PC-8 : PHYSICAL CHEMISTRY

UNIT-IV Solutions, Ionic equilibrium

Definition of Solution

A solution is a homogeneous mixture of two or more substances.

The component present in a larger amount is called the solvent.

The component present in a smaller amount is called the solute.

The solute particles are uniformly distributed at the molecular or ionic level in the solvent, so the solution appears as a single phase.

Types of Solutions Based on the Physical States of Solute and Solvent

The types depend on whether solute and solvent are in solid, liquid, or gaseous state:

Solute State	Solvent State	Example
Gas	Gas	Air (O_2 + N_2, etc.)
Gas	Liquid	Aerated drinks (CO_2 in water)
Gas	Solid	Hydrogen in palladium (H_2 in metal lattice)
Liquid	Gas	Moist air (water vapour in air)
Liquid	Liquid	Alcohol in water (ethanol + water)
Liquid	Solid	Amalgams (Hg in Na)
Solid	Gas	Camphor in air (sublimation vapors)
Solid	Liquid	Salt solution (NaCl in water), sugar solution
Solid	Solid	Alloys (brass = Cu + Zn, steel = Fe + C)

Liquid in Liquid Solutions (Classification by Miscibility)

Completely Miscible Liquids

Liquids that mix with each other in all proportions and form a single homogeneous phase.

Example: Alcohol in water (ethanol + water)

Acetone in water

Partially Miscible Liquids

Liquids that dissolve in each other only up to a certain limit. Beyond that, they separate into two layers.Miscibility depends on temperature.

Example:

Phenol + water (shows *Critical Solution Temperature – CST*)

Aniline + water

Immiscible Liquids

Liquids that do not dissolve in each other at all and form separate layers.

Example: Oil + water Mercury + water

Completely Miscible Liquids

When two liquids are miscible in all proportions, they form homogeneous liquid–liquid solutions.

These can be classified into Ideal solutions and Non-ideal solutions.

Ideal Solutions

Definition: A solution which strictly obeys Raoult's Law over the entire range of composition.

Raoult's Law:

The partial vapour pressure of each component is directly proportional to its mole fraction in the solution.

$P_A = P^0_A X_A$ & $P_B = P^0_B X_B$

where

P^0_A & P^0_B = vapour pressures of pure components

X_A & X_B = mole fractions of components

Total vapour pressure:
$P_{total} = P_A + P_B$
Characteristics of Ideal Solutions:
No heat change on mixing (ΔHmix = 0).
No volume change on mixing (ΔVmix = 0).
Intermolecular forces between A–B are similar to A–A and B–B.

Examples:

Benzene + Toluene (similar structure, same type of interactions)
n-Hexane + n-Heptane
Chlorobenzene + Bromobenzene

Non-Ideal Solutions

Definition: Solutions which do not obey Raoult's Law over the entire composition range.
Reason: Intermolecular forces between A–B are different from A–A and B–B interactions.
Types:

a) Positive Deviation from Raoult's Law

A–B interactions are weaker than A–A and B–B.
Escaping tendency of molecules increases → vapour pressure higher than ideal.
ΔHmix > 0 (endothermic), ΔVmix > 0.
Example:
Ethanol + Acetone
Carbon tetrachloride + Toluene

b) Negative Deviation from Raoult's Law

A–B interactions are stronger than A–A and B–B.
Escaping tendency decreases → vapour pressure lower than ideal.
ΔHmix < 0 (exothermic), ΔVmix < 0.
Example:
Acetone + Chloroform (H-bond formation)
Nitric acid + Water

Azeotropic Mixtures

Definition

An azeotrope (or constant-boiling mixture) is a mixture of two or more liquids that boils at a constant temperature and distills without any change in composition.This happens because the vapour phase has the same composition as the liquid phase.Azeotropes cannot be separated into pure components by simple fractional distillation.

Types of Azeotropes (Based on Boiling Temperature)

Minimum Boiling Azeotropes

Formed when the liquid mixture shows a positive deviation from Raoult's law.

Intermolecular forces between unlike molecules (A–B) are weaker than those in pure liquids (A–A, B–B).

Hence, vapour pressure ↑ and boiling point ↓ compared to both pure components.

Examples:

Ethanol–Water (95% ethanol, b.p. 351 K)

Acetone–Carbon disulphide

Maximum Boiling Azeotropes

Formed when the liquid mixture shows a negative deviation from Raoult's law.

Intermolecular forces between un-like molecules (A–B) are stronger than those in pure liquids.

Hence, vapour pressure ↓ and boiling point ↑ compared to both pure components.

Examples:

Hydrochloric acid–Water (20.2% HCl, b.p. 381 K)

Nitric acid–Water

Ethanol-water system.

Nature of the Mixture

Ethanol and water are completely miscible liquids.

They form a non-ideal solution because the intermolecular interactions between ethanol–water molecules differ from those of pure ethanol and pure water.

Type of Deviation

Ethanol–water solution shows a positive deviation from Raoult's Law.

Reason:

Ethanol molecules are hydrogen-bonded in pure state.

When mixed with water, some of these hydrogen bonds are broken, and A–B (ethanol–water) interactions are weaker compared to pure A–A or B–B interactions.

This increases the escaping tendency (vapour pressure ↑).

Azeotrope Formation

Due to positive deviation, the mixture forms a minimum boiling azeotrope.

Composition: 95.6% ethanol and 4.4% water (by weight).

Boiling Point: 351 K (78.1 °C), which is lower than the boiling points of both pure ethanol (78.4 °C) and pure water (100 °C).

Distillation Behaviour

During fractional distillation of ethanol–water mixture:

Vapour becomes richer in ethanol than the liquid.

But once composition reaches 95.6% ethanol, the vapour and liquid have identical composition.

Further distillation cannot increase ethanol concentration.

This composition is called azeotropic composition.

Industrial Importance

Absolute ethanol (100% pure ethanol) cannot be obtained by simple distillation due to azeotrope formation.

Methods used to break the azeotrope:

Adding benzene or cyclohexane (forms a ternary azeotrope, removing water).

Using molecular sieves.

Partially miscible liquids-phenol-water system.(System with an upper CST)

Definition

Two liquids are said to be partially miscible if they dissolve in each other only up to a certain limited extent.

Beyond that solubility limit, they separate into two distinct liquid layers.

Their mutual solubility is usually influenced by temperature.

Examples

Phenol + Water

Aniline + Water

Nicotine + Water

Phenol–Water System

1. Nature of Interaction

Phenol and water can form hydrogen bonds.

At low temperatures, this interaction is not strong enough to make them fully miscible, so two layers are formed.

As temperature increases, hydrogen bonding becomes more effective, and miscibility increases.

2. Critical Solution Temperature (CST)

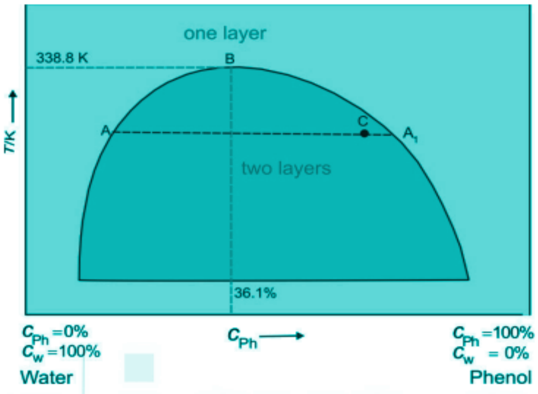
The **Critical Solution Temperature (CST)** is defined as the **lowest temperature at which two partially miscible liquids become completely miscible in every proportion**.

In the case of the **Phenol–Water system**, the CST is observed at about **66 °C (339 K)**. When the system is heated above this temperature, the mixture exists as a **single clear liquid phase**.

Experimental Procedure:

Take a clean, hard glass test tube and place a thermometer (up to 100 °C, with a precision of 0.1 °C) along with an aluminium stirrer. Avoid using copper stirrers. Transfer **5 mL of 80% phenol solution** into the test tube. Using a burette, add **0.5 mL of distilled water** to the phenol solution and observe whether the mixture is clear or turbid. If the mixture remains clear, add **1 mL of water** further. Place the test tube with the thermometer and stirrer in a water bath and heat the mixture gradually with continuous stirring. Record the temperature at which the **turbidity disappears** (solution becomes clear). Remove the tube from the water bath, allow it to cool while stirring, and note the temperature at which the **turbidity reappears**. Continue the experiment by adding additional increments of **0.5–1 mL water** each time, repeating the heating and cooling steps until approximately **30 mL water** has been added.

Finally, plot the average miscibility temperature against the **weight percentage of phenol** on graph paper. The **highest point on the curve** corresponds to the **Critical Solution Temperature (CST)** of the phenol–water system.



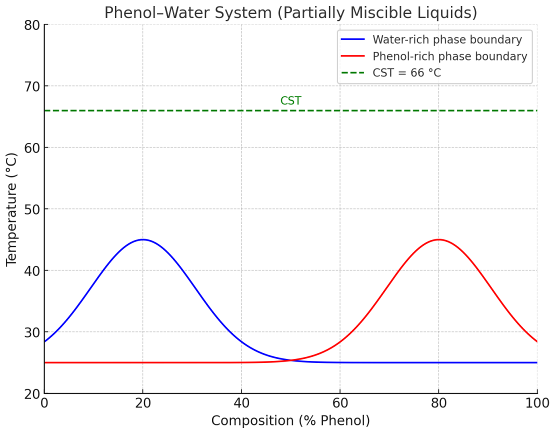
3. Phase Behaviour

Below CST → Two liquid layers exist: one phenol-rich and one water-rich.

At CST → The mutual solubility of phenol and water becomes complete.

Above CST → Only a single solution is formed at all compositions.

4. Phase Diagram (Explanation)



Above is the phase diagram of the Phenol–Water system showing the Critical Solution Temperature (CST ≈ 66 °C).

Region between the two curves → two layers (partially miscible).

Above CST → single homogeneous phase (complete miscibility).

Below CST → phenol-rich layer + water-rich layer.

5. Importance

CST helps in understanding liquid–liquid equilibria.

Useful in designing separation processes in industries.

Critical Solution Temperature (CST)

Definition

The Critical Solution Temperature (CST) is the temperature above which two partially miscible liquids become completely miscible in all proportions.

It is also called the consolute temperature.

Explanation

In some liquid–liquid systems, solubility depends strongly on temperature.

At low temperatures, the two liquids may form two separate layers (limited miscibility).

As temperature increases, mutual solubility increases.

At the CST, the miscibility becomes complete, and above this temperature, only a single homogeneous phase exists for all compositions.

Types of CST

Upper CST (UCST)

Occurs when liquids become completely miscible on heating.

Example: Phenol–Water system (UCST ≈ 66 °C).

Below 66 °C → two layers.

At 66 °C → complete miscibility.

Above 66 °C → homogeneous solution.

Lower CST (LCST)

Occurs when liquids are completely miscible at lower temperatures, but separate into two layers on heating beyond a certain temperature.

Example: Triethylamine–Water system (LCST ≈ 18 °C).

Miscible below 18 °C.

Separate into layers above 18 °C.

Both UCST and LCST

Some systems show both upper and lower CST, having complete miscibility only in the intermediate temperature range.

Example: Nicotine–Water system.

Examples of CST

Phenol–Water system → UCST at 66 °C.

Aniline–Water system → UCST at 168 °C.

Triethylamine–Water system → LCST at 18 °C.

Nicotine–Water system → both UCST and LCST.

Applications

CST studies help in:

Understanding molecular interactions between liquids.

Designing separation and purification processes.

Explaining temperature dependence of solubility in industrial and pharmaceutical formulations.

Nernst distribution law.

If we take two immiscible solvents A and B in a beaker, they form separate layers. When a solute X which is soluble in both solvents is added, it gets distributed or partitioned between them. Molecules of X pass from solvent A to B and from solvent B to A. Finally a dynamic equilibrium is set up. At equilibrium, the rate, at which molecules of X pass from one solvent to the other is balanced

$\frac{Concentration\ of\ X\ in\ A}{Concentration\ of\ X\ in\ B}$ = constant. For example, iodine distribution between carbon tetrachloride (CCl_4) and water – this is a very common alternative example.

Concentration of I_2 in CCl_4 (C_1)	**Concentration of I_2 in H_2O (C_2)**	$\frac{C_1}{C_2}$
0.050	0.0025	20.0
0.075	0.0038	19.7
0.100	0.0050	20.0
0.125	0.0062	20.2

STATEMENT OF NERNST'S DISTRIBUTION LAW

Nernst (1891) studied the distribution of several solutes between different appropriate pairs of solvents. He gave a generalization which governs the distribution of a solute between two non-miscible solvents. This is called Nernst's

Distribution law (or Nernst's Partition law) or simply Distribution law or Partition law. If a solute X distributes itself between two immiscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents,

$$\frac{Concentration\ of\ X\ in\ A}{Concentration\ of\ X\ in\ B} = K_D$$

If C_1 denotes the concentration of the solute in solvent A and C_2 the concentration in solvent B, Nernst's Distribution law can be expressed as $K_D = \frac{C_1}{C_2}$ The constant K_D (or simply K) is called the Distribution coefficient or Partition coefficient or Distribution ratio.

Applications of distribution law.

1. Solvent Extraction (Separation of Compounds)

- A practical application where an organic compound dissolved in water is extracted into an organic solvent (e.g., ether, chloroform).
- By repeated extractions with smaller volumes, almost complete transfer of solute can be achieved.
- Example: Extraction of benzoic acid from aqueous solution into benzene.

2. Determination of Association or Dissociation of Molecules

- If the solute associates (dimerizes/polymerizes) or dissociates in one solvent, the distribution law is modified.
- By studying deviations, degree of association/dissociation can be calculated.
- Example: Benzoic acid associates as dimers in benzene but remains monomeric in water. This behavior can be confirmed using the distribution law.

3. Determination of Equilibrium Constant

- Distribution law helps in calculating equilibrium constants of reactions between two immiscible solvents.
- Example: Partitioning of iodine between water and carbon disulfide can be used to determine equilibrium constants of complex formation.

4. Determination of Molecular Weight

- If the solute associates in one solvent, the extent of association can be used to determine its molecular weight.
- Example: Molecular weight of acetic acid in benzene (where it exists as dimers) can be determined.

5. Study of Complex Ion Formation

- Used to determine the stability constants of complexes formed in one of the solvents.
- Example: Distribution of iodine between water and CCl_4 changes in the presence of KI (due to formation of I_3^- ion). From this, stability constant of triiodide ion can be calculated.

6. Chromatography (Separation Technique)

- Partition chromatography is based directly on the principle of distribution law.
- A solute distributes between stationary liquid phase and mobile liquid/gaseous phase, enabling separation.
- Example: Paper chromatography, column chromatography.

7. Pharmaceutical Applications

- Distribution law helps in understanding drug solubility in water and lipids.
- The partition coefficient is crucial in drug design, as it affects absorption, distribution, and bioavailability of drugs.

- Example: Lipid-water distribution of anesthetics.

Ionic equilibrium

Definition

Ionic equilibrium refers to the state of dynamic balance established between ions and unionized molecules in a solution of weak electrolytes or in systems where ionic reactions take place.

- In such solutions, ions are constantly formed and recombined, but their concentrations remain constant once equilibrium is attained.

- This concept is similar to chemical equilibrium, but here it specifically involves ions in solution.

Explanation

Electrolytes

- ○ Substances which, when dissolved in water, produce ions are called electrolytes.
- ○ Strong electrolytes: Completely dissociate into ions (e.g., HCl, NaOH, NaCl).
- ○ Weak electrolytes: Partially dissociate into ions, establishing ionic equilibrium (e.g., CH_3COOH, NH_4OH).

Example of Ionic Equilibrium

- For acetic acid in water:

  $$CH_3COOH \rightleftharpoons H^+ + CH3COO^-$$

- Forward reaction: ionization of acid.

- Backward reaction: recombination of ions.

- At equilibrium, the rates of both reactions are equal, so concentrations remain constant.

Key Concepts in Ionic Equilibrium

- Degree of ionization (α): Fraction of molecules ionized.

- Ionization constant (Ka or Kb): Equilibrium constant for weak acids and bases.

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

- pH and pOH: Measure of acidity or alkalinity.

  $$p^H = -\log[H^+] \ \& \ p^{OH} = -\log[OH^-]$$

Ionic product of water (Kw):

Definition

The **ionic product of water (Kw)** is the product of the concentrations of hydrogen ions $[H^+]$ and hydroxide ions $[OH^-]$ in water at a given temperature.

At 25°C The experimentally measured value is:

$$K_w = [H^+][OH^-] = 1X\,10^{-14} \quad \text{(at 25◦C)}$$

Since in pure water: $[H^+] = [OH^-] = 1X\,10^{-7}$ (at 25◦C)

Importance of Ionic Equilibrium

- Helps in calculating pH of solutions.
- Explains buffer action (blood pH, pharmaceutical formulations).
- Determines solubility of salts (precipitation reactions).
- Useful in qualitative analysis of inorganic salts.

Common Ion Effect:

Suppression of ionization of a weak electrolyte by addition of a strong electrolyte having a common ion.

In other words, if two substances provide at least one same ion (common ion) in solution, the dissociation (ionization) of the weak electrolyte decreases.This is a direct consequence of **Le Chatelier's principle** applied to ionic equilibrium.

Explanation

- Consider acetic acid (CH_3COOH), a weak acid:

  $$CH_3COOH \rightleftharpoons H^+ + CH3COO^-$$

- Now, add a strong electrolyte like sodium acetate (CH_3COONa) which dissociates completely:

  $$CH_3COONa \rightleftharpoons Na^+ + CH3COO^-$$

- The solution now has an increased concentration of acetate ions (CH_3COO^-).
- According to Le Chatelier's principle, the equilibrium shifts to the left, i.e., ionization of acetic acid is suppressed.
- Therefore, fewer H^+ ions are produced → the solution becomes less acidic.

Solubility and solubility product.

1. Solubility

Definition

- Solubility is the maximum amount of a substance (solute) that can dissolve in a given amount of solvent (usually water) at a particular temperature to form a saturated solution.
- Expressed as grams of solute per litre or moles per litre (Molar solubility, S).

Example

- Solubility of **NaCl** in water at 25°C is about **36 g per 100 mL** of water.
- This means 36 g of NaCl dissolves in 100 mL of water at 25°C to give a saturated solution.

2. Solubility Product (Ksp)

Definition

- Solubility product is the **equilibrium constant** for the dissociation of a sparingly soluble salt into its ions in a saturated solution.
- If a salt AB dissolves slightly as:

$$AB(s) \rightleftharpoons A^+_{aq} + B^-_{aq}$$

$$Ksp = [A^+]\,[B^-]$$

Case 1: 1:1 Salt (AB) For salt AgCl:

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

If solubility = S, then: $[Ag^+] = [Cl^-] = S$

Then Ksp = $[Ag^+][Cl^-] = SXS = S^2$

Case 2: 1:2 Salt (AB_2) For salt **CaF_2**:

$CaF_{2(S)} \rightleftharpoons Ca^{+2} + 2F^{-1}$

If solubility = **S**, then: $[Ca^{+2}] = S$ & $[F^{-1}] = 2S$

Then Ksp = $[Ca^+][F^-]^2 = SX[2S]^2 = 4S^3$

Calculations based on solubility products.

Q: The solubility of AgCl in water at 25°C is $1.3X10^{-5}$ M Calculate Ksp.

Solution:

For AgCl , Ksp = $[Ag^+][Cl^-] = SXS = S^2$

Ksp = $[1.3X10^{-5}][1.3X10^{-5}] = [1.69X10^{-10}]$

Q:The solubility product of **CaF_2** is 4.0×10−11. Calculate its solubility in mol/L

Solution:

For CaF_2 , Ksp = $[Ca^+][F^-]^2 = SX[2S]^2 = 4S^3$

Ksp = $[Ca^+][F^-]^2 = SX[2S]^2 = 4S^3$

$S^3 = \frac{K_{sp}}{4}$

S = $\sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{4X10^{-11}}{4}} = 2.15X\,10^{-4}M$