SOCH BADLO BY MAK

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12TH GRADE CHEMISTRY

Chapter-3
CHEMICAL EQUILIBRIAM

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1. STRENGTH OF ACID:

Acid: The ability of a substance to donate protons is called **"Acid"**.

Strength of Acid: The degree to which different Bronsted acids give off protons is called "**strength of acid**".

Strong and weak acids: "**Strong acids**" are acids that completely ionize in water. **For Example:** Hydrochloric acid (HCl),Sulfuric acid (H_2SO_4), Nitric acid (HNO_3).

"**Weak acids**" are acids that partially ionize in water. **For Example:** Acetic acid (CH_3COOH), Carbonic acid (H_2CO_3), Citric acid ($C_6H_8O_7$).

Acid dissociation constant (Ka): The strength of acid is generally expressed in terms of **acid ionization constant (Ka).**

$$\textbf{Acid Strength} \propto \textbf{Ka}$$

- The greater the Ka, the stronger the acid.
- The smaller the Ka, the weaker the acid.

Consider the case of ionization of a general acid (HX) in water.

Reaction : $HX + H_2O \rightleftharpoons H_3O^+ + X^-$

The equilibrium constant K for this ionization process maybe written as:

$$K = \frac{[H3O^+]\,[X^-]}{[HX]\,[H2O]}$$

$$K\times[H_2O] = \frac{[H3O^{+}]\,[X^{-}]}{[HX]}$$

$$K_a = \frac{[H3O^{+}]\,[X^{-}]}{[HX]} \qquad \because K[H_2O] = K_a$$

Ka depends on temperature, For Example: **acetic acid** Ka=1.8×10^{-5} at 25°C

Definition of Ka:

- Ka is called the acid dissociation constant.
- It tells how much the acid ionizes in water at equilibrium.
- Higher Ka → stronger acid
- Lower Ka → weaker acid

⋆ Ka is usually inconvenient numbers, therefore, for convenience, these values are converted into **pK_a values**.

Relationship between K_a and pK_a:

$$pK_a = -\log K_a$$

Since pK_a refers to negative logarithm of K_a, so:

- smaller the value of pK_a = greater the value of K_a ⇒ Acid stronger.
- greater the value of pK_a = smaller the value of K_a ⇒ Acid weaker.

$$Ka \propto \frac{1}{pKa}$$

2. **STRENGTH OF BASE:**

Base: The ability of substance to accept the proton is called base.

Strength of base: The ability to accept proton from a solvent (usually water) is called **"strength of base"**

Strong and weak bases: **"Strong base"** is a base that completely dissociates in water to give hydroxide ions (OH^-). **For Example:** Sodium hydroxide (NaOH), Potassium hydroxide (KOH), Calcium hydroxide ($Ca(OH)_2$).

"Weak base" is a base that partially dissociates in water and gives fewer OH^- ions**. For Example:** Ammonia (NH_3), Magnesium hydroxide ($Mg(OH)_2$), Aluminium hydroxide ($Al(OH)_3$).

Base dissociation constant (Kb): The strength of base is generally expressed in terms of **base ionization constant (Kb).**

Base Strength $\propto$ Kb

- The greater the Kb, the stronger the base.
- The smaller the Kb, the weaker the base.

For a base B, an equilibrium reaction with water can be represented by the equation: $B + H_2O \rightleftharpoons BH^+ + OH^-$

$$Kc = \frac{[BH^+][OH^-]}{[B][H2O]}$$

$$Kc \times H_2O = \frac{[BH^+][OH^-]}{[B]}$$

$$Kb = \frac{[BH^+][OH^-]}{[B]} \qquad \because Kc[H_2O] = Kb$$

Definition of Kb:

- Kb is called base dissociation constant.
- it tells us how strongly a base ionizes (forms OH^- ions) in water.
- Strong Base → High Kb value
- Weak Base → Low Kb value

⋆ For convenience a parameter **pKb** has been devised to express the Kb value in convenient numbers.

Relationship between Kb and pKb:

pKb = – log Kb

$$\boxed{Kb \propto \frac{1}{pKb}}$$

Since pKb refers to negative logarithm of Kb, so:

- smaller the value of pKb = greater the value of Kb ⇒ Stronger base
- greater the value of pKb = smaller the value of Kb ⇒ weaker base

3. BUFFER SOLUTION:

"A solution in which there is no change in pH by adding a small amount of acid, base or dilution is added into it keeping it constant for a long time is known as buffer solution."

Importance of Buffer solution:

- Used to calibrate the pH meter.
- Biological catalyst enzymes are pH dependent, if we add acid or base with enzymes it deactivates then a buffer is used.

Types of buffer solution:

There are two types of buffer solution:

1. Acidic buffer : Mixture of weak acid and it's salt with strong base is called acidic buffer.

- Such solutions give pH less than 7.

For Example: $\underset{\text{Weak acid}}{CH_3COOH} + \underset{\text{Strong base}}{NaOH} \rightarrow \underset{\text{salt}}{CH_3COONa} + H_2O$

Acidic Buffer→ $CH_3COOH + CH_3COONa$ (weak acid + salt)

2. Basic buffer: Mixture of weak base and it's salt with strong acid is called basic buffer.

- Such solutions give pH more than 7.

For Example: $\underset{\text{Weak base}}{NH_4OH} + \underset{\text{Strong acid}}{HCl} \rightarrow \underset{\text{salt}}{NH_4Cl} + H_2O$

Basic Buffer → $NH_4OH + NH_4Cl$ (weak base + salt)

Buffer Action: Method by which a buffer can maintain it's pH is called buffer action.

Components of Buffer:

- CH_3COOH (weak acid)
- CH_3COONa (salt of the weak acid).

By Common ion effect:

- $CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$ (complete dissociation)
- $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ (partial dissociation)
- Extra CH_3COO^- from salt suppresses ionization of CH_3COOH.

(i) Addition of HCl (strong acid):

- $HCl \rightarrow H^+ + Cl^-$
- $H^+ + CH_3COO^- \rightarrow CH_3COOH$
- As H^+ does not exist in free form in solution it reacts with CH_3COO^- ion and

forms CH_3COOH which does not ionize to a greater extent so pH has negligible change.

(ii) Addition of NaOH (strong base):

- $NaOH \rightarrow Na^+ + OH^-$
- $OH^- + H^+ \rightarrow H_2O$
- $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ (to replace H^+)
- When base is added to OH^- from base combines with H^+ of buffer form water and it's weak electrolyte and doesn't produce H^+.

<u>Calculation of pH of Buffer Solution:</u>

Conjugate Base Supply:

- The salt (e.g., CH_3COONa) is a strong electrolyte.
- It fully dissociates to give the conjugate base (CH_3COO^-).

Concentration Assumption:

- Concentration of conjugate base ≈ concentration of salt
- Concentration of acid remains approx. equal to its initial value (CH_3COOH ≈ original [acid]).

pH Calculation:

Use the **Henderson-Hasselbalch** Equation:

$$\mathbf{pH = pKa + \log\left(\frac{[Salt]}{[Acid]}\right)}$$

Example – 3.2

(a) Calculate the pH of an acetic acid-sodium acetate buffer solution containing 1.0 moles of each component.

(b) What will be the pH of this solution after the addition of 0.01 mole of hydrochloric acid (HCl) to 1 dm^3 of the solution? Assume that the volume of the solution remains unchanged with the addition of hydrochloric acid. (Ka for acetic acid = 1.8×10^{-5}).

Solution: **(a) The pH of the buffer solution can be calculated by assuming the equilibrium concentration of the acid and its conjugate base as the starting concentration.**

Thus, $[CH_3COOH] = 1.0M$ $[CH_3COO^-] = 1.0M$

For acetic acid dissociation:

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$Ka = \frac{[CH3COO^-][H^+]}{[CH3COOH]} \qquad \because Ka = 1.8 \times 10^{-5}$$

$$1.8 \times 10^{-5} = \frac{1M\,[H]^+}{1M} \qquad \text{(1M will be cancelled)}$$

$[H^+] = 1.8 \times 10^{-5}$

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

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

$pH = 4.745$

Thus, the pH of the buffer solution is 4.76.

(b) *After HCl addition:*

$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

0.01 mole 0.01 mole 0.01 mole

Initially, there were 1.0 mole of CH_3COOH and 1.0 mole of CH_3COO^- present per dm^3 of the solution.

After the addition of HCl, 0.01 mole of CH_3COO^- ions is combined with the H^+ ions formed from the dissociation of 0.01 mole of added HCl. This can be written as:

$CH_3COO^- + H^+ \rightarrow CH_3COOH$

0.01 mole 0.01 mole 0.01 mole

Thus, the numbers of moles of salt and acetate ions, after the addition of HCl are:

$CH_3COOH = (1.0 + 0.01)$ mole = 1.01 mole

$CH_3COO^- = (1.0 - 0.01)$ mole = 0.99 mole

The equilibrium expression for the new solution can be written as:

$$Ka = \frac{[H^+][CH3COO^-]}{[CH3COOH]}$$

$$[H^+] = \frac{Ka\,[CH3COO^-]}{[CH3COOH]}$$

$$[H^+] = \frac{1.8 \times 10^{-5}\,[1.01M]}{[0.99M]}$$

$[H^+] = 1.83 \times 10^{-5}$

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

$pH = -\log (1.836 \times 10^{-5})$

$pH = 4.736$

Notice:

There is a slight change in pH from 4.76 to 4.736 which is only a difference of 0.009. Thus, a buffer does its job by limiting the change in pH to a very small amount.

<u>Applications of buffer solution:</u>

1. Buffer System in Blood Plasma

- The bicarbonate buffer system maintains blood pH between 7.35 – 7.45.
- pH below 6.8 or above 7.8 can cause death.

Main Reactions:

(a) Formation of carbonic acid:

$CO_2 + H_2O \rightleftharpoons H_2CO_3$

(b) Dissociation of carbonic acid:

$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$

- These reactions are catalyzed by the enzyme carbonic anhydrase (present in red blood cells).
- The system maintains a balance between CO_2, H_2CO_3, HCO_3^-, and H^+ in the blood.

Neutralization of Acids:

When excess H^+ (acid) is present:

$HCO_3^- + H^+ \rightarrow H_2CO_3$

Neutralizes extra acidity.

Neutralization of Bases:

When excess OH^- (base) is present:

$OH^- + H_2CO_3 \rightarrow HCO_3^- + H_2O$

Neutralizes extra base.

Importance:

- Maintains stable pH in blood.
- Supports enzyme activity and other biological functions.
- Regulated by both the respiratory and renal systems.

2. Household Cleaning Products:

- Detergents and cleaners contain buffers to maintain a stable pH.
- Ensures effective cleaning without damaging surfaces or skin.

3. Personal Care Products

- Shampoos and soaps use buffers to keep pH skin-friendly.
- Helps prevent irritation and keeps the product gentle.

4. Swimming Pools

- Buffers help maintain stable pH of pool water.
- Prevents corrosion of pool equipment and ensures swimmer comfort.

5. Food and Beverage Industry

(a) Food Preservation:

Buffers control acidity and maintain flavour & stability in food products.

(b) Beverage Production:

Used to maintain consistent taste and prevent spoilage by stabilizing pH.

6. Photography

- Photographic developer solutions contain buffers.
- Maintain stable pH for consistent film/print development.

4. SOLUBILITY PRODUCT AND PRECIPITATION REACTION.

SOLUBILITY PRODUCT: Product of molar concentration of opposite charge ion in equilibrium with solid state is called solubility product.

When an excess of slightly soluble ionic compound is mixed with water:

- Some dissolve.
- Rest stays undissolved at the bottom.
- A **dynamic equilibrium** is established between undissolved solid and dissolved ions.

Example:

When **CaF_2** is mixed with water:

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

Equilibrium Constant Expression:

$$Kc = \frac{[Ca^{+2}][F]^{-2}}{[CaF2]}$$

$Kc[CaF_2] = [Ca^{2+}][F^{-}]^2$ $\because Kc[CaF_2] = Ksp$

But since CaF_2 is a solid (and slightly soluble), its concentration is **constant**.

So we define a new constant:

Ksp (Solubility Product Constant)

$Ksp = [Ca^{2+}][F^-]^2$

Definition of Ksp:

Ksp is the **product of the equilibrium concentrations of** ions, each raised to the power of their coefficients in the balanced equation.

For a general salt:

A☒B☒$_{(s)}$ $\rightleftharpoons$ **m**$\mathbf{A^{n+}}$ **+ n**$\mathbf{B^{m-}}$

$Ksp = [A^{n+}]^m[B^{m-}]^n$

Note: Higher the Ksp → greater the solubility in water.

The value before coefficient will go into the power and outside the bracket. Like :

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

$Ksp = [Ca^{+2}][F^-]^2$

As, Ca has 1 before it so it will be $[Ca^{+2}]$ and F has 2 before it so 2 will go into power $[F^-]^2$.

CONCEPT ASSESSMENT – 3.1

Write the dissociation reaction and the solubility product constant expression for each of the following solids:

(a). $PbSO_4$

Dissociation Reaction:

$PbSO_{4(s)} \rightleftharpoons Pb^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

Solubility Product (Ksp) Expression:

$Ksp = [Pb^{+2}][SO_4^{-2}]$

(b). $Al(OH)_3$

Dissociation Reaction:

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

Solubility Product (Ksp) Expression:

$Ksp = [Al^{+3}][OH^-]^3$

(c). $BaSO_4$

Dissociation Reaction:

$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

Solubility Product (Ksp) Expression:

Ksp = $[Ba^{+2}][SO_4^{-2}]$

CALCULATING CONCENTRATIONS OF IONS:

Given:

Ksp for AgBr = 1.60×10^{-10}

Step-by-Step Calculation:

1. Write the dissociation equation:

$AgBr \rightleftharpoons Ag^+ + Br^-$

2. Let x = solubility of AgBr, Then:

$[Ag^+] = x$, $[Br^-] = x$

3. Ksp Expression:

Ksp = $[Ag^+][Br^-]$

$1.60 \times 10^{-10} = x \times x = x^2$

4. Solve for x:

$x^2 = 1.60 \times 10^{-10}$

$x = \sqrt{(1.60 \times 10^{-10})}$

$x = 1.26 \times 10^{-5}$ M

So, $[Ag^+] = [Br^-] = 1.26 \times 10^{-5}$ M

Steps to Calculate Ion Concentration using Ksp:

1. Write the dissociation equation for the salt.
2. Set up the Ksp expression.
3. Solve for ion concentrations using stoichiometry.

CONCEPT ASSESSMENT – 3.2

Q.1) Ksp for PbF_2 is 4×10^{-8}. Calculate the concentration Pb^{+2} and F^- ions in solution.

dissociation equation :

$\mathbf{PbF_{2(s)} \rightleftharpoons Pb^{2+}{}_{(aq)} + 2F^-{}_{(aq)}}$

Let the solubility of PbF_2 be = **x mol/dm³**

Then at equilibrium:

→ $[Pb^{2+}]$ = **x**

→ $[F^-]$ = **2x**

Write the Ksp expression

$Ksp = [Pb^{+2}][F^{-}]^{2}$

Calculation:

$Ksp = (x)^{1}(2x)^{2}$

$Ksp = 4x^{3}$ $\because Ksp = 4 \times 10^{-8}$

$4 \times 10^{-8} = 4x^{3}$

Dividing both sides by 4

$\frac{4}{4} \times 10^{-8} = \frac{4}{4} x^{3}$

$1 \times 10^{-8} = x^{3}$

Taking cube root on both sides

$\sqrt[3]{1 \times 10^{-8}} = \sqrt[3]{x^{3}}$

$(1 \times 10^{-8})^{1/3} = x$

$X = 2.5 \times 10^{-3}$ mol/dm³

$[Pb^{2+}] = 2.5 \times 10^{-3}$ mol/dm³

$[F^{-}] = 2x = 2(2.5 \times 10^{-3})$

$[F^{-}] = 4.3 \times 10^{-3}$ mol/dm³

Q2: Ksp for $BaSO_4$ is 1×10^{-10}. Write the equation and equilibrium expression for the dissolving of barium sulfate. Also calculate the concentration of each ion.

Dissociation equation

$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

Let solubility = **x mol/dm³**

Then:

→ $[Ba^{2+}]$ = **x**

→ $[SO_4^{2-}]$ = **x**

Ksp expression:

$Ksp=[Ba^{2+}][SO4^{2-}]$

Calculation :

$Ksp = [Ba^{2+}][SO4^{2-}]$

Ksp = x.x

$Ksp = x^2$ $\quad\because Ksp = 1\times 10^{-10}$

$1 \times 10^{-10} = x^2$

Taking square root on both sides:

$$\sqrt{1 \times 10^{-10}} = \sqrt{x^2}$$

$X = 1 \times 10^{-5}$

$[Ba^{2+}] = [SO_4^{2-}] = 1 \times 10^{-5}$ mol/dm^3

5. **COMMON ION EFFECT:**

"Decrease in solubility or ionization of an electrolyte by the addition of another strong electrolyte having a common ion is called **Common Ion Effect**."

- It occurs due to **Le Chatelier's Principle.**
- The equilibrium shifts backward (left) to reduce the effect of added common ions.

Explanation:

- A **weak electrolyte** dissociates partially.
- A **strong electrolyte** dissociates completely.
- When both are in solution, the **common ion from the strong electrolyte** increases.
- This **suppresses the ionization** of the weak electrolyte.

EXAMPLES:

1). Hydrofluoric Acid (HF) + Sodium Fluoride (NaF)

Equilibrium:

$HF \rightleftharpoons H^+ + F^-$ *(weak electrolyte)*

$NaF \rightarrow Na^+ + F^-$ *(strong electrolyte)*

Effect:

- NaF increases F^- in solution
- Equilibrium shifts left → Less HF ionizes

Electrolyte: It is a substance which produces ion/electricity. It has two types:

Strong electrolyte ⇒ has high ionization

Weak electrolyte ⇒ has less ionization.

Non–Electrolyte: It is a substance which doesn't produce ion/electricity

Le Chatelier's Principle:

"If an external change is applied to a system at equilibrium, the system shifts to counteract that change."

So, if a product (ion) increases, the reaction shifts left, reducing ionization.

- [HF] increases, $[H^+]$ and $[F^-]$ decrease from HF

2). NaCl + HCl (Brine + Acid)

Equilibrium Reaction:

- $NaCl \rightleftharpoons Na^+ + Cl^-$ *(weak electrolyte)*
- $HCl \rightarrow H^+ + Cl^-$ *(strong electrolyte)*

Common Ion: Cl^-

Effect:

- HCl adds more Cl^- ions to solution.
- According to Le Chatelier's Principle, equilibrium shifts left.
- NaCl starts to crystallize/precipitate out of the solution.

This method is used to purify NaCl (common salt).

3). NH_4OH + NH_4Cl

Equilibrium Reaction:

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ *(weak electrolyte)*

$NH_4Cl \rightarrow NH_4^+ + Cl^-$ *(strong electrolyte)*

Common Ion: NH_4^+

Effect:

- NH_4Cl increases NH_4^+ ions in solution.
- Equilibrium shifts left, reducing OH^- production.
- So, ionization of NH_4OH decreases.

4). $KClO_4$ + KCl

Equilibrium Reaction:

$KClO_4 \rightleftharpoons K^+ + ClO_4^-$ *(moderately soluble salt)*

$KCl \rightarrow K^+ + Cl^-$ *(highly soluble salt)*

Common Ion: K^+

Effect:

- KCl adds extra K^+ ions.
- Equilibrium shifts left.
- So, $KClO_4$ solubility decreases and it precipitates out.

We can know solubility of salt by using solubility table:

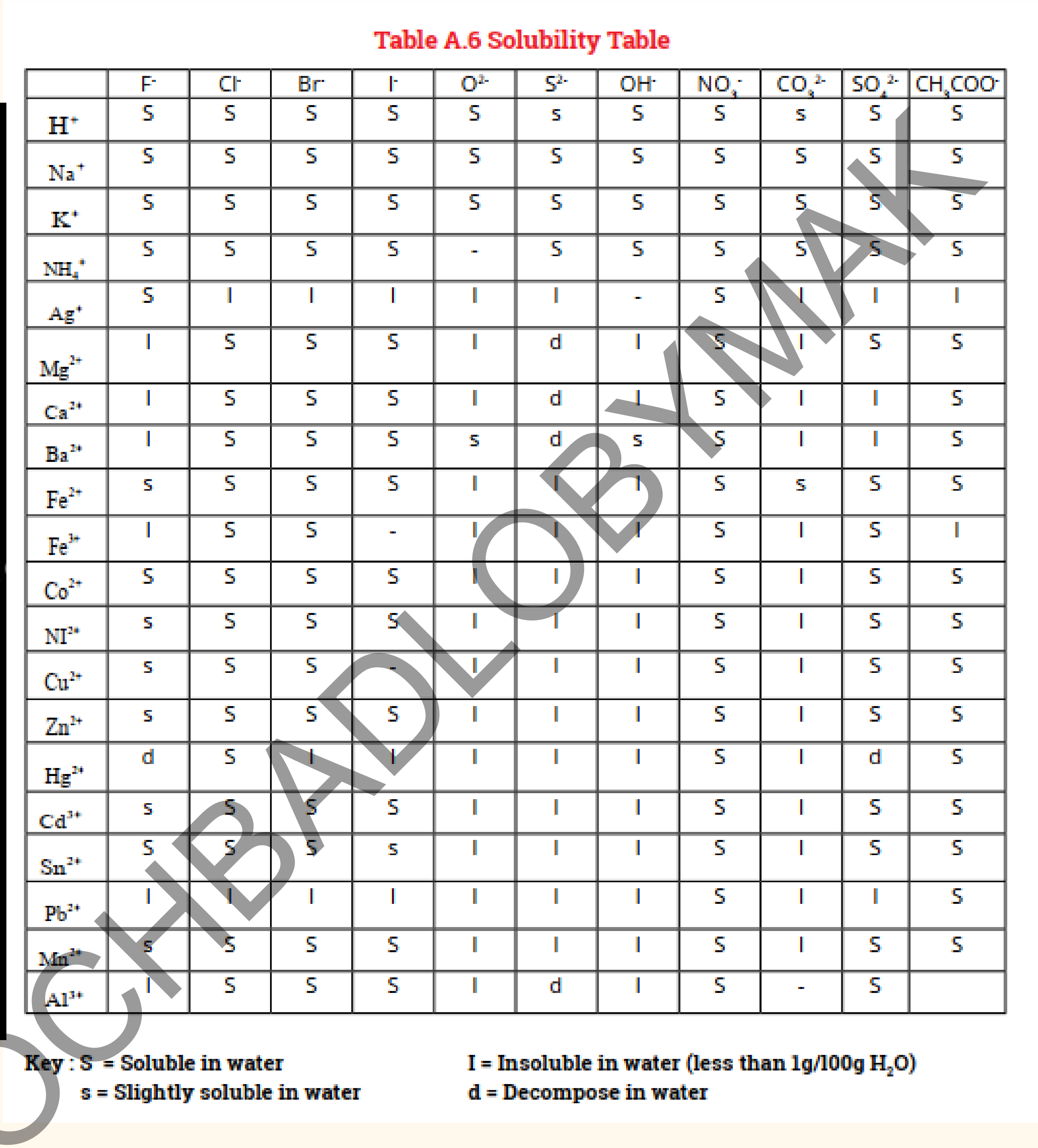


Table A.6 Solubility Table

	F^-	Cl^-	Br^-	I^-	O^{2-}	S^{2-}	OH^-	NO_3^-	CO_3^{2-}	SO_4^{2-}	CH_3COO^-
H^+	S	S	S	S	S	s	S	S	s	S	S
Na^+	S	S	S	S	S	S	S	S	S	S	S
K^+	S	S	S	S	S	S	S	S	S	S	S
NH_4^+	S	S	S	S	-	S	S	S	S	S	S
Ag^+	S	I	I	I	I	I	-	S	I	I	I
Mg^{2+}	I	S	S	S	I	d	I	S	I	S	S
Ca^{2+}	I	S	S	S	I	d	I	S	I	I	S
Ba^{2+}	I	S	S	S	s	d	s	S	I	I	S
Fe^{2+}	s	S	S	S	I	I	I	S	s	S	S
Fe^{3+}	I	S	S	-	I	I	I	S	I	S	I
Co^{2+}	S	S	S	S	I	I	I	S	I	S	S
NI^{2+}	s	S	S	S	I	I	I	S	I	S	S
Cu^{2+}	s	S	S	-	I	I	I	S	I	S	S
Zn^{2+}	s	S	S	S	I	I	I	S	I	S	S
Hg^{2+}	d	S	I	I	I	I	I	S	I	d	S
Cd^{2+}	s	S	S	S	I	I	I	S	I	S	S
Sn^{2+}	S	S	S	s	I	I	I	S	I	S	S
Pb^{2+}	I	I	I	I	I	I	I	S	I	I	S
Mn^{2+}	s	S	S	S	I	I	I	S	I	S	S
Al^{3+}	I	S	S	S	I	d	I	S	-	S	

Key : S = Soluble in water

s = Slightly soluble in water

I = Insoluble in water (less than 1g/100g H_2O)

d = Decompose in water

CONCEPT ASSESSMENT – 3.3

Q1). Ammonium Chloride, NH_4Cl is a water soluble salt. What will happen if this salt is added to a solution containing ammonium hydroxide?

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

Ans). Equilibrium reaction for NH_4Cl:

$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$

Common Ion:

NH_4^+ (comes from both NH_4OH and NH_4Cl)

Effect of Adding NH_4Cl:

- NH_4Cl increases the concentration of NH_4^+ ions in the solution.
- According to Le Chatelier's Principle, equilibrium will shift left to reduce this increase.
- As a result, OH^- ion concentration decreases.
- Ionization of NH_4OH is suppressed → it dissociates even less.

Q2). Carbonic acid is a weak acid. It ionizes in water as follows:

$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{-2}$$

What will happen if a strong electrolyte such as Na_2CO_3 is added to a solution containing carbonic acid?

Ans). Reaction for Na_2CO_3:

$$Na_2CO_3 \rightarrow 2\,Na^+ + CO_3^{2-}$$

Common Ion:

CO_3^{2-} is common between Na_2CO_3 and H_2CO_3 system.

Effect of Adding Na_2CO_3:

- CO_3^{2-} ions increase in the solution.
- According to Le Chatelier's Principle, equilibrium shifts to left to reduce excess CO_3^{2-}.
- Ionization of H_2CO_3 is suppressed.
- Concentration of H^+ ions decreases.
- pH of the solution increases (becomes more basic)
- Carbonic acid becomes even weaker.

6. THE PARTITION COEFFICIENT:

"A ratio that describes how a compound distributes itself between two immiscible solvents, typically oil and water."

Symbolic representation: Kpc

Mathematical representation:

$$\text{Kpc} = \frac{[concentration\ of\ solute\ in\ organic\ layer]}{[concentration\ of\ solute\ in\ aqueous\ layer]}$$

Let solute be X

$$\text{Kpc} = \frac{[X\ in\ ether]}{[X\ in\ water]}$$

X(in water) ⇌ X(in ether)

Equilibrium will be developed.

Conditions for Kpc:

- If X is polar then it will be soluble in aqueous solvent.
- If X is non–polar then it will be soluble in organic solvent.
- If Kpc>1 compound will be more soluble in non-polar solvent.
- If Kpc<1 compound will be more soluble in polar solvent.

Significance of Kpc:

1. Predict drug absorption.
2. Helps in separation technique.
3. Used in environmental chemistry for pollutant distribution.
4. It is temperature dependent,

$$\textbf{Solubility} \propto \textbf{Temperature}$$

(More heat = more solute dissolves)

Unit of Kpc: It has no unit

Explanation:

- When two immiscible liquids like ether and water are mixed with a solute X and shaken in a separating funnel, solute X dissolves in both layers.
- After standing, the layers separate again.
- The solute is distributed between both solvents and an equilibrium is established.
- At this point, the concentration of X becomes

Nernst Distribution Law:
"This law states that a solute distributes itself between two immiscible liquids in a fixed ratio, provided the temperature is constant and the solute exists in the same molecular form in both solvents."

constant in both layers.

- This equilibrium follows the Nernst Distribution Law.

ACTIVITY – 3.1

Calculating the partition coefficient.

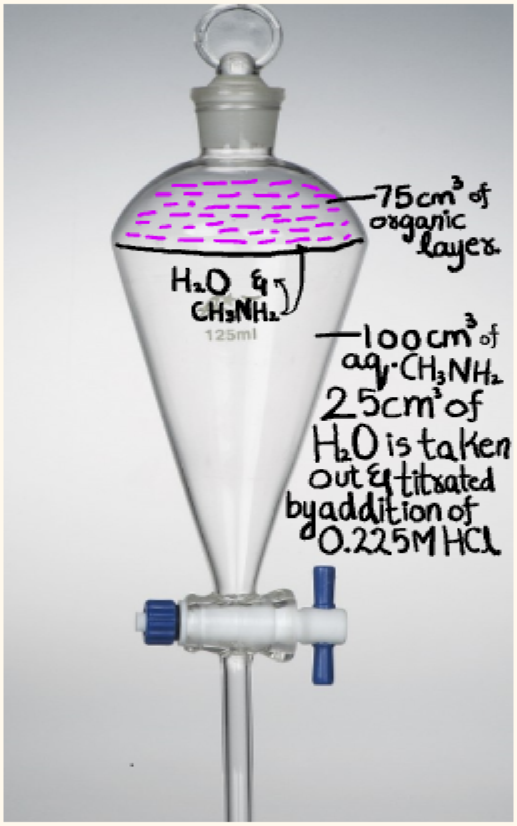
Procedure:

- Take 100 cm^3 of 0.150 M methylamine solution (CH_3NH_2) and pour it into a separating funnel.
- Add 75 cm^3 of an organic solvent into the same funnel.
- Shake gently but well so the solute can move between the two liquids.
- Let it sit for 5–10 minutes to reach equilibrium.
- Once the two layers form, separate them into two different beakers.
- Measure the concentration of the solute (methylamine) in each layer.

Calculations:

When 100 cm^3 of 0.150 mol/dm^3 methylamine solution is mixed with 75.0 cm^3 of an organic solvent in a separating funnel and left to reach equilibrium,

25 cm^3 of the water layer is taken out and titrated using 0.225 mol/dm^3 HCl. It took 7.05 cm^3 of HCl for neutralization.



Data for Calculation:

- Volume of aqueous methylamine solution = 100 cm^3
- Initial concentration of methylamine = 0.150 mol/dm^3
- Volume of organic solvent = 75.0 cm^3
- Volume of aqueous layer taken = 25.0 cm^3
- Volume of HCl used in titration = 7.05 cm^3
- Concentration of HCl = 0.225 mol/dm^3

Solution:

STEP – 1: Write down equilibrium equation

$CH_3NH_{2\,(aq)} \rightleftharpoons CH_3NH_{2\,(ORGANIC\ SOLVENT)}$

STEP – 2: Write Kpc expression

$$Kpc = \frac{[CH3NH2(organic\ layer)]}{[CH3NH2\ (aqueous\ layer)]}$$

STEP – 3: Determine total moles of CH_3NH_2 in original solution

According to formula:

$$M = \frac{n}{Vdm^3}$$

$$\Rightarrow n = M \times Vdm^3$$

$$n = 0.150 \times 100$$

$$n = 15dm^3$$

To convert into cm^3, we will divide by 1000

$$n = \frac{15}{1000}$$

$$n = 0.015 \text{ moles}$$

These moles will be distributed between two layers.

STEP – 4: Determine the no. of moles CH_3NH_2 in H_2O.

$$CH_3NH_{2\,(aq)} + HCl_{(aq)} \rightarrow CH_3NH_3Cl_{(aq)}$$

$25cm^3$ of aqueous layer reacted with $7.05cm^3$ of 0.225M HCl

$$n = M \times Vdm^3$$

$$n = 0.225 \times \frac{7.05cm^3}{1000}$$

$$n = 0.001586 \text{ mol}$$

$$25cm^3 = 0.001586$$

$$100cm^3 = x$$

By cross multiplication:

$$x = \frac{0.001586 \times 100}{25}$$

$$x = 0.00634 \text{ mol}$$

So , $100cm^3 = 0.00634$ mol

STEP – 5: Determine no. of moles of CH_3NH_2 present in organic solvent.

Mol CH_3NH_2 (organic layer) = mol CH_3NH_2 (total) – mol CH_3NH_2(aq layer)

Mol CH_3NH_2 (organic layer) = 0.015 mol – 0.00634 mol

Mol CH_3NH_2 (organic layer) = 0.00867 mol.

STEP – 6: Change the no. of moles into concentrations:

Concentration (CH_3NH_2 in aqueous layer) = $0.0063 \times \frac{1000}{100}$

Concentration (CH_3NH_2 in aqueous layer) = 0.063 mol dm^{-3}

Concentration (CH_3NH_2 in organic layer) = $0.0867 \times \frac{1000}{75}$

Concentration (CH_3NH_2 in organic layer) = 0.116 mol dm^{-3}

STEP – 7: Substitute the values into Kpc expression:

$$\text{Kpc} = \frac{[CH3NH2(organic\ layer)]}{[CH3NH2(aqueous\ layer)]}$$

$$\text{Kpc} = \frac{0.116}{0.063}$$

Kpc = 1.83

- As, Kpc value is greater than 1 so CH_3NH_2 is more soluble in organic solvent than water.

Hence proved.

CONCEPT ASSESSMENT – 3.4

When 2 grams of a solute is shaken with a mixture of 150 cm3 of water and 20 cm3 of chloroform. After shaking, 1.5 grams of the solute is found in the chloroform layer. Calculate the partition coefficient.

Given:

Total solute = 2 g
Solute in chloroform = 1.5 g
Solute in water = 2 – 1.5 = 0.5 g
Volume of water = 150 cm^3 = 0.150 dm^3
Volume of chloroform = 20 cm^3 = 0.020 dm^3

Solution:

STEP – 1: Write down equilibrium equation

$$\text{Solute(aq)} \rightleftharpoons \text{Solute(org)}$$

STEP – 2: Write Kpc expression

$$\text{Kpc} = \frac{Concentration\ in\ organic\ layer\ (chloroform)}{Concentration\ in\ aqueous\ layer}$$

According to formula:

$$\text{Concentration} = \frac{Mass}{Volume}$$

$$\text{Kpc} = \frac{\frac{Mass\ in\ organic}{Volume\ in\ organic}}{\frac{Mass\ in\ aqueous}{Volume\ in\ aqueous}}$$

$$\text{Kpc} = \frac{\frac{1.5}{0.020}}{\frac{0.5}{0.150}}$$

$$\text{Kpc} = \frac{75}{3.33}$$

Kpc = 22.5

So, the solute is more soluble in the organic layer.

<u>Factors affecting the numerical value of Partition Coefficient:</u>

1. Polarity of the Solute

- Polar solutes dissolve better in polar solvents (like water).
- They form hydrogen bonds or dipole interactions.

Example: Ethanol is more soluble in water than in octanol → favors polar phase.

2. Polarity of the Solvent

"Like dissolves like":

- Polar solutes prefer polar solvents.
- Non-polar solutes prefer non-polar solvents.

Example: Benzene (non-polar) dissolves better in octanol (non-polar) than in water → high Kpc in non-polar phase.

3. Temperature

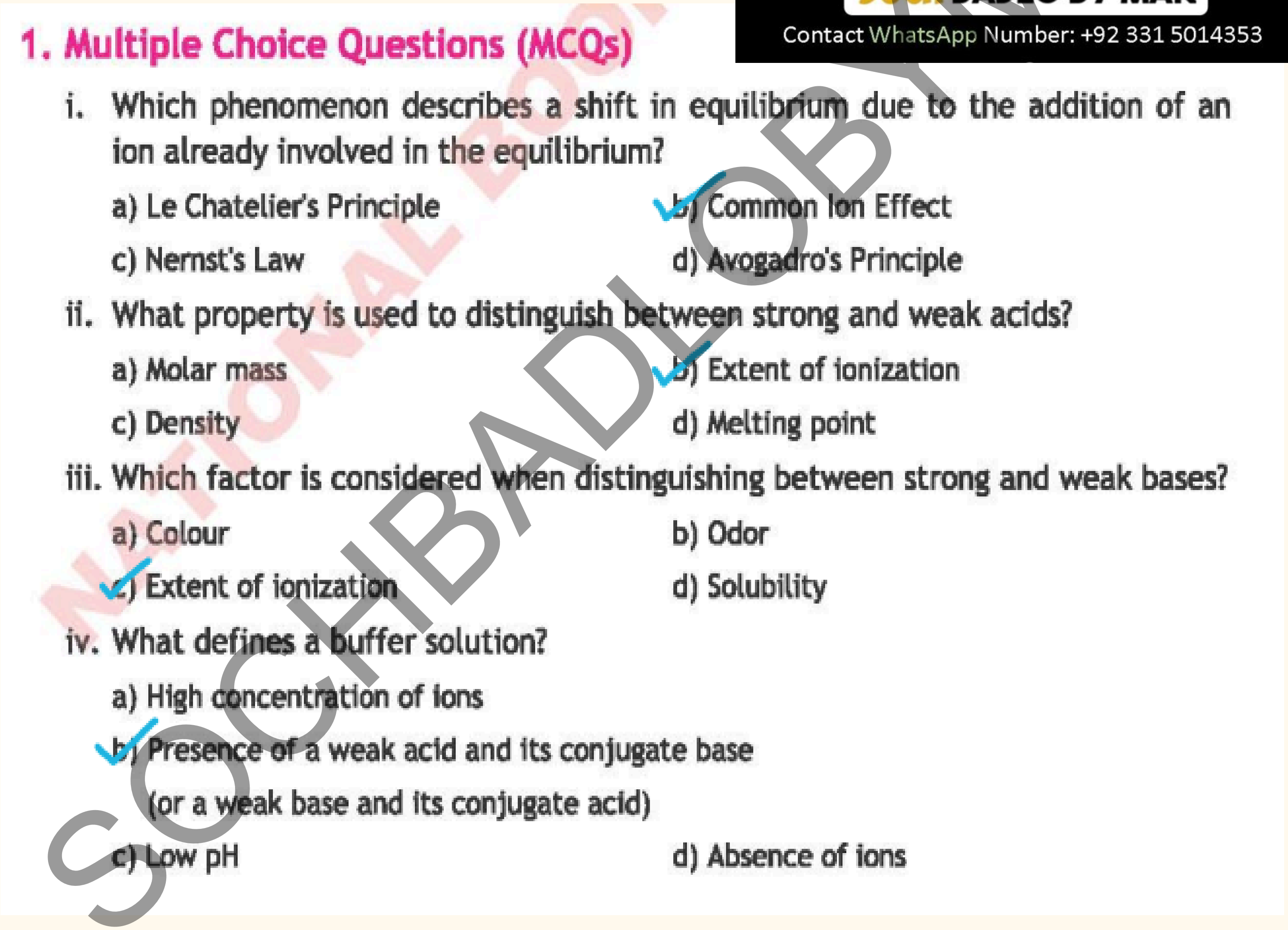
- Higher temperature = higher solubility (usually).
- Can increase solubility in either solvent, depending on the solute.

Example: Aspirin becomes more soluble in water at high temp → Kpc shifts toward the polar phase.

4. Molecular Size & Structure

- Bigger molecules may face steric hindrance → harder to dissolve.
- Functional groups also affect how the molecule interacts with each solvent.

Example: Butyl acetate (larger) may have a lower Kpc than ethyl acetate due to size.



1. Multiple Choice Questions (MCQs)

i. Which phenomenon describes a shift in equilibrium due to the addition of an ion already involved in the equilibrium?

a) Le Chatelier's Principle [✓ b) Common Ion Effect]
c) Nernst's Law d) Avogadro's Principle

ii. What property is used to distinguish between strong and weak acids?

a) Molar mass [✓ b) Extent of ionization]
c) Density d) Melting point

iii. Which factor is considered when distinguishing between strong and weak bases?

a) Colour b) Odor
[✓ c) Extent of ionization] d) Solubility

iv. What defines a buffer solution?

a) High concentration of ions
[✓ b) Presence of a weak acid and its conjugate base (or a weak base and its conjugate acid)]
c) Low pH d) Absence of ions

v. How can a buffer solution be made?

a) Mixing strong acids and bases

[✓ b) Mixing a weak acid and its conjugate base (or a weak base and its conjugate acid)]

c) Diluting a strong acid d) Adding water to a strong base

vi. What role does HCO_3^- play in controlling pH in blood?

[✓ a) Neutralization of acids] b) Buffering against changes in pH

c) Catalysing reactions d) Enhancing oxygen transport

vii. How is the concentration of a slightly soluble salt calculated?

[✓ a) Using the solubility product constant (K_{sp})]

b) Titration with a strong base

c) Measuring density

d) Conductivity measurement

viii. Which term is used to describe the strength of an acid in terms of its ionization in water?

a) Acid Concentration [✓ b) Acid Dissociation Constant (Ka)]

c) Acid Molarity d) Acid Equilibrium Constant

ix. Which type of solvent would favour the partitioning of a polar solute?

a) Non-polar solvent b) Hydrophobic solvent

[✓ c) Polar solvent] d) Aprotic solvent

x. What is the partition coefficient defined as?

[✓ a) Ratio of solute concentration in one solvent to the other]

b) Ratio of solute concentration in a single solvent

c) Ratio of solute mass in one solvent to the other

d) Ratio of solute mass in a single solvent

SHORT ANSWER QUESTIONS:

Q1). Explain the common ion effect with a suitable example.

Ans). "Common ion effect is the suppression of ionization of a weak electrolyte by adding a strong electrolyte having a common ion".

Example:

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

adding $NaCH_3COO$ (which gives CH_3COO^-) suppresses ionization of acetic acid.

Q2). Differentiate between strong and weak acids using the extent of ionization and Ka.

Ans). Strong acids ionize completely in water, meaning they release all their hydrogen ions (H^+), so their extent of ionization is nearly 100%, and their Ka value is large.

Weak acids, on the other hand, only partially ionize in water, releasing fewer H^+ ions. Hence, their extent of ionization is low, and their Ka value is small.

Q3). Differentiate between strong and weak bases using extent of ionization and Kb.

Ans). Strong bases fully ionize in water and produce a high concentration of OH^- ions. So, they have a high extent of ionization and a large Kb value.
Weak bases ionize only partially, giving fewer OH^- ions. Therefore, their extent of ionization is low, and their Kb value is small.

Q4). Define a buffer solution and provide an example of how it can be made.

Ans). A buffer solution resists changes in pH when small amounts of acid or base are added.

Example: A mixture of CH_3COOH and CH_3COONa forms an acidic buffer.

Q5). How does a buffer solution control pH? Include chemical equations in your explanation.

Ans). Buffer works by neutralizing added acids or bases.

In CH_3COOH / CH_3COONa buffer:

If acid (H^+) is added:

$CH_3COO^- + H^+ \rightarrow CH_3COOH$

If base (OH^-) is added:

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

Q6). Describe the uses of buffer solutions in various applications.

Ans). Buffers are used in:

- Blood to maintain pH ~7.4
- Shampoos & cosmetics to avoid skin irritation
- Pharmaceuticals to ensure drug stability
- Biological research to control pH in experiments

Q7). Explain how HCO_3^- plays a role in controlling pH in the blood.

Ans: HCO_3^- acts as a buffer in blood.

If H^+ increases:

$HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow CO_2 + H_2O$

If OH^- increases:

$\mathbf{H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O}$

This keeps blood pH stable around 7.35–7.45

Q8). Calculate the concentration of a slightly soluble salt given its Ksp.

Ans). (Example):

If Ksp of AB = x^2,

Then:

Solubility = $\sqrt{Ksp}$

Example:

If Ksp = 4×10^{-6},

then Solubility = $\sqrt{(4 \times 10^{-6})} = 2 \times 10^{-3}$ mol/L

<u>CONCEPTUAL/SLO BASED QUESTIONS:</u>

Q1: Why does a strong acid not form an effective buffer solution when mixed with its salt?

Answer: A strong acid fully ionizes in water, so it doesn't leave enough un-ionized acid to neutralize added base. Buffers need a weak acid and its salt so they can resist pH changes by reacting with added H^+ or OH^-.

Q2: How does the common ion effect influence the solubility of a sparingly

soluble salt?

Answer: When a common ion is added from another source, it shifts equilibrium backward (Le Chatelier's Principle), which decreases the solubility of the salt.

Example: Adding Cl^- to AgCl solution reduces AgCl solubility.

Q3: Why do weak acids have a lower Ka value than strong acids?

Answer: Weak acids partially ionize, so they produce fewer H^+ ions — that means their Ka (ionization constant) is smaller. Strong acids completely ionize, so their Ka is large.

Smaller Ka = weaker acid.

Q4: Why NH_3 a stronger base than water?

Answer: Because NH_3 (ammonia) has a lone pair on nitrogen that it can easily donate to accept a proton (H^+). Nitrogen is less electronegative than oxygen, so it holds onto its lone pair more loosely, making it more available for bonding with H^+.

On the other hand, water (H_2O) has lone pairs too, but oxygen is more electronegative, so it holds them tighter, making water less willing to donate its lone pair.

Q5: A solution has a very low pH but does not ionize completely — what does this say about the strength of the acid?

Answer: It's a concentrated weak acid, the low pH comes from high concentration, but since it doesn't ionize fully, it's not strong.

Strength ≠ pH; strength = ionization ability.

Q6: How can we find solubility of a compound?

Answer: We can find solubility of a compound by a solubility table.
