alpha^2 c$

ii. Percent dissociation = $\alpha \times 100$

Calculation:

c = 0.01 M = 1×10^{-2} M

Using formula (i),

$$\therefore \quad \alpha = \sqrt{\frac{K_a}{c}}$$

$$= \sqrt{\frac{1.8 \times 10^{-5}}{1 \times 10^{-2}}} = \sqrt{1.8 \times 10^{-3}} = \sqrt{18 \times 10^{-4}}$$

$= 4.242 \times 10^{-4}$

Using formula (ii),

Percent dissociation = $\alpha \times 100$

$= 4.242 \times 10^{-2} \times 100 =$ **4.242%**

$K_a = (0.05)^2 \times (0.1) = 2.5 \times 10^{-4}$

Ans: Percent dissociation of 0.01 M acetic acid solution is **4.242%**.

3.5 Autoionization of water

Q.27 Derive an expression for ionic product of water.

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

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

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

$$K = \frac{[H_3O^+][OH^-]}{[H_2O(l)]^2} \quad ...(i)$$

or $K[H_2O]^2 = [H_3O^+][OH^-]$ ...(ii)

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. (ii) we get,

$K \times K' = [H_3O^+][OH^-]$ ...(iii)

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

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.

Q.28 What will be the value of K_w at 298K?

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

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

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

Q.29 Internet my friend.

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

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

Ans : The values of K_w at various temperatures are:

Temperature	Value of K_w
273 K	0.114×10^{-14}
283 K	0.292×10^{-14}
293 K	0.681×10^{-14}
303 K	1.47×10^{-14}
313 K	2.92×10^{-14}
323 K	5.47×10^{-14}

3.6 pH Scale

Q.30 Define pH and pOH. and give their expressions.

Ans :

i. pH of a solution is defined the pH of a solution as the negative logarithm to the base 10, of the concentration of H^+ ions in solution in mol dm^{-3}.

ii. Expressed mathematically as
$pH = -\log_{10}[H^+]$

iii. *pOH* of a solution can be defined as the negative logarithm to the base 10, of the molar concentration of OH^- ions in solution.
pOH is expressed mathematically as
$pOH = -\log_{10}[H^-]$

★ Q.31 Derive the relation pH + pOH = 14.

Ans : Relationship between pH and pOH

The ionic product of water is

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

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

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

Taking logarithm of both the sides, we write

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

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

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

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

$pH + pOH = 14$

★ Q.32 Define pH and pOH. Derive the relationship between pH and pOH.

Ans : *Refer Q.30 and Q.31.*

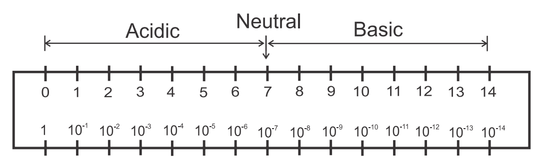
Q.33 Explain pH scale in brief.

Ans :

i. **Neutral solution:** For pure water or any aqueous neutral solution at 298 K
$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ M
Hence,
$pH = -\log_{10}[H^+] = -\log_{10}[1 \times 10^{-7}] = 7$

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

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



Q.34 Use brain power

i. Suppose that pH of monobasic and dibasic acid is the same. Does this mean that the molar concentrations of both acids are identical?

Ans : No, it does not mean that the molar concentrations of boh acids are identical.
Consider a strong monobasic acid (HA) and a strong dibasic acid (H_2A), both having the same molar concentration (c).
The dissociate as given below:

$$\underset{c}{HA} \rightarrow \underset{c}{H^+} + \underset{c}{A^-}$$

$$H_2A \rightarrow 2H^+ + A^{2-}$$

c 2c c

here c is molar concentration of acid
The dibasic acid gives 2 times the number of H+ ions as compared to monobasic acid.
So, if both the acids have same pH, then the molar concentration of dibasic acid would be half that of monobasic acid.

ii. How pH of pure water vary with temperature? Explain.

Ans : The pH of pure water decreases as the temperature increases.
pH is measure of H_3O^+ ions in a solution. As concentration of H_3O^+ ions increase, pH

decreases.

When (H_2O) dissociates, it forms H_3O^+ and OH^- ions.

$$2H_2O_{(l)} \rightleftharpoons H_2O^+_{(aq)} + H_2O^-_{(aq)}$$

The equilibrium constant for this reaction is known as K_w.

When temperature increases, the value of K_w increases. Hence, there are more (H_3O^+) ions in water. As a result, pH of water decreases.

Do you know?

i. pH is crucial for digestion of food and other biochemical reactions in our body.

ii. pH of gastric juice is about 2.

iii. pH of blood is maintained within range 7.36 to 7.42.

iv. Enzymes function effectively only at a certain pH. For example trypsin acts best for alkaline pH.

Type-2

Numericals based on pH and pOH

Q.1 Calculate *pH* and *pOH* of 0.01 M HCl solution.

Solution:

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

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+{}_{(aq)} + Cl^-{}_{(aq)}$$

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

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

We know that $pH + pOH = 14$

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

Q.2 Calculate the pH of 0.01 M sulphuric acid.

Solution:

Given: Concentration of sulphuric acid = 0.01 M

To find pH

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

Calculation: Sulphuric acid (H_2SO_4) is a strong acid. It dissociates almost completely in water as:

$$H_{2SO_{4(aq)}} + 2H_2O_{(l)} \rightarrow 2H_2O^+_{(aq)} + 2H_2O^{2-}_{4(aq)}$$

Hence,

$[H_3O+] = 2 \times c = 2 \times 0.01\ M = 2 \times 10^{-2}\ M$

From formula (i),

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

$= -\log_{10}2 - \log_{10}10^{-2} = -\log_{10}2 + 2 = 2 - 0.3010$

$pH = 1.699$

Ans : The pH of 0.01 M sulphuric acid is **1.699**.

Q.3 *pH* of a solution is 3.12. Calculate the concentration of H_3O^+ ion.

Solution:

pH is givent by

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

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

$= -3.12$

$= -3 - 0.12 + 1 - 1$

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

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

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

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

Q.4 The pH of a solution is 6.06. Calculate its H^+ ion concentration.

Solution:

Given: pH of solution = 6.06

To find H^+ ion concentration

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

Calculation: From formula,

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

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

$= -6.06 = -6 - 0.06 + 1 - 1$

$= (-6 - 1) + 1 - 0.06 = -7 + 0.94$

$= \bar{7}.94$

Thus, $[H_3O^+] = \text{Antilog}_{10} [\bar{7}.94]$

$= 8.710 \times 10^{-7}\ M$

Ans: The H^+ ion concentration of the solution is **8.710×10^{-7} M**

Q.5 In NaOH solution $[OH^-]$ is 2.87×10^{-4}. Calculate the pH of solution.

Solution:

Given: $[OH-] = 2.87 \times 10^{-4}\ M$

To find: pH of the solution

Formula: i. $pOH = -\log_{10}[OH^-]$

ii. $pH + pOH = 14$

Calculation: From formula (i),

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

$pOH = -\log_{10}[2.87 \times 10^{-4}]$

$= -\log_{10}2.87 - \log_{10} 10^{-4}$

$= -\log_{10}2.87 + 4 = 4 - 0.4579$

$pH = 3.5421$

From formula (ii),

$pH + pOH = 14$

$pH = 14 - pOH = 14 - 3.5421 = 10.4579.$

Ans : pH of the solution is **10.4579**.

Q.6 A weak monobasic acid is 0.04% dissociated in 0.025 M solution. What is *pH* of the solution?

Solution:

A weak monobasic acid HA dissociates as:

$$HA + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

Percent dissociation $= \alpha \times 100$

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

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

Now $[H_3O^+] = \alpha \times c$

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

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

Q.7 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:

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

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

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

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

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

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

for monoacidic base,

$$BOH_{(aq)} \rightleftharpoons B^+_{(aq)} + OH^-_{(aq)}$$

$[OH^-] = \alpha c$

$$\alpha = \frac{[OH^-]}{c} = \frac{1.858 \times 10^{-3}}{0.02} = 0.07925$$

Percent dissociation $= \alpha \times 100$

$= 0.07925 \times 100$

$= 7.925\%$

Q.8 The pH of rain water collected in a certain region of Maharashtra on particular day was 5.1. Calculate the H^+ ion concentration of the rain water and its percent dissociation.

Solution:

Given: pH of rain water = 5.1

To find: i. H^+ ion concentration

ii. Percent dissociation

Formula:

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

ii. Percent dissociation $= \alpha \times 100$

Calculation: From formula (i)

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

$\therefore$ $\log_{10}[H_3O^+] = -5.1$

$= -5 - 0.1 + 1 - 1 = (-5 - 1) + 1 - 0.1$

$= -6 + 0.9 = \bar{6}.9$

$\therefore$ $[H_3O^+] = \text{Antilog}_{10}[\bar{6}.9]$

$= 7.943 \times 10^{-6}$ M

Considering that pH of rain water is due to dissociation of monobasic strong acid (HA), we have

$$HA_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + A^-_{(aq)}$$

$\therefore$ $[H_3O^+] = \alpha$

$\alpha = 7.943 \times 10^{-6}$

From formula (ii),

Percent dissociation $= 7.943 \times 10^{-6} \times 100$

$= 7.943 \times 10^{-4}$

Ans: i. H^+ ion concentration is $\mathbf{7.943 \times 10^{-6}}$ **M**.

ii. Percent dissociation is $\mathbf{7.943 \times 10^{-4}}$.

Q.9 pH of a week monobasic acid is 3.2 in its 0.02 M solution. Calculate its dissociation constant.

Solution:

Given: pH of weak monobasic acid = 3.2,

Concentration of solucion (c) = 0.02 M

To find: Dissociation constant (K_a)

Formula:

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

ii. $K_a = \alpha^2 c$

Calculation: From formula (i)

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

$\therefore$ $\log_{10}[H_3O^+] = -3.2$

$= -3 - 0.2 + 1 - 1 = (-3 - 1) + 1 - 0.2$

$= -4 + 0.8 = \bar{4}.8$

$\therefore$ $[H_3O^+] = \text{Antilog}_{10}[\bar{4}.8]$

$= 6.310 \times 10^{-4}$ M

A weak monobasic acid HA dissociates as:

$$HA + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

∴ $[H_3O^+] = \alpha \times c$

$\alpha = 7.943 \times 10^{-6}$

$$\alpha = \frac{[H_3O^+]}{c} = \frac{6.310 \times 10^{-4}}{0.02} = 3.16 \times 10^{-2}$$

From formula (ii),

$K_a = a^2 c = (3.16 \times 10^{-2})^2 \times 0.02 = 2.0 \times 10^{-5}$

Ans: Dissociation constant of the acid is **2.0×10^{-5}**.

3.7 Hydrolysis of Salts

Q.35 What are different types of salts. Give examples.

Ans : **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.

Q.36 Explain the concept of hydrolysis.

Ans :

i. When a salt is dissociated in water, it dissociates completely into its constituent ions.

ii. The solvent water dissociates slightly as,

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

iii. Pure water is neutral and $[H_3O^+] = [OH^-]$.

iv. If the ions of the salt do not interact with water the hydronium and hydroxyl ion concentrations remain equal and the solution is neutral.

v. When one or more of the salt ions react with water, the equality of concentrations of H_3O^+ and OH^- ions is disturbed.

vi. The solution, does not remain neutral and becomes acidic or basic depending on the type of the salt.

vii. Such a reaction between the ions of salt and the ions of water is called hydrolysis of salt.

viii. 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).

Q.37 Explain why the salt of strong acid and strong base does not undergo hydrolysis.

Ans :

i. 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.

$NaCl_{(aq)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$

ii. The ions Na^+ and Cl^- 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.

iii. In other words,

$$Na^+_{(aq)} + Cl^-_{(aq)} + H_2O \rightarrow \underset{\text{(strong acid)}}{HCl_{(aq)}} + \underset{\text{(strong base)}}{NaOH_{(aq)}}$$

[Possible products]

$$HCl_{(aq)} + NaOH_{(aq)} + H_2O \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)}$$

iv. 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.

v. Equality $H_3O^+ = OH^-$ produced by ionization of water is not disturbed and solution is neutral.

vi. It may be concluded that salt of strong acid and strong base does not undergo hydrolysis.

Q.38 Why is KCl solution neutral to litmus paper?

Ans : KCl is a salt of strong acid (HCl) and a strong base (KOH). Hence it do not undergo hydrolysis and it is neutral to litmus.

Q.39 Write a short note on the hydrolysis of salt of strong acid and weak base.

Ans :

i. $CuSO_4$ 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,

$CuSO_{4(aq)} \rightarrow Cu^{2+}_{(aq)} + SO_4{}^{2-}_{(aq)}$

ii. $SO_4{}^{2-}$ ions of salt have no tendency to react with water because the possible product H_2SO_4 is strong electrolyte.

iii. The reaction of Cu^{2+} ions with OH ions form unionized $Cu(OH)_2$.

iv. The hydrolytic equilibrium for $CuSO_4$ is then written as,

$$Cu^{2+}(aq) + 4H_2O_{(l)} \rightleftharpoons Cu(OH)_{2(aq)} + 2H_3O^+_{(aq)}$$

v. Due to the presence of excess of H_3O^+ ions, the resulting solution of $CuSO_4$ becomes acidic and turns blue litmus red.

★ Q.40 Why it is necessary to add H_2SO_4 while preparing the solution of $CuSO_4$?

Ans :

i. Formation of sparingly soluble $Cu(OH)_2$ by hydrolysis makes the aqueous solution of $CuSO_4$ turbid.

ii. If H_2SO_4, that is H_3O^+ ions are added, the hydrolytic equilibrium shifts to the left.

iii. A turbidity of $Cu(OH)_2$ dissolves to give a clear solution.

iv. To get clear solution of $CuSO_4$, the addition of H_2SO_4 would be required.

Q.41 Explain the hydrolysis of salt of weak acid and strong base.

Ans :

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

$$CH_3COONa_{(aq)} \rightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

ii. Water dissociates slightly as,

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

iii. Solution of CH_3COONa contains Na^+, H_3O^+, CH_3COO^-, OH^-.

iv. The Na^+ ions of salt have no tendency to react with OH^- ions of water since the possible product of the reaction is NaOH, a strong electrolyte.

v. On the other hand the reaction of CH_3COO^- ions of salt with the H_3O^+ ions from water produces unionized CH_3COOH.

vi. $$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$$

vii. Thus, the hydrolytic equilibrium for CH_3COONa is,

$$CH_3COONa_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)}$$

viii. As a result of excess OH ions produced the solution becomes basic. The solution of CH_3COONa is therefore basic.

Q.42 Can you tell?
Why an aqueous solution of NH_4Cl is acidic while that of HCOOK basic ?

Ans :

i. NH_4Cl is salt of strong acid HCl and weak base NH_4OH. When dissolved in water, it dissociates completely as,

$$NH_4Cl_{(aq)} \rightarrow NH^+_{4(aq)} + Cl^-_{(aq)}$$

ii. Cl– ions of salt have no tendency to react with water because the possible product HCl is strong electrolyte.

iii. The reaction of NH ions with OH^- ions form unionized NH_4OH. The hydrolytic equilibrium for NH_4Cl is then written as,

$$NH^+_{4(aq)} + 2H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H_3O^+_{(aq)}$$

iv. Due to the presence of excess of H_3O ions, the resulting solution of NH_4Cl becomes acidic.

v. Similarly, HCOOK is a salt of weak acid HCOOH and strong base KOH. When dissolved in water, it dissociates completely.

$$HCOOK_{(aq)} \rightarrow HCOO^-_{(aq)} + K^+_{(aq)}$$

vi. The K^+ ions of salt have no tendency to react with OH^- ions of water since the possible product of the reaction is KOH, a strong electrolyte.

vii. On the other hand, the reaction of $HCOO^-$ ions of salt with the H_3O^+ ions from water produces unionized HCCOH.

$$HCOO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HCOOH_{(aq)} + OH^-_{(aq)}$$

Thus, the hydrolytic equilibrium for HCOOK is,

$$HCOOK_{(aq)} + H_2O_{(l)} \rightleftharpoons HCOOH_{(aq)}$$

$$+ K^{+}_{(aq)} + OH^{-}_{(aq)}$$

viii. As a result of excess OH^- ions produced, the resulting solution of HCOOK becomes basic.

Q.43 Aqueous solution of sodium carbonate is alkaline whereas aqueous solution of ammonium chloride is acidic. Explain.

Ans :

i. Sodium carbonate (Na_2CO_3) is a salt of weak acid H_2CO_3 and strong base NaOH. It dissociates completely in water

$$Na_2CO_{3\,(aq)} \rightarrow 2Na^{+}_{(aq)} + CO_{3\,(aq)}^{2-}$$

ii. The Na^+ ion of salt have no tendency to react with OH^- ion at water because the possible product of the reaction is NaOH, which is a strong electrolyte.

iii. Whereas, the reaction of CO_3^{2-} ions of salt with H_3O^+ ion of water produce unionized H_2CO_3.

$$CO_{3\,(aq)}^{2-} + 2H_2O_{(2)} \rightleftharpoons H_2CO_{3\,(aq)} + 2OH^{-}_{(aq)}$$

iv. Thus, the hydrolytic equilibrium for Na_2CO_3 is

$$Na_2CO_{3\,(aq)} + H_2O_{(2)} \rightleftharpoons H_2CO_{3\,(aq)} + 2Na^{+}_{(aq)} + 2OH^{-}_{(aq)}$$

v. As a result, excess of OH– ions are produced, the resulting solution of Na_2CO_3 is alkaline.

vi. Similarly, ammonium chloride (NH_4Cl) is a salt of strong acid HCl and weak base NH_4OH. When NH_4OH is dissolved in water. It dissociates completely.

$$NH_4CO_{(aq)} \rightarrow NH^{+}_{4\,(aq)} + Cl^{-}_{(aq)}$$

vii. $Cl^-_{(aq)}$ ion have no tendency to react with water because me possible product is HCl which is a strong electrolyte.

viii. The NH_4^+ ion of salt reacts with OH^- ions and forms unionized NH_4OH. The hydrolytic equilibrium for NH_4Cl is written as

$$NH_4{}^{+}{}_{(aq)} + 2H_2O_{(2)} \rightleftharpoons NH_4OH_{(aq)} + H_3O + (aq)$$

Q.44 Explain hydrolysis of salt of weak acid and weak base.

Ans :

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

$BA_{(aq)} \rightarrow B^{+}{}_{(aq)} + A^{-}(aq)$

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

$$B^{+}{}_{(aq)} + A^{+}{}_{(aq)} + H_2O \rightleftharpoons \underset{\text{(weak base)}}{BOH} + \underset{\text{(weak acid)}}{HA}$$

iii. 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.

Q.45 Explain: Solution of NH_4F turns blue litmus red.

Ans :

i. NH_4F is a salt of weak acid HF ($K_a = 7.2 \times 10^{-4}$) and weak base NH_4OH ($K_b = 1.8 \times 10^{-5}$).

ii. Here, K_a is greater than K_b. The salt hydrolyses as

$$NH_4{}^{+}{}_{(aq)} + F^{-}{}_{(aq)} + H_2O \rightleftharpoons \underset{\text{(weak base)}}{NH_4OH_{(aq)}} + \underset{\text{(weak acid)}}{HF_{(aq)}}$$

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

$$NH_4{}^{+}{}_{(aq)} + 2H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H_3O^{+}{}_{(aq)} \quad ...(i)$$

$$F^{-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons HF_{(aq)} + OH^{-}{}_{(aq)} \quad ...(ii)$$

iv. The NH_4^+ ions hydrolyse to a slightly greater extent than the F^- ions. That means the reaction produces more H_3O^+ ions than the OH^- ions produced in reaction.

v. In other words, NH_4^+ ions are slightly stronger as acid than F^- ions as base.

vi. The solution of NH_4F is thus only slightly acidic and turns blue litmus red.

Q.46 Explain: Solution of NH_4CN turns red litmus red.

Ans :

i. 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

$$NH_4^+{}_{(aq)} + CN^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons \underset{\text{(weak base)}}{NH_4OH_{(aq)}} + \underset{\text{(weak acid)}}{HCN_{(aq)}}$$

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

$$NH_4^+{}_{(aq)} + H_2O_{(l)} + \rightleftharpoons NH_4OH_{(aq)} + H_2O^+{}_{(aq)} \quad ..(i)$$

$$CN^-{}_{(aq)} + H_2O^-{}_{(l)} \rightleftharpoons HCN_{(aq)} + OH_{(aq)} \quad ..(ii)$$

The CN^- ions hydrolyse to a greater extent than NH_4^+ ions, The reaction (ii) produces more OH^- ions than the H_3O^+ ions produced in reaction (i). The solution of NH_4CN is, basic and turns red litmus blue.

Q.47 Explain: Hydrolysis of salt of weak acid and weak base for which $K_a = K_b$.

Ans :

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

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

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

$$CH_3COO^-{}_{(aq)} + NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons \underset{\text{(weak acid)}}{CH_3COOH_{(aq)}} + \underset{\text{(weak base)}}{NH_4OH_{(aq)}}$$

The ions of the salt react with water as

i. $$CH_3COO^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-{}_{(aq)}$$

ii. $$NH_4^+{}_{(aq)} + 2H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H_3O^+{}_{(aq)}$$

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^+ produces as many H_3O^+ ions as that of CH_3COO^- produces OH^- ions.

★ Q.48 What is meant by hydrolysis? A solution of CH_3COONH_4 is neutral. Why?

Ans :

i. Hydrolysis of salt is defined as the reaction in which cations or anions or both ions of a salt reacts with ions of water to produce acidity or alkalinity (or sometimes even neutrality).

Refer Q.47.

3.8 Buffer solutions

Q.49 Define buffer solutions.

Ans : 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.

+50 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?

Ans : Sodium benzoate inhibits the growth of potentially harmful bacteria, mold and other microbes in food.

Q.51 What is an acidic buffer solution? Give Henderson Hasselbalch equation to calculate pH of acidic buffer solution?

Ans :

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

ii. 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

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

where $pK_a = -\log_{10}K_a$

and K_a is the dissociation constant of the acid.

Q.52 What is an basic buffer solution?

Ans :

i. **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,

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

where $pK_b = -\log_{10}K_b$ and

K_b is the dissociation constant for the base.

Q.53 How are basic buffer solutions prepared?

Ans : Basic buffer solutions are prepared by mixing aqueous solutions of a weak base and its salt with strong acid.

★ Q.54 Classify the following buffers into different types:

i. $CH_3COOH + CH_3COONa$

ii. $NH_4OH + NH_4Cl$

iii. Sodium benzoate + benzoic acid

iv. $Cu(OH)_2 + CuCl_2$

Ans :

	Buffer	Type
i.	$CH_3COOH + CH_3COONa$	Acidic buffer
ii.	$NH_4OH + NH_4Cl$	Basic buffer
iii.	Sodium benzoate + benzoic acid	Acidic buffer
iv	$Cu(OH)_2 + CuCl_2$	Basic buffer

Q.55 Explain buffer action with the help of an example.

Ans :

i. Consider sodium acetate - acetic acid buffer.

ii. Here sodium acetate is a strong electrolyte which dissociates completely in water producing large concentration of CH_3COO as follows:

$$CH_3COONa_{(aq)} \rightarrow CH_3COO_{(aq)} + Na^+_{(aq)}$$

iii. On the other hand since the acetic acid is a weak acid, the concentration of undissociated CH_3COOH molecules is usually high.

iv. If a strong acid is added to this solution the added H^+ ions will be consumed by the conjugate base CH_3COO^- present in large concentration.

v. Similarly, if small amount of base is added, the added OH ions will be neutralized by the large concentration of acetic acid as shown in the following reactions:

$$\underset{\text{(large concentraion)}}{CH_3COO^-_{(aq)}} + \underset{\text{(added acid)}}{H^+_{(aq)}} \rightarrow CH_3COOH_{(aq)}$$

$$\underset{\text{(large concentraion)}}{CH_3COOH_{(aq)}} + \underset{\text{(added acid)}}{OH^-_{(aq)}} \rightarrow CH_3COO^-_{(aq)} + H_2O_{(l)}$$

vi. The acid or base added thus can not change the $[H^+]$ or $[OH^-]$ concentrations and, pH of the buffer remains unchanged.

vii. Dilution does not have any effect on pH of buffer.

viii. This is because the concentration ratio term in Henderson Hasselbalch equation and remains the same. The dilution does not change this ratio.

Q.56 Give the properties of buffer solution.

Ans : 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.

★ Q.57 Write one property of a buffer solution.

Ans : The pH of a buffer solution does not change even if it is kept for a long time.

+Q.58 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?

Ans : Yes, it is enough to add a few mL of a buffer solution to maintain its pH. The pH of a buffer solution is independent of the volume of the solution.

Q.59 Mention the application of buffer solution.

Ans :

i. 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

($HCO_3^- + H_2CO_3$) 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.

Type-3

Numericals based on pH of buffer solution

+Q.1 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

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

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

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

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

Substitution in the above equation gives

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

$= 3.1427 + \log 3.33$

$= 3.1427 + 0.5224 = 3.6651 \approx 3.67.$

+Q.2 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

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

$pK_b = -\log_{10} K_b$

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

$= 5 - 0.2553 = 4.7447$

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

substitution of these in the above equation gives

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

$= 4.7447 + 0.3010 = 5.0457$

$pH = 14 - \text{pOH} \quad = 14 - 5.0457$

$= 13.9543 \approx 13.95$

3.9 Solubility product

+60 Can you recall ?

i. What is solubility of a compound ?

Ans : Solubility is the relative ability of a solute to dissolve into a solvent.

ii. What is saturated solution ?

Ans : A saturated solution is a solution in which there is no much solute that if there was any more, it would not dissolve.

iii. What is meant by the sparingly soluble salt ?

Ans : Sparingly soluble salts are those salts whose solubility is very low.

Q.61 Explain solubility product with the help of a suitable example.

Ans :

i. 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.

ii. 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^+ and Cl^-.

iii. A dynamic equilibrium exists between undissolved solid AgCl and the dissolved ions, Ag^+ and Cl^-, in the saturated solution.

iv. This equilibrium, called solubility equilibrium, is represented as :

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

The expression for its equilibrium constant is:

$$K = \frac{[Ag^+][Cl^-]}{K'} \quad ...(i)$$

The concentration of undissolved solid AgCl is constant we may write

[AgCl] = constant = K'

Substituting in Eq. (i) we write

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

$$K \times K' = [Ag^+][Cl^-]$$

The product of K × 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}.

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

For the general salt solubility equilibrium

$$B_xA_{y\,(s)} \text{ -- } xB^{y+}_{(aq)} + yA^{x-}_{(aq)}$$

The solubility product is

$$K_{sp} = [B^{y+}]^x[A^{x-}]^y \quad ...(ii)$$

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.

Q.61 Give the K_{sp} expression for the following salts.

i. $BaSO_4$ **ii. Bi_2S_3**

iii. CaF_2 **iv. $Ca_3(PO_4)_2$**

Ans :

Salt	Solubility equilibrium	K_{sp} Expression
$BaSO_4$	$BaSO_{4(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4\,(aq)}$	$K_{sp} = [Ba^{2+}][SO_4^{2-}]$
Bi_2S_3	$Bi_2S_{3(s)} \rightleftharpoons 2Bi^{3+}_{(aq)} + 3S^{2-}_{(aq)}$	$K_{(sp)} = [Bi^{3+}]^2[S^{2-}]^3$
CaF_2	$CaF_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2F^-_{(aq)}$	$K_{(sp)} = [Ca^{2+}][F^-]^2$
$Ca_3(PO_4)_{2(s)}$	$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4\,(aq)}$	$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$

Q.62 What is solubility product?

Ans : 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).

Q.63 What is molar solubility?

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

molar solubility (mol/L)

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

Q.64 Derive the relationship between solubility and solubility product.

Ans :

Consider once again the solubility equilibrium for B_xA_y,

$$B_xA_{y\,(s)} \rightleftharpoons xB^{y+}_{(aq)} + yA^{x-}_{(aq)}$$

The solubility product is given as

$$K_{sp} = [B^{y+}]^x[A^{x-}]^y \quad ...(i)$$

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

$[B^{y+}]$ = xS mol/L

$[A^{x-}]$ = xS mol/L

From Eq. (i)

$K_{sp} = [xS]^x[yS]^y = x^xy^yS^{x+y}$

Q.65 What is the relationship between molar solubility and solubility product for salts given below.

i. $AgCrO_3$ **ii. $Ca_3(PO_4)_2$**

iii. $Cr(OH)_3$

Ans : i. For AgBr,

$$AgBr_{(s)} \rightleftharpoons Ag^+_{(aq)} + Br^-_{(aq)}$$

Here, x = 1, y = 1

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

ii. For PbI_2,

$$PbI_{2(s)} \text{ -- } Pb^{2+}_{(aq)} + 2I^-_{(aq)}$$

Here, x = 1, y = 2

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

iii. $Al(OH)_3$,

$$Al(OH)_{3(s)} \text{ -- } Al3^+_{(aq)} + 3OH^-_{(aq)}$$

Here, x = 1, y = 3

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

Q.66 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. $Cr(OH)_3$

Ans :

i. For Ag_2Br_4,

$$Ag_2CrO_{4(s)} \rightleftharpoons 2Ag^{+}_{(aq)} + CrO^{2-}_{4(aq)}$$

Here, x = 2, y = 1

$K_{sp} = x^x y^y S^{x+y} = (2)^2 (1)^1 S^{2+1} = 4S^3$

ii. For $Ca_3(PO_4)_2$,

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3CA^{2+}_{(aq)} + 2PO^{3-}_{4(aq)}$$

Here, x = 3, y = 2

$K_{sp} = x^x y^y S^{x+y} = (3)^3 (2)^2 S^{3+2}$

$= 27 \times 4 \times S^5 = 108S^5$

iii. For $Cr(OH)_3$,

$$Cr(OH)_{3(s)} \rightleftharpoons Cr^{3+}_{(aq)} + 3OH^{-}_{(aq)}$$

Here, x = 1, y = 3

$K_{sp} = x^x y^y S^{x+y} = (1)^2 (3)^3 S^{1+3}$

$= 1 \times 27 \times S^4 = 27S^4$

★Q.67 Explain the relation between ionic product and solubility product to predict whether a precipitate will form when two solutions are mixed?

Ans :

i. Ionic product (IP) of an electrolyte is defined in the same way as solubility product (K_{sp}).

ii. 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.

Type-4

Numericals based on Solubility product

+Q.1 A solution is prepared by mixing equal volumes of 0.1 M $MgCl_2$ and 0.3 M $Na_2C_2O_4$ 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,

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

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

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

$$Mg^{2+}(aq) + C_2O^{2-}_{4\,(aq)} \rightleftharpoons MgC_2O_{4(s)}$$

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.

+Q.2 If 20.0 cm^3 of 0.050 M $Ba(NO_3)_2$ are mixed with 20.0 cm^3 if 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

$20 + 20 = 40\ cm^3$

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

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

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

Therefore $[Ba^{2+}] = 0.025$ and

$[F^-] = 0.010$ M

Hence ionic product of BaF_2 is

$IP = [Ba^{2+}]\ [F^-]^2$

$= 0.025 \times (0.01)^2$

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

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

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

+Q.3 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 :

$$AgBr_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Br^{-}_{(aq)}$$

x = 1, y = 1

$K_{sp} = [Ag^+][Br^-] = S^2$

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

$= 7.2 \times 10^{-7}$ 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}

3.10 Common ion effect

Q.68 Explain common ion effect using an example.

Ans :

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

ii. CH_3COOH is weak acid, dissociates only slightly in solution

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

iii. CH_3COONa being a strong electrolyte dissociates almost completely in solution.

$$CH_3COONa_{(aq)} \rightarrow CH_3COO + Na^+$$

iv. Both the acid and the salt produce CH_3COO ions in solution. CH_3COONa dissociates completely.

v. Therefore it provides high concentration of CH_3COO ions.

vi. According to Le-Chatelier principle, the addition of CH_3COO from CH_3COONa to the solution of CH_3COOH, shifts equilibrium of dissociation of CH_3COOH to left.

vii. Thus reverse reaction is favoured in which CH_3COO combines with H^+ to form unionised CH_3COOH.

viii. Hence dissociation of CH_3COOH is supressed due to presence of CH_3COONa containing a common CH_3COO 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.

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

Ans :

i. NH_4OH is a weak electrolyte. It will dissociates only slightly in solution.

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

ii. NH_4Cl being a strong electrolyte dissociates almost completely in solution.

$$NH_4Cl_{(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-_{(aq)}$$

iii. Both acids and the salt produce NH_4^+ ions in the solution. NH_4Cl dissociates completely. Therefore it provides high concentration of NH_4^+ ions.

iv. According to Le-Chatelier principle, the addition of NH_4^+ from NH_4Cl to the solution of NH_4OH, shifts equilibrium of dissociation of NH_4OH to left.

v. Thus reverse reaction is favoured in which NH_4^+ combines with OH^- to form unionized NH_4OH.

vi. Hence dissociation of NH_4OH is suppressed due to presence of NH_4Cl containing a common NH_4^+ ion.

★ Q.70 The dissociation of H_2S is suppressed in the presence of HCl. Name the phenomenon.

Ans : Due to common ion effect the dissociation of H_2S is suppressed in the presence of HCl is known as common ion effect.

★ Q.71 Dissociation of HCN is suppressed by the addition of HCl. Explain.

Ans :

i. HCN is a weak elecrolyte, it dissociates only slightly in solution.

$$HCN_{(aq)} \rightleftharpoons H^+_{(aq)} + CN^-$$

ii. HCl being a strong electrolyte dissociates almost completely in solution.

iii. HCN and HCL both dissociate to produce H^+

ion which are common to both.

iv. The concentration of H^+ ion in the solution increases due to the complete dissociation of HCl.

v. According to Le-Chatelier's principle, the addition of H^+ ions from HCl shifts equilibrium of dissociation of HCN to the left.

vi. H^+ ion combines with CN^- ions to produce unionized HCN. Thus, the dissociation of HCN is suppressed by the addition of HCl.

★ Q.72 Solubility of sparingly soluble salt get effected in presence of a soluble salt having one common ion. Explain.

Ans :

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

$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl_{(aq)}$

The solubility product of AgCl is

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

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

$AgNO_{3(aq)}$ -- $Ag^+_{(aq)} + NO_{3(aq)}$

The dissociation of AgCl and $AgNO_3$ produce a common Ag^+ ion. The concentration of Ag^+ ion in the solution increases owing to complete dissociation of $AgNO_3$.

According to Le-chatelier's principle the addition of Ag^+ 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.

★ Q.73 Sulphides of cation of group II are precipitated in acidic solution (H_2S + HCl) whereas sulphides of cations of group IIIB are precipited in ammoiacal solution of H_2S. Comment on the relative values of the solubility product of sulfides of these.

Ans :

i. Group II and group III B cations are precipitated as their sulphides.

ii. However, the solubility product of sulphids of group II cations is lower than group III B cations.

iii. Therefore, for the precipitation of cation of group II, only a small concentration of sulphide ion is required.

iv. This is achieved by passing H_2 gas in the presence of strong electrolyte HCl, which has a common ion (H^+) with H_2S.

v. Due to the common ion effect, the dissociation of H_2S is suppressed and thus, the concentration of S^{2-} ions decreases.

vi. This results only in the precipitation of sulphides of group II while sulphides of the higher group remain in as solution as they require a higher concentration of S^{2-} ions for precipitation.

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