Types and Properties of solutions

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Solution: A solution is usually defined as a homogeneous mixture of two or more substances whose composition can be varied over certain ranges.

Dilute solution: If the concentration of the solute in a solution is very low, the solution is called a dilute solution.

Types of solution:

1. Gas in gas
2. Gas in liquid
3. Gas in solid
4. Liquid in liquid
5. Liquid in solid
6. Solid in solid
7. Solid in Liquid

Different unit of concentration:

① % by weight (W)
② Mole fraction (X)
③ Molarity (M)
④ Normality (N)
⑤ Molality
⑥ PPm, PPb, PPt

Unit of concentration: ~~By weight or weight (wt)~~

Molarity ($mol L^{-1}$): The molarity of a solution is the number of moles of the solute dissolved in 1000 mL of the solution.

⇒ If 60 g (1 mole) of urea is dissolved in 1000 mL H_2O solution then Molarity is 1 molar.

Molality: The molality of a solution is the number of moles of the solute dissolved in 1000g of the solvent.

⇒ 60 g urea (1 mole) is dissolved in 1000g H_2O creates 1 mulal solution.

Normality: The number of grams equivalent to solute that is present in a one-liter solution.

Mole fraction: Mole fraction represents the number of molecules of a particular component in a mixture divided by the total number of moles in the given mixture.

$$X_A = \frac{n_A}{n_A + n_B}$$

Liquid-liquid solution: When two liquids are mixed together there is an energy change involved in the system. This is due to the movement of the solvents and solute molecules to form solutions.

⇒ sometimes energy is absorbed and sometimes energy is released.

colligative properties: The word colligative is derived from latine word colligatus that means to bind together or going together.

The essential part of this is that they depend only on the number of solute particle present in solution.

Defn: Those properties of solutions ~~is~~ which depend only upon the total number of molecules of solute

per unit volume and on its chemical nature and being closely related to each other through a common explanation are called colligative properties.

Four main colligative properties of solutions are follows:

① Lowering of vapour pressure.
② Elevation of Boiling point.
③ Depression of freezing point.
④ Somotic pressure.

The colligative properties are widely used for the determined of molecular mass of substances.

Elevation of Boiling point is a colligative property:

The thermodynamic expression of elevation of boiling point given as below:

$$\Delta T_b = \frac{R T_0^2}{L_e} \times X_2$$

$$\Delta T_b = \frac{R T_0^2}{L_e} \cdot \frac{n_2}{n_1} \quad \left[\text{For dilute solution, } X_2 = \frac{n_2}{n_1}\right]$$

From the above equation it is clear that, Boiling points depend only on the number of moles but does not depend on its nature.

Thus, the elevation of boiling point is a colligative property.

The lowering of vapour pressure is colligative property:

According to the Raoult's law for lowering of vapour pressure –

" The relative lowering of vapour pressure of a solvent by a non valatile solute is equale to the molefraction of the solute in solution"

Mathematically it may be written,

$$\frac{P_0 - P}{P_0} = \frac{n_2}{n_1 + n_2}$$

where,

P_0 = Vapour pressure of solvent

P = Vapour pressure of solution

n_1 = mole ~~pressure~~ number of solvent

n_2 = mole number of solution

From the above equation it is clear that the lowering of vapour pressure depends only on the mole number of solute in a solution but independent of its nature. Thus the lowering of vapour pressure is a colligative property.

When are the laws on colligative properties valid?

1. When the solution is dilute.
2. When the solute is non-volatile and non-electrolytes.
3. When the solute in the solution doesn't undergo molecular association and disassociation.
4. When the solution is metal.

What are the causes of deviations of coligative properties in a solution from ideal behaviour?

1. When the concentration of the solution is high, i.e, the solution is concentrated.
2. When the solute in the solution is associated.
3. When the solute in the solution suffers electrolytic disassociation.
4. When the solution is non-metal.

Raoult's law: The statement of Raoult's law is -

"The relative lowering of vapour pressure of a solvent due to the addition of a non volatile and non-electrolyte solute is equal to the mole fraction of the solute present in the solution"

Explanation: If P_0 and P are the vapour pressure of the solvent and the solution respectively, the relative lowering of vapour pressure is $\frac{P_0 - P}{P_0}$. In a solution

containing n_2 moles of solute in n_1 moles of solvent into the mole fraction of the solution is $\frac{n_2}{n_1+n_2}$.

Then according to raoult's law,

$$\frac{P_0-P}{P_0} = \frac{n_2}{n_1+n_2} = x_2$$

where x_2 is the mole of the solute. This is the mathematical expression of Raoult's law.

For very dilute solution, n_2 can be neglected in comparison with n_1 and no Raoult's law takes the form, $\frac{P_0-P}{P_0} = \frac{n_2}{n_1}$

Alternative expression of Raoult's law:

From the mathematical expression of Raoult's law of lowering of vapour pressure, we get,

$$\frac{P_0-P}{P_0} = x_2$$

$$\text{or, } 1 - \frac{P}{P_0} = x_2$$

$$\text{or, } \frac{P}{P_0} = 1 - x_2 \quad \text{---(1)}$$

If x_1 is the mole fraction of solvent and x_2 is that of the single solute, it follows that for a binary solution, $x_1 + x_2 = 1$

$$\text{or, } x_1 = -x_2$$

Now, from equation ① we get,

$$\frac{P}{P_0} = x_1$$

or, $P = P_0 x_1$ —— ②

$\therefore P \propto x_1$

Thus, the vapour pressure of solution is directly proportional to the molefraction of solvent. This is taken as an alternative way of stating Raoult's law.

From eqn ② we get,

The vapour pressure of the solvent over any solution is equal to the vapour pressure of the pure solvent multiplied by the mole fraction of the solvent.

④ Molecular weight from Raoult's law of lowering of vapour pressure:

From Raoult's law, $\frac{P_0 - P}{P_0} = \frac{n_2}{n_1 + n_2} = x_2$

For a dilute solution, $\frac{n_2}{n_1 + n_2}$ may be replaced by $\frac{n_2}{n_1}$ as, n_2 is negligiable,

$$\therefore \frac{P_0 - P}{P_0} = \frac{n_2}{n_1}$$

If w_2 gm of solute of Molecular weight M_2 be present. w_1 gm of solvent of molecular weight M_1 then,

$$\frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1}$$

And the equation becomes,

$$\frac{P_0 - P}{P_0} = \frac{w_2/M_2}{w_1/M_1}$$

By mesing P_0 and P for a solution of known concentration M_2 may be obtained.

Ideal solution: The solution which obey Raoult's law at any temperature and pressure is called ideal solution.

when ideal solution is prepared-

1. It doesn't absorb heat
2. It doesn't evolve heat
3. No volume change occurs.

Thermodynamic criteria of ideal solution:

1. Volume of mixing, $\Delta V_{mix} = 0$
2. Enthalpy of mixing, $\Delta H_{mix} = 0$
3. Entropy of mixing, $\Delta S_{mix} = 0 - \Sigma x_i R \ln x_i$

⇒ When the ideal solution is prepared by two compound A and B. The Intermolecular forces between A-A and B-B and A-B must be same.

Non-ideal solution: A solution which shows deviation from Raoult's law is called non-ideal solution.

Reason of solution may not behave ideally:

1. If the concentration of the solution be high.
2. If the solution is associated or dissociated in solution.

3. If the internal pressure be different in solution.
4. If compound is formed between solvent and solute.

⇒ It doesn't obey Raoult's law. . .

$\therefore \Delta V_{mix} \neq 0$ and $\Delta H_{mix} \neq 0$

V.P composition plots of the system:

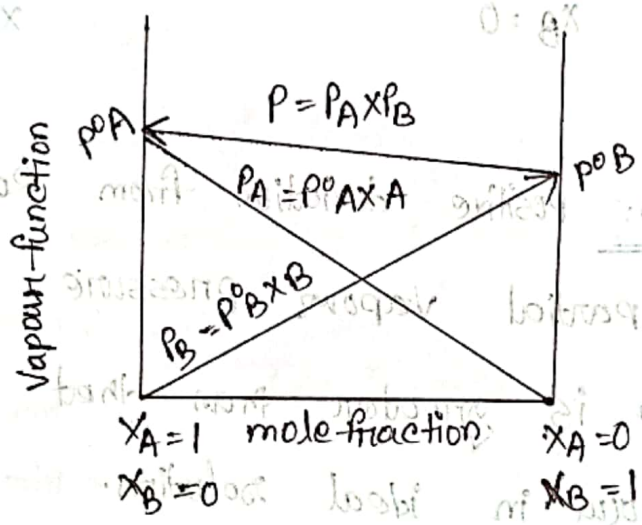
Curve for ideal solution:

$\Delta H_{mix} = 0$

$\Delta V_{mix} = 0$

$\Delta S_{mix} = 0$

A-B = A-A = A=B



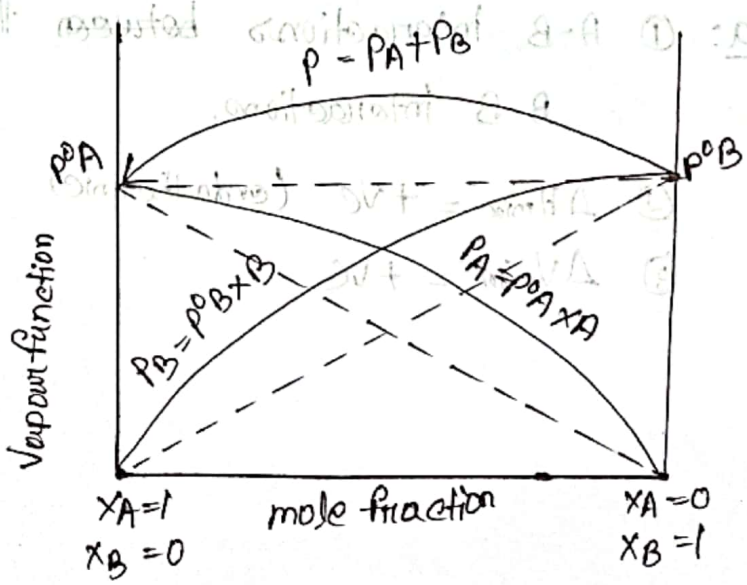
Curve for non ideal solution (positive):

ΔH_{mix} = +Ve

ΔV_{mix} = +Ve

ΔS_{mix} = +Ve

A-B) A-A / B-B



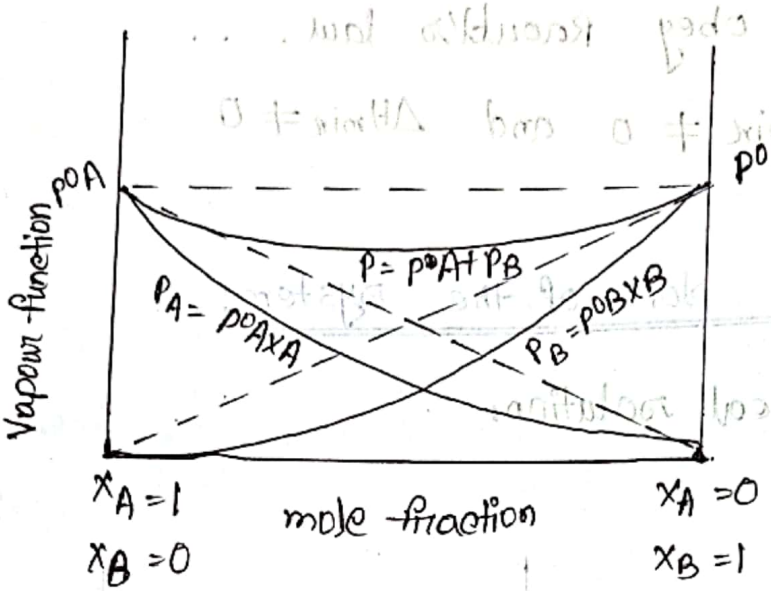
Curve for non-ideal solution (Negative):

$\Delta H_{mix} = -Ve$

$\Delta V_{mix} = -Ve$

$\Delta S_{mix} = -Ve$

$A-B < A-A / B-B$



Positive deviation: Positive deviation from Raoult's law means that partial vapour pressure exerted by a component is greater than that exerted by Raoult's law in ideal solution.

i.e, $P_A > P_A^0 x_A$

Criteria: ① A-B interactions lower than A-A and B-B interactions.

② $\Delta H_{mix} = +Ve$ (endothermic)

③ $\Delta V_{mix} = +Ve$

Physical significance: The positive deviation from the ideal behaviour occurs due to repulsion between solvent and solute molecule mutually and thereby the fugacity of the molecule increases which causes high vapour pressure.

Ex: Aceton- CS_2, C_6H_{12} - CCl_4.

Negative deviation: Negative deviation from Raoult's law means that partial vapour pressure exerted by a component is less than that exerted by the Raoult's law in ideal solution.

i.e, $P_A < P_A^0 \times A$

Criteria: ① A-B interaction is greater than A-A and B-B interactive

② ΔH_{mix} = -ve (exothermic)

③ ΔV_{mix} = -ve

Physical significance: The reason for negative deviation is mutual attraction between solute and solvent molecules. This causes the evaluation of heat and the volume of the mixture decreases and vapour pressure also decreases.

Ex: Acetone- cholofrom

water- Methanol

Henry' law: The mass of gas dissolved by a given volume of solvent, at constant temperature is proportional to the pressure of the gas which it is in equilibrium. If stated mathematically,

$$w \propto p$$
$$\Rightarrow w = kp$$

w = Mass of the gass dissolved in a unit volume of the solvent.

P = Pressure of the gas in equilibrium with the solvent.

K = constant, called henry's law constant.

Application: The influence of partial pressure on salubility is utilized in making carbonated beverages (পানীয়) like beer, champagne and many soft drinks. so called 'soda water' is bottled under a carbon dioxide pressure of about 4 atm. When the bottle is opened to the air, the partial pressure of CO_2 above the solution decreased about 0.01 atm and bubbles out.

Limitations and validity of Henry's law:

1. It is obeyed fairly satisfactorially by many gases of low solubility. provided the pressure is not too high no the temp. is not too low.
2. It holds good for dilute solutions of gases which do not react with solvent.
3. This law is strictly applicable to those gases where the molecular species are the same in the liquid phases.

Nernst distribution law:

If a solute is shaken up with two immiscible liquids in both of which the solute is soluble, then the solution distributes itself between the two liquids in such a way that the ratio of its concentrations in the two liquid phases in constant independent of the amount of the solid or the solvent.

Mathematically, $\frac{c_1}{c_2} = K$ = constant at constant T

$\Rightarrow$ c_1 and c_2 are the molar concentration of the solute in the two phases respectively.

$\Rightarrow$ K = constant called distribution coefficient or partition so called.

"This law is called the Nernst distribution law and Henry's law for gases in a special cases."

→ This law is only valid if no association, dissociation or chemical combination between the solute and

and solvent takes places.

Application: ① The distribution law has been successfully applied to the study of association or dissociation of a solute in a solvent.

② It can be used to determine the equilibrium constant kc for a complex reaction.

$(KI + I_2 \rightleftharpoons KI_3)$

③ It finds numerous applications in the process of extraction (fractional) of a solute from solvent both in the laboratory and in the industry.

④ It can be used to determine the solubilities of a solute.

⑤ It can be used to confirmatory test for bromide and Iodide.

⑥ It can be applied to purify the Lubricating oil.

Limitation :

① The temperature is kept constant throughout the experiment.

② The solution must be dilate.

③ The two solvent must be immiscible.

④ The concentration of the solute are noted after the equilibrium has been reached.