Semester-VI

MJC-10 (T): Colligative Properties of Dilute Solutions, Chemica Kinetics and Photochemistry (T)

Course Outcomes

After completion of the course, studentswill be able to understand:-

CO1: Colligative properties of dilute solutions and determination of these properties.

CO2: Abnormal colligative properties and molar mass.

CO3: Azeotropes, maximum and minimum boiling azeotropic mixture.

CO4: Kinetics of simple and complex reactions.

CO5: Jablonski diagram and laws of photochemistry.

Colligative Properties of Dilute Solutions, Chemical Kinetics and Photochemis (Theory: 4 credits)

Unit	Topics to be covered	No. o Lectur
1.	**Colligative Properties of Dilute Solutions:** Colligative properties of solutions, Henry's law, Raoult's law (thermodynamic derivation), ideal and non-ideal solutions, azeotropes, thermodynamic derivation and experimental determination of relative lowering in vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure, abnormal colligative properties due to association and dissociation of solutes in solutions, van't Hoff's factor, abnormal molar mass, applications of colligative properties in determining molar mass of solutes, degree of dissociation and association.	15
2.	**Kinetics of Elementary Reactions:** Rate laws of first, second, third and zero order reactions, methods of determination of order of reactions, temperature dependance of reaction rate, Arrhenius equation, Activation energy. Collision theory and transition state theory of reaction rates. **Catalysis:** Theory and applications.	12
3.	**Kinetics of Complex Reactions:** Steady state approximation, integrated rate expression (first order only) for the 1. Opposing reactions 2. Parallel reactions and 3. Consecutive reactions.	12
4.	**Photochemistry:** Introduction, consequences of light absorption, Lambert-Beer's law, laws of photochemistry, Grotthus-Draper law, Stark-Einstein law of photochemical equivalence, quantum yield, photochemical reactions ($H_2 + Cl_2$, $H_2 + Br_2$, decomposition of HI), photochemical rate laws, energy transfer in photochemical reactions, Jablonski diagram, photosensitization, fluorescence, phosphorescence and chemiluminescence.	09
	TOTAL	48

Suggested Readings:

1. Physical Chemistry: P.W. Atkins (ELBS)
2. Comprehensive Physical Chemistry: Hemant Snehi
3. Theoretical Physical Chemistry: Gladstone

22.9.23

22/9/23

22.09.23

22-09-23

22/09/23

22/9/2023

২২/০৯/২০২৩

4. Physical Chemistry: G.M. Barrow.
5. Modern Electrochemistry: JOM Bakris and A.K.N. Reddy
6. Text Books of Polymer Science: F.W. Billmayer Jr.
7. Advanced Physical Chemistry: Gurdeep Raj

2.9.23

22/9/23

22.09.23

22.09.23

Ksahi

22/9/2023

22.9.23

22/09/2023

Semester - VI

MJC - 10(T)

Naiyara Kafil Hafizee
Department of Che

Colligative Properties of Solutions

1. Introduction : colligative properties are the properties of dilute solutions that depend only on the number of solute particles present in the solution and not on the nature of the solute.

These properties are mainly observed in dilute solutions where the solute is non-volatile.

The four important colligative properties are :-

1. Relative lowering of vapour pressure
2. Elevation of boiling point
3. Depression of freezing point
4. Osmotic pressure

2. Relative Lowering of Vapour Pressure :- When a non-volatile solute is added to a solvent, the vapour pressure of the solvent decreases.

According to Raoult's law:

$$P_1 = P_1^\circ X_1$$

Where:

P_1 = vapour pressure of solvent in solution
P_1° = vapour pressure of pure solvent
X_1 = mole fraction of solvent

Relative lowering of vapour pressure is:-

$$\frac{P_1^0 - P_1}{P_1^0} = X_2$$

Where X_2 is the mole fraction of solute.
It depends only on the number of solute particles.

3. Elevation of Boiling Point :-

Boiling point is the temperature at which vapour pressure becomes equal to atmospheric pressure.

When solute is added:-

- vapour pressure decreases
- Higher temperature is required to boil
- Boiling point increases

Elevation in boiling point:

$$\Delta T_b = K_b m$$

Where:-

ΔT_b = elevation in boiling point
K_b = molal boiling point constant
m = molality

Unit of K_b: $K\ Kg\ mol^{-1}$

4. Depression of Freezing Point :—

Freezing point is the temperature at which solid and liquid phases are in equilibrium.

Addition of solute:

- Lowers freezing point
- Solution freezes at lower temperature than pure solvent

Depression in freezing point:

$$\Delta T_f = K_f m$$

Where:—

ΔT_f = depression in freezing point

K_f = molal freezing point constant

m = molality

Unit of K_f : K Kg mol^{-1}

5. Osmotic Pressure :—

Osmosis is the flow of solvent through a semi-permeable membrane from dilute solution to concentrated solution.

Osmotic pressure (π) is the pressure required to stop osmosis.

$$\pi = CRT$$

Where:

π = osmotic pressure
C = molar concentration
R = gas constant
T = temperature in Kelvin

Osmotic pressure is very useful for determining molar mass of macromolecules like proteins and polymers.

6. Abnormal Colligative Properties :–

Sometimes observed values are higher or lower than expected due to :

- Association (e.g, acetic acid in benzene)
- Dissociation (e.g, NaCl in water)

This is explained using Van't Hoff factor (i) :

$$i = \frac{\text{Observed colligative property}}{\text{Calculated value}}$$

Modified equations :–

$$\Delta T_b = i K_b m$$

$$\Delta T_f = i k_f m$$

$$\pi = i C R T$$

7. Applications :—

- Determination of molar mass
- Antifreeze in cars (ethylene glycol)
- Salting of roads in winter
- Preservation of food
- Reverse osmosis (water purification)

Henry's Law

1. **Introduction:** Henry's Law explains the relationship between pressure of a gas and its solubility in a liquid.

It tells us how much gas can dissolve in a liquid at a given temperature.

2. **Statement of Henry's Law:**

At constant temperature, the amount of gas dissolved in a liquid is directly proportional to the pressure of that gas above the liquid.

In simple words:

If pressure increases, more gas dissolves.
If pressure decreases, less gas dissolves.

3. **Mathematical Expression:**

Henry's Law is written as:

$$P = K_H x$$

Where:

P = Partial pressure of the gas
x = Mole fraction of gas in solution
K_H = Henry's law constant

OR,

$$C = K_H P$$

Where,

C = concentration of dissolved gas.

P = Pressure of gas
K_H = Henry's constant

4. Important Points

- Temperature must remain constant.
- Henry's constant (K_H) depends on:-
  - Nature of gas
  - Nature of liquid
  - Temperature
- Higher temperature → Gas solubility decreases
- Different gases have different K_H values.

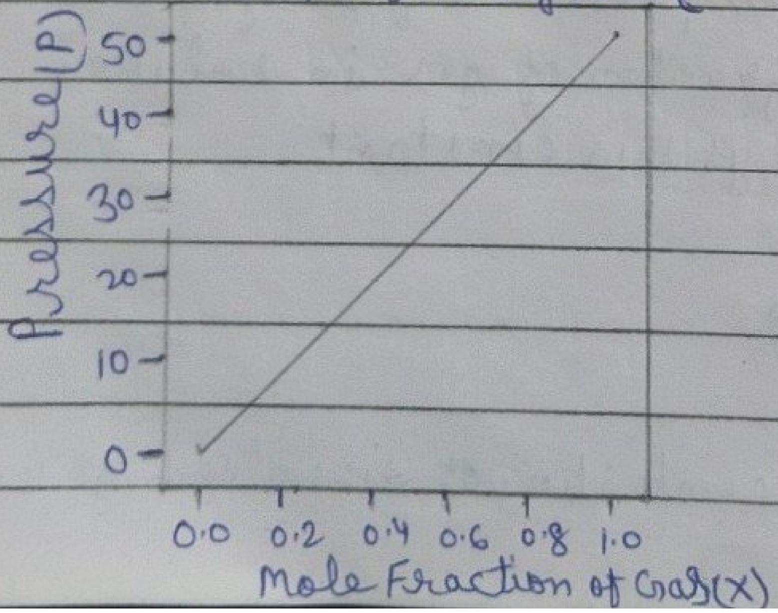
5. Graph of Henry's Law :-

If we draw a graph between:

- Pressure (P) on Y-axis
- Mole fraction (X) on X-axis

We get a straight line passing through origin.

Graph of Henry's Law ($P = K_H X$)



This shows direct proportionality.

6. Applications of Henry's Law :-

1. Cold Drinks :- carbonated drinks are prepared by dissolving CO_2 under high pressure.
When bottle is opened → pressure decreases → gas comes out as bubbles.

2. Scuba Diving :- At high pressure underwater, more nitrogen dissolves in blood.
If diver comes up quickly → pressure drops → gas bubbles form → causes "bends".

3. High Altitude :- At high altitude, atmospheric pressure is low → less oxygen dissolves in blood → breathing difficulty.

7. Limitations :-

- works mainly for dilute solutions.
- Not applicable when gas reacts with liquid.
- Deviates at very high pressure.

Raoult's Law :- (Thermodynamic Derivation)

- Statement of Raoult's Law :-

For an ideal solution, the partial vapour pressure of each volatile component is directly proportional to its mole fraction in the liquid phase.

For component A;

$$P_A = X_A P_A^0$$

Where

P_A = Partial vapour pressure of A in sol^n.
X_A = mole fraction of A in solution
P_A^0 = vapour pressure of pure A

Thermodynamic Derivation of Raoult's Law

We derive Raoult's law using chemical potential.

Step 1 :- Condition of Equilibrium

At equilibrium between liquid and vapour

$$\mu_A(\text{liquid}) = \mu_A(\text{vapour})$$

Step 2 :- Chemical Potential in Vapour Phase

For an ideal gas

$$\mu_A(\text{vapour}) = \mu_A^0(\text{vapour}) + RT \ln P_A$$

Where,

R = gas constant

T = temperature
P_A = Partial pressure

Step 3:- Chemical Potential in Liquid Phase (ideal solution)

For an ideal solution
$\mu_A(\text{liquid}) = \mu_A^0(\text{liquid}) + RT \ln X_A$

Step 4:- At Equilibrium

$\mu_A^0(\text{liquid}) + RT \ln X_A = \mu_A^0(\text{vapour}) + RT \ln P_A$

Rearranging,
$RT \ln X_A = RT \ln P_A + \mu_A^0(\text{vapour}) - \mu_A^0(\text{liquid})$

Step 5:- For pure component at Equilibrium

For pure A,
$\mu_A^0(\text{liquid}) = \mu_A^0(\text{vapour}) + RT \ln P_A^0$

Substitute into above equation:
$RT \ln X_A = RT \ln P_A - RT \ln P_A^0$

Divide by RT:
$\ln X_A = \ln P_A - \ln P_A^0$

Using log rule:
$\ln X_A = \ln\left(\frac{P_A}{P_A^0}\right)$

Taking antilog

$$x_A = \frac{p_A}{p_A^0}$$

So,

$$p_A = x_A p_A^0$$

This is Raoult's Law (Thermodynamic Derivation).

Ideal and Non-Ideal Solutions :—

Ideal Solutions :—

Definition:— An ideal solution is a solution that obeys Raoult's Law at all concentrations and temperatures.

Characteristics of ideal Solutions :—

1. Obey Raoult's Law at all compositions.
2. No heat is absorbed or released during mixing.

$\Delta H_{mix} = 0$

$\Delta V_{mix} = 0$

Examples of Ideal Solutions :—

- Benzene + Toluene
- n-Hexane + n-Heptane

Non-Ideal Solutions

Definition:— A non-ideal solution is a solution that does not obey Raoults law over the entire concentration range.

Types of Non-ideal solutions :—

1. **Positive Deviation from Raoult's Law:** When actual vapor pressure is greater than predicted by Raoult's law.

Reason:-

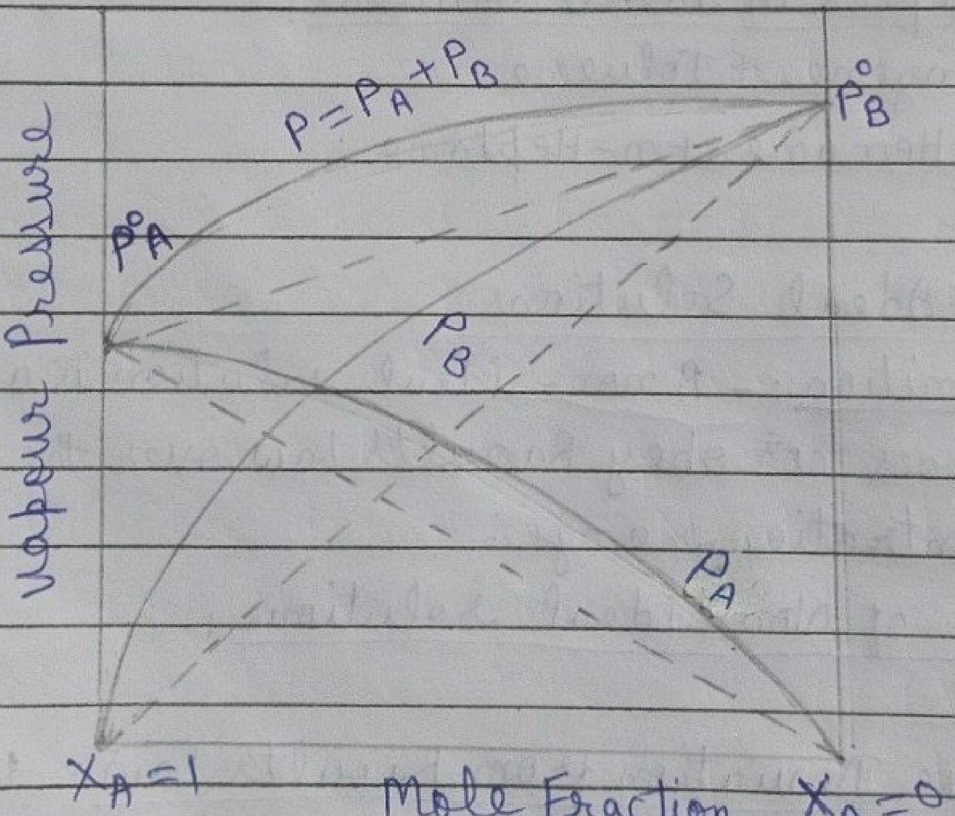
- A-B attraction is weaker than A-A and B-B attraction.
- Moleculer escape easily into vapor phase.

Effects:-

- $\Delta H_{mix} > 0$ (Heat absorbed, endothermic)
- $\Delta V_{mix} > 0$ (volume increases)

Examples:-

- Ethanol + water
- Acetone + Ethanol



~~Positive deviation~~ from Raoult's law

2. **Negative Deviation from Raoult's Law:** When actual vapor pressure is less than predicted.

Reason:-

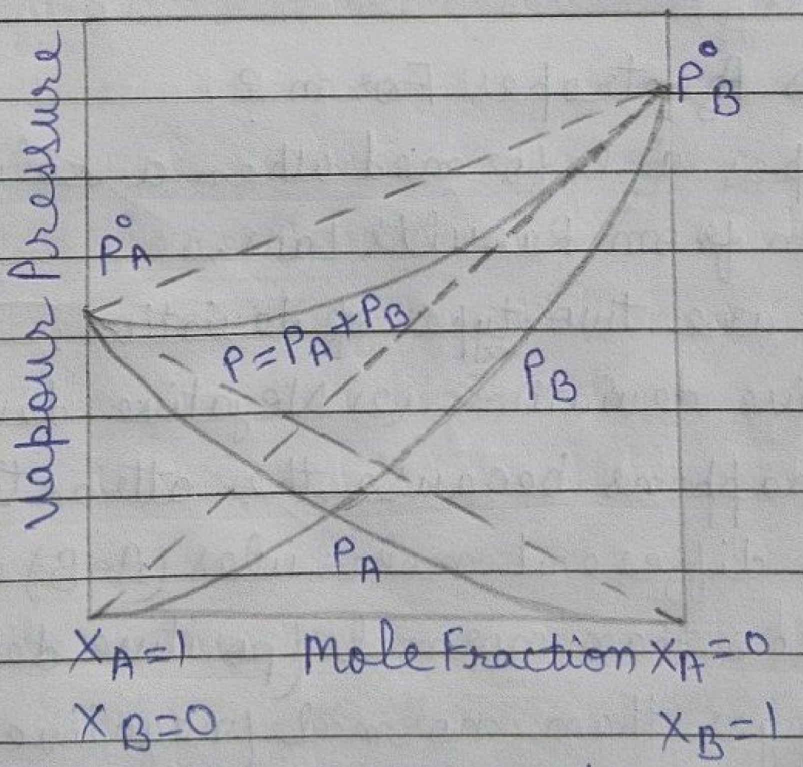
- A-B attraction is stronger than A-A and B-B.
- Molecules hold each other strongly and do not escape easily.

Effects:-

- $\Delta H_{mix} < 0$ (Heat released, exothermic)
- $\Delta V_{mix} < 0$ (Volume decreases)

Examples:-

- Acetone + Chloroform
- Nitric acid + water



Negative deviation from Raoult's law

Azeotropes:-

1. What is an Azeotrope?

An azeotrope is a special type of liquid mixture that:-

- Boils at a constant temperature
- Has the same composition in liquid and vapor phase.
- Cannot be separated by simple distillation

In Simple words:- When the mixture boils, the vapour formed has exactly the same composition as the liquid. So, separation becomes impossible by ordinary distillation.

It is also called a constant boiling mixture.

2. Why Do Azeotropes Form?

Azeotropes are formed when a solution shows deviation from Raoult's Law.

There are two types of deviation:-

(1) Positive deviation (2) Negative deviation

This happens because the attractive forces between different molecules (A-B) are either;

- Weaker than normal (positive deviation), or
- Stronger than normal (negative deviation)

3. Types of Azeotropes:

A. Minimum Boiling Azeotrope

Characteristics:

- Shows positive deviation from Raoult's law
- Boiling point is lower than both pure components
- Intermolecular forces are weaker
- Evaporates more easily

Example:

Ethanol + water (95.6% ethanol)

This mixture boils at 78.1°C and cannot give pure ethanol by simple distillation.

B. Maximum Boiling Azeotrope

Characteristics:

- Shows negative deviation from Raoult's Law.
- Boiling point is higher than both pure components
- Intermolecular forces are stronger
- Harder to evaporate

Example:
- Nitric acid + water
- HCl + water

Thermodynamic derivation and experimental determination of relative lowering in vapour pressure :

Definition :- When a non-volatile solute is added to a solvent, the vapour pressure of the solvent decreases.

Thermodynamic Derivation :

Let

P_A^0 = vapour pressure of pure solvent
P_A = vapour pressure of solution
X_A = mole fraction of solvent

According to Raoult's law :-

$$P_A = X_A P_A^0$$

Relative lowering of vapour pressure;

$$\frac{P_A^0 - P_A}{P_A^0} = 1 - X_A$$

Since,

$$1 - X_A = X_B$$

For dilute solution;

$$\frac{P_A^0 - P_A}{P_A^0} = \frac{n_B}{n_A}$$

Hence, RLVP depends only on number of solute particles.

Experimental Determination

Ostwald - Walker Method

- Dry air is passed through pure solvent and solution
- Loss in mass is measured
- Vapour pressures are calculated from mass loss.

Elevation in Boiling Point

Definition :- Increase in boiling point of a solution compared to pure solvent.

Thermodynamic Derivation :-

- Boiling point = temperature at which vapour pressure equals atmospheric pressure
- Adding solute lowers vapour pressure
- Higher temperature is needed to boil

$$\Delta T_b = K_b m$$

Where,

ΔT_b = elevation in boiling point
K_b = molal elevation constant
m = molality.

Experimental Determination :-

Beckmann Boiling Point Apparatus

- Measure boiling point of solvent
- Measure boiling point of solution
- Difference gives ΔT_b

Depression in Freezing Point

Definition:- Decrease in freezing point of solution compared to pure solvent.

Thermodynamic Derivation

- Freezing occurs when chemical potential of solid = liquid
- Solute lowers chemical potential of liquid
- Freezing point decreases

$\Delta T_f = K_f m$

where,

ΔT_f = depression in freezing point
K_f = molal depression constant

Experimental Determination

Beckmann Freezing Point Apparatus

- Measure freezing point of solvent
- Measure freezing point of solution
- Difference gives ΔT_f

Osmotic Pressure

Definition:- Pressure required to stop the flow of solvent through a semipermeable membrane.

Thermodynamic Derivation

- Osmosis continues till chemical potential become equal
- Pressure developed = osmotic pressure

$\pi V = nRT$

or,

$\pi = CRT$

Where,

π - osmotic pressure

C = molar concentration

R = gas constant

T = temperature

Experimental Determination

Osmometer Method :-

- Solution and solvent separated by semi-permeable membrane
- Height / pressure difference is measured
- Osmotic pressure calculated

Abnormal Colligative Properties due to Association and Dissociation of solutes in solutions:

Introduction:- Colligative properties of solutions depend only on the number of solute particles present in the solution and not on their nature.

Normally, colligative properties follow theoretical laws.

But in some solutions, the observed values of colligative properties are different from the calculated values.

Such behavior is called abnormal colligative properties.

Abnormality occurs due to:

1. Association of solute molecules
2. Dissociation of solute molecules

Normal Colligative Properties

When solute neither associates nor dissociates, the observed colligative properties are equal to the calculated values and such solutions are called ideal solutions.

Abnormal Colligative Properties :-

When solute molecules associate or dissociate in solution, the number of solute particles changes. This leads to abnormal values of :-

- Relative lowering of vapour pressure
- Elevation in boiling point
- Depression in freezing point
- Osmotic pressure

Abnormality due to Association of Solutes

Definition :→ Association is the process in which two or more solute molecules combine together to form a single larger molecule in solution.

Effect of Association

Due to association :

- Number of solute particles decreases
- Colligative properties show lower values than expected
- Molecular mass calculated becomes higher than actual

Example : Acetic acid in benzene shows association.

$2CH_3COOH \rightarrow (CH_3COOH)_2$

Van't Hoff Factor (i)

Van't Hoff factor is used to explain abnormal behavior.

$$i = \frac{\text{Observed Colligative Property}}{\text{Calculated Colligative Property}}$$

For association;

$i < 1$

Relation between i and Degree of Association (α)

For dimerisation;

$$i = 1 - \frac{\alpha}{2}$$

Where,

α = degree of association

Abnormality due to Dissociation of Solutes

Definition: Dissociation is the process in which a solute molecule splits into two or more ions in solution.

Effect of Dissociation:- Due to dissociation:

- Number of solute particles increases

- Colligative properties show higher values than expected
- Molecular mass calculated becomes lower than actual

Example :- Sodium chloride in water

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

Van't Hoff Factor

For dissociation

$i > 1$

Relation between i and Degree of Dissociation(α)

$$i = 1 + \alpha$$

Comparison between Association and Dissociation

	Point	Association	Dissociation
(1)	Nature	Molecules combine	Molecules split
(2)	No. of particles	Decreases	Increases
(3)	Colligative property	Lower than normal	Higher than normal
(4)	Van't Hoff factor	$i < 1$	$i > 1$
(5)	Molecular mass	Appears higher	Appears lower

Conclusion :- Abnormal colligative properties arise when solute molecules undergo association or dissociation in solution.

This abnormal behavior can be explained using the van't Hoff factor, which corrects the values of colligative properties and molecular mass.

Van't Hoff Factor (i)

Introduction :- Some solutions do not follow normal colligative property laws.
This abnormal behavior is explained by Van't Hoff factor (i).

Definition :- Van't Hoff factor (i) is defined as the ratio of the actual number of particles present in solution to the number of particles expected from the solute formula.

Mathematical Expression :-

$$i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

OR

$$i = \frac{\text{Actual number of particles}}{\text{Expected number of particles}}$$

Normal value of i :- For non-electrolytes like glucose, urea, there is no association or dissociation.
So,

$$i = 1$$

Abnormal value of i :-

(A) $i > 1$ (Dissociation)

When a solute breaks into ions in solution, the number of particles increases.

Example:-

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

Expected particles = 1

Actual particles = 2

So,

$i = 2$

This happens due to dissociation.

(B) $i < 1$ (Association):-

When solute molecules combine together, the number of particles decreases.

Example:-

$2\,CH_3COOH \rightarrow (CH_3COOH)_2$

Expected particles = 2

Actual particles = 1

So,

$i < 1$

This happens due to association

Relation of i with Degree of Dissociation (α):-

For dissociation,

$i = 1 + (n-1)\alpha$

Where,
n = number of ions formed
α = degree of dissociation

Effect on Colligative Properties:—

$$\Delta T_b = i\, K_b m$$

$$\Delta T_f = i K_f m$$

$$\pi = i C R T$$

Importance of van't Hoff Factor:—

- Explains abnormal colligative properties
- Helps in molecular weight determination
- Useful for electrolyte solutions
- Important for numerical problems

Conclusion:— van't Hoff factor is a correction factor used in colligative property equations. Its value depends on association or dissociation of solute particles.

Abnormal Molar Mass :-

Abnormal molar mass means that the molar mass calculated from colligative properties is not equal to the actual molar mass of the solute. This abnormality occurs because the solute associates or dissociates in solution.

Normal Molar Mass :- When solute particles neither associate nor dissociate in solution:

- Number of particles remains same
- Calculated molar mass = Actual molar mass
- No abnormality

Example :- Glucose in water

Causes of Abnormal Molar Mass

1. Association of Solute :-

Association means two or more solute molecules combine together to form a bigger molecule.

Effect of association :-

- Number of particle decreases

- Colligative property value decreases
- Calculated molar mass becomes greater than actual

Examples:— • Acetic acid in benzene
• Benzoic acid in benzene

Result;— Abnormally high molar mass

2. **Dissociation of Solute:—** Dissociation means one solute molecule splits into two or more ions.

Effect of dissociation:—

- Number of particles increases
- Colligative property value increases
- Calculated molar mass becomes less than actual

Example:— • $NaCl \rightarrow Na^{+} + Cl^{-}$
• KCl, $CaCl_2$ in water

Result:— Abnormally low molar mass

Van't Hoff Factor (i):— Van't Hoff factor explains abnormal molar mass.

Formula:— $$i = \frac{\text{Observed colligative propert}}{\text{Normal colligative property}}$$

OR

$$i = \frac{\text{Actual molar mass}}{\text{Observed molar mass}}$$

Value of Van't Hoff Factor

Condition	Value of i
Normal Solute	$i = 1$
Association	$i < 1$
Dissociation	$i > 1$

Degree of Association (α) :-

For association:

$$i = 1 - \alpha\left(1 - \frac{1}{n}\right)$$

Where,

α = degree of association

n = number of molecules associated

Degree of Dissociation (α) :-

For dissociation:

$$i = 1 + \alpha(n-1)$$

Where,

α = degree of dissociation

n = number of ions formed

Applications of colligative properties in determining molar mass of solutes:

Introduction:- Colligative properties are the properties of dilute solutions which depend only on the number of solute particles, not on their nature. These properties are used to determine the molar mass of unknown solutes, especially substances with high molecular weight.

Why colligative Properties are Important

- Useful for finding molar mass of non-volat le solutes
- Applicable for large molecules like proteins and polymers
- Results are accurate and reliable
- Depend only on number of particles

Main Colligative Properties used :-

1. Relative lowering of vapour pressure
2. Elevation in boiling point
3. Depression in freezing point
4. Osmotic pressure

1. Relative Lowering of vapour pressure method

When a non-volatile solute is added to a solvent the vapour pressure of solvent decreases.

Principle:- Relative lowering of vapour pressure is directly proportional to mole fraction of solute.

Formula:-

$$\frac{P^0 - P}{P^0} = \frac{w_2 \times M_1}{w_1 \times M_2}$$

Where,

P^0 = vapour pressure of pure solvent
P = vapour pressure of solution
w_2 = Mass of solute
w_1 = Mass of solvent
M_1 = Molar mass of solvent
M_2 = Molar mass of solute

By rearranging the formula, molar mass of solute is calculated.

2. Elevation in Boiling Point Method :

Addition of solute increases the boiling point of solvent.

Principle:- Elevation in boiling point depends on molality of solution.

Formula:- $\Delta T_b = K_b \times \frac{w_2}{M_2} \times \frac{1000}{w_1}$

Where,

ΔT_b = Elevation in boiling point

K_b = Molal elevation constant

Molar mass of solute is obtained by rearranging the formula.

3. Depression in Freezing Point Method

Freezing point of solution is lower than that of pure solvent.

Principle :- Depression in freezing point is proportional to number of solute particles.

Formula : $\Delta T_f = K_f \times \frac{w_2}{M_2} \times \frac{1000}{w_1}$

Where,

ΔT_f = Depression in freezing point

K_f = Molal depression constant

This method is commonly used for organic compounds.

4. Osmotic Pressure Method

Osmotic pressure is developed when solution and solvent are separated by a semipermeable membrane.

Principle :- Osmotic pressure is directly proportional to molar concentration.

Formula :-

$$\pi = \frac{w_2}{M_2} \times \frac{RT}{V}$$

Where,

π = Osmotic pressure
R = Gas constant
T = Absolute temperature
V = volume of solution

Best method for high molecular weight substances like proteins.

Advantages of Osmotic Pressure Method

- Works at room temperature
- Suitable for very dilute solutions
- Highly accurate for large molecules

Conclusion :- Colligative properties play an important role in determining molar mass of solutes.

Among all methods, osmotic pressure method is most reliable for high molar mass compounds.

These methods are widely used in chemistry, biology and pharmaceutical sciences.

Degree of Dissociation and Degree of Association

Degree of Dissociation (α)

Definition: Degree of dissociation (α) is the fraction of total solute molecules that dissociate (break into ions) in solution.

It is represented by α (alpha).

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{Total moles initially taken}}$$

Value of α:

- If no dissociation $\rightarrow \alpha = 0$
- If complete dissociation $\rightarrow \alpha = 1$
- If partial dissociation $\rightarrow 0 < \alpha < 1$

Example: For electrolyte like KCl

$$KCl \rightarrow K^+ + Cl^-$$

If 1 mole KCl is taken and 0.8 mole dissociates,

$$\alpha = \frac{0.8}{1} = 0.8$$

Relation with van't Hoff factor(i)

For dissociation:

$i = 1 + (n-1)\alpha$

Where,

- i = van't Hoff factor
- n = number of ions formed after dissociation
- α = degree of dissociation

Example: For Nacl:

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

Here $n = 2$

$i = 1 + (2-1)\alpha = 1 + \alpha$

Degree of Association (α)

Definition: Degree of association (α) is the fraction of total solute molecules that combine (associate) to form bigger molecules in solution

Example: Acetic acid in benzene forms dimer

$2CH_3COOH \rightarrow (CH_3COOH)_2$

If 1 mole is taken and 0.3 mole associates,

$\alpha = 0.3$

Relation with van't Hoff factor (i)

For association:

$i = 1 - \frac{(n-1)\alpha}{n}$

where, • i = Van't Hoff factor
- n = number of molecules combining
- α = degree of association

For dimerization ($n=2$):

$$i = 1 - \frac{\alpha}{2}$$

Example: (Acetic acid in benzene)

$$2CH_3COOH \rightarrow (CH_3COOH)_2$$

If,

$$\alpha = 0.3$$

$$i = 1 - \frac{0.3}{2} = 1 - 0.15 = 0.85$$

Important Points :-
- Dissociation increases number of particles
$\rightarrow i > 1$
- Association decreases number of particles
$\rightarrow i < 1$
- These cause abnormal molar mass
- Important in colligative properties

Conclusion :-
- Degree of dissociation and association explain why experimental molar mass differs from

normal molar mass.

- It is closely related to van't Hoff factor (i).
- Very important in colligative properties.