SOLUTION & COLLIGATIVE PROPERTIES

COLLIGATIVE PROPERTIES AND DETERMINATION OF MOLAR MASS

COLLIGATIVE PROPERTIES AND DETERMINATION OF MOLAR MASS SOLUTIONS WITH NEGATIVE DEVIATION:

Negative deviation:

In these solutions, the interactions between A and B are more robust than the interactions within the pure A-A and B-B liquids comprising the solution. Due to the heightened A-B interactions, molecules of both A and B exhibit a diminished inclination to escape from the solution compared to their escape from pure liquids. Consequently, following Raoult's law, each component of the solution demonstrates a partial vapor pressure that falls below the anticipated values. The overall vapor pressure in such cases is lower than the vapor pressure that would be projected in an ideal solution with an equivalent composition.

 $H_{mixing} < 0$ for negative deviation

The following are some examples of solutions with positive deviations:

- chloroform and methyl acetate
- ➤ acetic acid and pyridine

COLLIGATIVE PROPERTIES ARE THE PROPERTIES OF DILUTE SOLUTION

Lowering Of Vapour Pressure:

When a non-volatile solute is dissolved in a pristine solvent, the vapor pressure of the solvent decreases, meaning that the vapor pressure of the solution is consistently lower than that of the pure solvent. This is because the escape tendency of solvent molecules diminishes, attributed to the reduced surface area available for evaporation in the solution.

If at a certain temperature P^o is the vapour pressure of pure solvent, and P_s is the vapour pressure of solution then Lowering of vapour pressure = $P^o - P_s$

Relative lowering of vapour pressure = $\frac{P^{o} - P_{s}}{P^{o}}$

from equation (8)

$$\frac{P^0 - P_S}{P^0} = \frac{n_A}{n_A + n_B}$$

for a more dilute solution $n_{\text{A}} < < < n_{\text{B}}$

so

$$\frac{\frac{P^{0}-P_{S}}{P^{0}} = \frac{n_{A}}{n_{B}}}{\frac{\Delta P}{P^{0}} = \frac{P^{0}-P_{S}}{P^{0}} = \frac{n_{A}}{n_{B}}}$$
$$\frac{\Delta P}{P^{0}} = \frac{n_{A}}{n_{B}} \qquad \dots \dots (11)$$
or

relative lowering of vapour pressure

$$= \frac{\mathbf{P}^0 - \mathbf{P}_{\mathsf{S}}}{\mathbf{P}^0} = \frac{\mathbf{n}_{\mathsf{A}}}{\mathbf{n}_{\mathsf{B}}} = \frac{\mathbf{w}_{\mathsf{A}}}{\mathbf{m}_{\mathsf{A}}} \times \frac{\mathbf{m}_{\mathsf{B}}}{\mathbf{w}_{\mathsf{B}}}$$

 \Rightarrow

Chemistry

Ex. Calculate wt. of urea which must be dissolved in 400 gm of water so final solutions has

V.P. 2% less than V.P. of pure water:

Sol. Let V.P be V. of water

$$P^{0} - P_{s} = .02 V$$

$$Ps = 0.98 V$$

$$\frac{0.02}{0.98} = \frac{w}{60} \times \frac{18}{400} \text{ ; where } w = \text{weight of urea.}$$

$$w = \frac{2 \times 60 \times 400}{18 \times 98} \text{ gm}$$

LIMITAIONS OF RAOULT'S LAW:

Raoult's Law is applicable exclusively to ideal solutions, with very dilute solutions adhering to Raoult's Law to a reasonable approximation.

(1) Ideal Solutions:

Ideal solutions are those that adhere to Raoult's law. When the forces of attraction between A-A and B-B are comparable to those between A-B, A and B will constitute an ideal solution



That means that it takes the same amount of energy for solvent molecules to break away from the surface in either case.

Properties of ideal solution:

- (i) Raoult's law is obeyed
- (ii) $\Delta H_{mix} = 0$, i.e., there should not be enthalpy change when components of ideal solutions are mixed.
- (iii) $\Delta V_{mix} = 0$, (1L + 1L = 2L) i.e., there should not be change in volume on mixing. e.g.; n-hexane and n-heptane; ethyl bromide and ethyl iodide; benzene and toluene; chlorobenzene and bromobenzene form ideal solutions.

(2) Non-Ideal Solutions

Those solutions which do not obey Raoult's law are called non-ideal solutions. When the forces of attraction between A — A, B — B is different from A — B then 'A' and 'B' form non-ideal solutions.

For these solutions:

(i) Raoult's law is not obeyed. (ii) $\Delta H_{mix} \neq 0$. (iii) $\Delta V_{mix} \neq 0$.

TYPES OF NON-IDEAL SOLUTIONS

(A) Non-Ideal Solutions Showing Positive Deviation from Raoult's Law

- (i) In this scenario, the partial pressure of each component A and B surpasses the values predicted by Raoult's law, leading to an overall pressure over the solution that is higher than expected for an ideal solution, as illustrated in the figure.
- (ii) The boiling point of such a solution is comparatively lower than the boiling points of both A and B.



Note: Dotted lines depict vapor pressures and total pressure associated with an ideal solution.

Ex.: Water and ethanol, chloroform and water, ethanol and CCl₄, methanol and chloroform, benzene and methanol, acetic acid and toluene, acetone and ethanol, methanol and water, C₂H₅OH + cyclohexane.

Explanation: The elevated vapor pressure observed in these blends indicates that molecules are separating more readily than in their pure liquid forms. This is due to weaker intermolecular forces between molecules of A and B compared to those in the pure liquids. This phenomenon becomes apparent when the liquids are combined. The establishment of new attractions during mixing releases less heat than what was absorbed to break the original interactions. Consequently, heat is absorbed during the mixing of liquids, resulting in an endothermic enthalpy change.

(B) Non-Ideal Solutions Showing Negative Deviation from Raoult's Law

- (i) In this instance, the partial pressure of each component A and B falls below the values predicted by Raoult's law, leading to an overall pressure over the solution that is also lower than expected for an ideal solution, as depicted in the figure.
- (ii) The boiling point of such a solution is comparatively higher than the boiling points of both A and B.



- **Note:** Dashed lines represent vapour pressures and total pressure corresponding to ideal solution
- **Ex.:** chloroform and acetone, chloroform and methyl acetate, water and hydrochloric acid, water and nitric acid, acetic acid and pyridine, chloroform and benzene.

Explanation: In these instances, the molecules exhibit a reduced tendency to separate from the mixture compared to their behavior in pure liquids. The mixture must possess new, stronger forces than those present in the original liquids. This is evident when mixing the liquids, as there is an evolution of heat. More heat is released during the formation of the new, stronger bonds than the amount absorbed in breaking the initial, weaker bonds.

IDEAL SOLUTION	NON - IDEAL SOLUTIONS		
	+ VE DEVIATION FROM	+ VE DEVIATION FROM RAOULTS	
	RAOULTS LAW	LAW	
1. Which follow	Which do not follow	Which do not obey Rault's law	
Raoult's law and at	Raoult's law(i) $P_{T,exp} >$	$(i)P_{T,exp} < (x_A P_A^o + x_A P_B^o)$	
all compositions	$(x_A P_A^o + x_A P_B^o)$		
$P_{T} = X_{A}P_{A}^{o} + X_{a}P_{a}^{o}$ 2. Process of	(ii) $A A = A - B$ B B = A - B	(ii) $\begin{array}{c} AA \\ BB \end{array} > A - B$	
attraction between	Weaker force of attraction	Stronger force of attraction between A-	
A-B are exactly	between A-B than in pure	B thanin pure A-A & B-B	
same as A-A & B-B	A-A & B-B.		
AA = A			
$\mathbf{B} = \mathbf{B} - \cdots - \mathbf{B}$	(11) $\Delta H_{mtc} = +$ ve energy	(111) $\Delta H_{mtc} = -$ ve energy absorbed	
	absorbed	(iv) $\Delta V_{mtc} = -ve (1L + 1L > 2L)$	
$3. \Delta H_{mtc} = 0$	$(iv) \Delta V_{mtc} = + ve (1L + 1L)$	$(v) \Delta S_{mtc} = + ve$	
4. $\Delta V_{\rm mtc} = 0$	> 2L)	$(vi) \Delta G_{mtc} = -ve$	
5. $\Delta S_{mtc} = +$ ve as for	$(v) \Delta S_{mtc} = + ve$		
process to Proceed.	(vi) $\Delta G_{\rm mtc} = - ve$		
6. $\Delta G_{mtc} = -ve$			
eg.	eg.	eg.	
	H_2O+CH_3OH	H ₂ O+HCOOH	

Chemistry

Class-12th

(1) Benzene +	$H_2O+C_2H_5OH$	H_2O+CH_3COOH
Toluene	C ₂ H ₅ OH cyclohexane	H ₂ O+HNO ₃
(2) Hexane + heptane	$CHCl_3 CCl_4 \rightarrow dipole$	CHCl ₃ CH ₃ OCH ₃
(3) $C_2H_5Br + C_2H_5I$	dipole interaction becomes weak	CH_3 $C = OH - C - CI CH_3$ $C = O - H - C - CI $

Azeotropic Mixtures: Significant deviations from ideal behavior result in a distinct category of mixtures referred to as azeotropes, azeotropic mixtures, or constant-boiling mixtures.

Azeotropes: Liquid mixtures that undergo distillation without alterations in composition are termed constant boiling mixtures, azeotropes, or azeotropic mixtures. A boiling liquid mixture at the azeotropic composition generates a vapor with precisely the same composition, and the liquid maintains its composition throughout the evaporation process. Two categories of azeotropes are recognized.

(1) Minimum Boiling Azeotropes:

Non-ideal solutions exhibiting significant positive deviations from Raoult's law give rise to minimum boiling azeotropes, which have boiling points lower than those of their individual components A and B.

Examples include water and benzene, chloroform and methanol. The diagrams below illustrate the temperature vs. composition (at constant pressure) phase diagram on the left side and the pressure vs. composition (at constant temperature) phase diagram for a minimum-boiling azeotropic mixture of chloroform and methanol.

Note: The detailed values in the diagram are not important. Only the qualitative shape of the diagram is important.



At the nadir of the temperature vs. composition phase diagram, the concentration in the vapor phase equals that in the liquid phase (y = x). This concentration is referred to as the azeotropic composition. At this juncture, the mixture boils consistently at a fixed temperature without any alteration in composition.

(2) Maximum Boiling Azeotropes:

Non-ideal solutions displaying substantial negative deviations from Raoult's law give rise to maximum boiling azeotropes, which have boiling points higher than those of their individual components A and B. An example is the mixture of HCl and H₂O. The left side depicts a temperature versus composition phase diagram, while the right side shows a pressure versus composition diagram for the maximum boiling azeotrope.



(3) Separation of Azeotropic Mixtures

Once the azeotropic composition is achieved, the condensate matches the composition of the azeotropic liquid. The vapor phase does not contain a higher concentration of any component than the liquid phase. Consequently, azeotropic mixtures cannot be further separated through distillation beyond the azeotropic composition.

INTRODUCTION OF OSMOSIS AND OSMOTIC PRESSURE: OSMOSIS AND OSMOTIC PRESSURE

Osmosis:

Osmosis is defined as the spontaneous flow of solvent molecules through semipermeable

membrane from a dilute solvent to a solution or from a dilute to a concentrated solution.

Osmotic presssure (π **)**

The hydrostatic pressure developed as a result of osmosis is a measure of osmotic pressure of the solution.

or

The hydrostatic pressure built up on the solution which just stops the osmosis. osmotic pressure = hydrostatic pressure $\pi = hdg$



Chemistry

h = increase in level in the tube of unit cross section.

d = density of solution,

g = acceleration due to gravity

or

The osmotic pressure is the external pressure that needs to be exerted on the solution to halt the flow of the solvent into the solution through a semipermeable membrane.



Reverse Osmosis

If an external pressure greater than the osmotic pressure is applied, the movement of solvent molecules can be directed from the solution toward the pure solvent, essentially reversing the usual osmotic direction. Reverse osmosis is employed for desalinating seawater to obtain fresh drinking water.

Ideal Solutions: An ideal solution is one that precisely follows Raoult's law under all concentrations and temperatures. Key characteristics of an ideal solution include:

- (i) Zero Volume Change of Mixing: The volume change of mixing should be zero; $\Delta V_{mix} = 0$; $V_{solvent} + V_{solute} = V_{solution}$.
- (ii) Zero Heat Change on Mixing: The heat change during mixing should be zero; $\Delta H_{mix} = 0$ (neither absorbed nor evolved).
- (iii) Absence of Chemical Reaction: There should be no chemical reaction between the solvent and solute.
- (iv) Non-Dissociation of Solute Molecules: Solute molecules should not dissociate in the ideal solution.
- (v) Non-Association of Solute Molecules: Solute molecules should not associate in the ideal solution.
- (vi) Adherence to Raoult's Law: An ideal solution must comply with Raoult's law at all concentrations.
- Ex.: (i) Benzene and toluene
 - (ii) Carbon tetrachloride and silicon tetra chloride.
 - (iii) n Hexane and n heptane
 - (iv) Ethylene dibromide and ethylene dichloride.

Non-Ideal solutions

For such solutions:

Those solutions which do not obey Rault's law are called non-ideal solutions.

$$PA \neq P_A^o X_A$$

$$P_B \neq P_B^o X_B$$

Non ideal solutions are formed when the components differ much in their structures and polarities.

$\Delta H_{mixing} \neq zero$

$\Delta V_{mixing} \neq zero$

Non ideal solutions show either positive or negative deviations from Rault's law

WATER PURIFICATION:

Reverse Osmosis (RO) stands out as a pivotal water purification technology. The process involves pushing water through a semi-permeable membrane under pressure to eliminate contaminants, resulting in purified water suitable for consumption. RO is widely utilized, including in the desalination of seawater, making it a dependable source for obtaining potable water. Key features and applications of RO include:

- > The process effectively removes dissolved and suspended impurities, including bacteria.
- > The semi-permeable membrane allows solvent molecules to pass through while preventing the passage of large ions or molecules through its pores.
- > Polymer membranes, particularly cellulose acetate, are employed for desalinating seawater.
- Cellulose acetate, as a semi-permeable membrane, facilitates the passage of water molecules while remaining impermeable to impurities.
- RO technology finds diverse applications in the military, wastewater purification, the food industry, landfill leachate purification, and more.

ABNORMAL MOLAR MASSES:

The calculated molecular masses, derived from the colligative properties of solutions, may deviate from experimentally determined values, leading to what is known as abnormal molar masses. Van't Hoff proposed an explanation for this phenomenon by highlighting the dissociation of solutes into ions when dissolved in a solvent. Since colligative properties rely solely on the number of solute particles, the dissociation of solute molecules into ions increases the particle count, thereby influencing colligative properties.

For instance, when 1 mole of NaCl dissolves in 1 kg of water and fully dissociates, the resulting solution contains 1 mole of Cl^- ions and 1 mole of Na^+ ions, totalling 2 moles of ions. However, in calculating molar mass using colligative properties, only 1 mol of NaCl is considered present in the solution.

Certain substances exhibit association in the aqueous state, leading to fewer ions or molecules in the solution compared to the actual number of molecules. Consequently, for substances that dissociate, the observed molar mass is lower than the actual mass, while for substances that associate, the real mass is lower than the observed molar mass.

The abnormality in molecular mass is explained as follows:

- The dissociation of solute molecules into multiple ions increases the number of particles, subsequently elevating colligative properties.
- As molar mass is inversely proportional to colligative properties, its value tends to be lower than anticipated.
- Conversely, when solute particles associate, the total particle count decreases, resulting in a reduction of colligative properties. In such cases, the observed molar mass values are higher than expected.

VANT'S HOFF'S THEORY OF DILUTE SOLUTION:

The osmotic pressure (P or π) of a solution exhibits a direct proportionality to its concentration (C) at a constant temperature. The concentration of a solution containing one gram mole in V litters is equivalent to 1/V.

thus $P \propto C$ (when temperature is constant)

or

$$1 \propto \frac{P}{V}$$

PV = constant or πV = constant

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Gay - Lussac - Van't Hoff law (Pressure - Temperature law)

Concentration remaining same, the osmotic pressure of a dilute solution directly proportional to its absolute temperature

(T), i.e., P \propto T

or $\frac{P}{T} = consant$ or $\frac{\pi}{T} = consant$

Combining the two laws, i.e., when concentration and temperature both are changing, the osmotic pressure will be given by:

or

$$P \propto C T$$

$$P = kCT$$
or

$$P = k. \frac{1}{v}.T \quad (since, C = \frac{1}{v})$$
or

$$PV = ST \quad or \quad \pi V = ST$$

S is called molar solution constant.

In this context, V represents the volume of the solution containing one gram mole of the solute. The calculated value for S is 0.082 liter atm K^{-1} mol⁻¹, aligning with the value of R, the molar gas constant. If the solution contains n gram moles in V liters, the general equation would be modified as follows:

PV = nST $\pi V = nST$

or

DEPRESSION IN FREEZING POINT OF SOLVENT. (CRYOSCOPY)

The freezing point of a liquid is the temperature at which the liquid and its solid state coexist in equilibrium. Another way to define it is as the temperature at which the liquid and solid states of a substance share the same vapor pressure. When a non-volatile, non-electrolyte is dissolved in a pure solvent, the vapor pressure of the solvent decreases. If T_0 is the freezing point of the pure solvent and $(T_f)_s$ is the freezing point of its solution, then,

$$(T_f)_s < T_o$$

The difference in the freezing point of pure solvent and solution is the depression of freezing point (ΔT_f) Thus,

$$\Gamma_{\rm o} - (T_{\rm f})_{\rm s} = \Delta T_{\rm f}$$

Depression in freezing point is directly proportional to the lowering of vapour pressure of solution.

$$\Delta T_{\rm f} \propto P^0 - P_{\rm s}$$

from Raoult's law for dilute solution:

$$\frac{P^{o} - P_{s}}{P^{o}} = \frac{W_{A}}{m_{A}} \cdot \frac{m_{B}}{W_{B}}$$
$$P^{o} - P_{s} = \frac{W_{A}}{m_{A}} \cdot \frac{m_{B}}{W_{B}}.P$$

for the pure solvent, P⁰ and m_B are constant. therefore –

$$P^{o} - P_{s} \propto \frac{W_{A}}{m_{A}W_{B}}$$
$$\Delta P \propto \frac{W_{A}}{m_{A}W_{B}} \propto \Delta T$$
$$\Delta T_{f} = K \frac{W_{A}}{m_{A}W_{B}}$$

or

or

Where K is a constant, called depression constant.

Chemistry

$$\begin{array}{ll} \mbox{When} \frac{W_A}{m_A} = 1 \mbox{ (one mole of solute)} \\ \mbox{And} & w_B = 1 g. \\ \mbox{Then} & \Delta T_f = K \\ \mbox{If} & \frac{W_A}{m_A} = 1 \mbox{ and } w_B = 100 \mbox{ g} \\ \mbox{Then,} & \Delta T_f = \frac{K}{100} = K' \\ \end{array}$$

K' is called molecular depression constant. It is defined as the depression of freezing point produced when 1 mole of the solute is dissolved in 100 g of the solvent.

Thus K' = 100 K

If

Then

K_f is called molal depression constant.

K_f is defined as the depression of freezing point produced when 1 mole of solute is dissolved in 1000 g of the solvent.

Or
$$\Delta T_{f} = \frac{1000K_{f} \times W_{A}}{m_{A} \times W_{B}}$$
Or
$$\Delta T_{f} = \text{molality} \times K_{f}$$

0r

K_f is characteristic of a particular solvent and can be calculated from the thermodynamical relationship

$$K_{f} = \frac{0.002T_{f}^{2}}{L_{f}}$$

$$\begin{split} \Delta T_{f} &= \frac{100 \text{K}' \times \text{W}_{A}}{\text{m}_{A} \times \text{W}_{B}} \\ \frac{\text{W}_{A}}{\text{m}_{A}} &= 1 \text{ and } \text{w}_{B} = 1000 \text{ g} \\ \Delta T_{f} &= \frac{\text{K}}{1000} = \text{K}_{f} \end{split}$$

Where, T_f is the freezing point of solvent in absolute scale and L_f the latent heat of fusion in calories per gram of the solvent. For water,

$$K_f = \frac{0.002 \times (273)^2}{80} = 1.86$$

the molal depression constant for some common solvents are given in the following table

SOLVENT	F.P.(°C)	MOLAL DEPRESSION SOLVENTS
Water Ethyl alcohol Chloroform Carbon tetra chloride Benzene	0.0	1.86
	- 114.6	1.99
	- 63.5	4.70
	- 22.8	29.80
	5.5	5.12
Camphor	179.0	39.70