

Types of Solutions

On the basis of Raoult's Law, liquid-liquid solutions are classified into two types of solutions, they are:

- Ideal Solutions
- Non-ideal Solutions

Ideal and Non – Ideal Solutions

The solutions which obey Raoult's law at all compositions of solute in solvent at all temperature are called **ideal solutions**.

Ideal solutions can be obtained by mixing two components with identical molecular size, structure and they should have almost same inter molecular attraction e.g., two liquids A and B form an ideal solution when A –A and B–B molecular attractions will be same and hence A–B molecular attraction will be almost same as A–A and B–B molecular attraction.

An ideal solution should have following characteristics

- ❖ It should obey Raoult's law i.e., the partial pressure of components A and B in a solution will be $p_A = x_A P_A^0$ and $p_B = x_B P_B^0$. Where P_A^0 and P_B^0 are respective vapour pressure in pure form; x_A and x_B are respective mole fractions of components A and B.
- ❖ The enthalpy of mixing of two components should be zero, $\Delta_{mix}H = 0$, i.e. This signifies that no heat is released or absorbed during mixing of two pure components to form an ideal solution
- ❖ The volume of the mixing is equal to zero that is $\Delta_{mix}V = 0$. This means that total volume of solution is exactly same as the sum of the volume of solute and solution. Adding further, it also signifies that there will be contraction or expansion of the volume while the mixing of two components is taking place.
- ❖ The solute-solute interaction and solvent-solvent interaction is almost similar to the solute-solvent interaction.

Examples of Ideal solutions

- Ethyl chloride and ethyl bromide
- n-hexane and n-heptane
- CCl_4 and SiCl_4

Non-ideal solutions

The solution which deviates from ideal behaviour are called **non-ideal solution** or **real solutions** and they do not obey Raoult's law over entire range of composition.

It has been found that on increasing dilution, a non ideal solution tend to be ideal.

For non-ideal solutions,

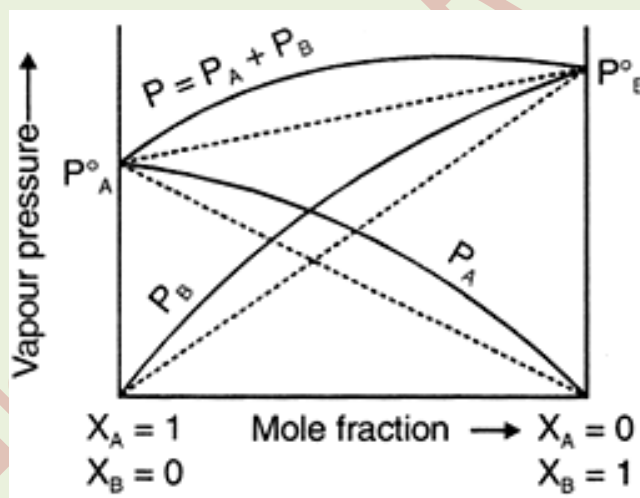
- ❖ $p_A \neq x_A P_A^0$ and $p_B \neq x_B P_B^0$
- ❖ $\Delta_{mix}H \neq 0$
- ❖ $\Delta_{mix}V \neq 0$

Non-ideal solutions are of two types:

- Non-ideal solutions showing **positive deviation** from Raoult's Law
- Non-ideal solutions showing **negative deviation** from Raoult's Law

i) Positive Deviation from Raoult's Law

Positive Deviation from Raoult's Law occurs when the vapour pressure of the component is greater than what is expected in Raoult's Law. For Example, consider two components A and B to form non-ideal solutions. Let the vapour pressure, pure vapour pressure and mole fraction of component A be p_A, P_A^o and x_A respectively and that of component B be p_B, P_B^o and x_B respectively. These liquids will show positive deviation when Raoult's Law when: $p_A > x_A P_A^o$ and $p_B > x_B P_B^o$, as the total vapour pressure ($x_A P_A^o + x_B P_B^o$) is greater than what it should be according to Raoult's Law. The solute-solvent forces of attraction is weaker than solute-solute and solvent-solvent interaction that is, $A - B < A - A$ or $B - B$. The enthalpy of mixing is positive that is, $\Delta_{mix}H > 0$ because the heat absorbed to form new molecular interaction is less than the heat released on breaking of original molecular interaction. The volume of mixing is positive that is, $\Delta_{mix}V > 0$ as the volume expands on the dissolution of components A and B.

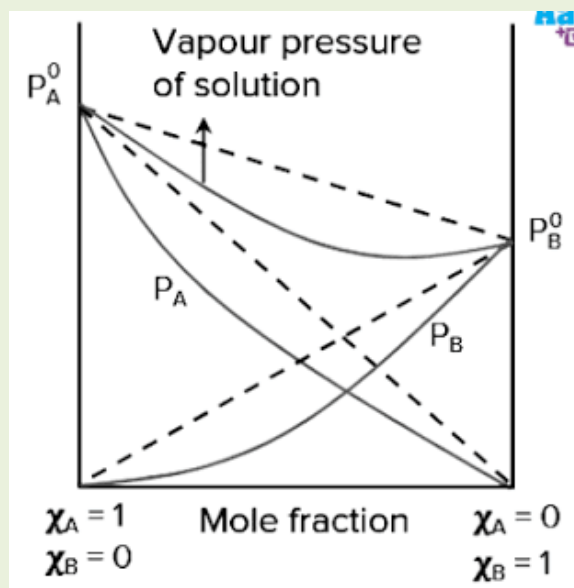


Examples of Positive Deviation

- a. Methyl Alcohol and Water
- b. Acetone and Ethanol
- c. Ethanol and Water

ii. Negative Deviation from Raoult's Law

Negative Deviation occurs when the total vapour pressure is less than what it should be according to Raoult's Law. Considering the same A and components to form a non-ideal solution, it will show negative deviation from Raoult's Law only when: $p_A < x_A P_A^o$ and $p_B < x_B P_B^o$ as the total vapour pressure ($x_A P_A^o + x_B P_B^o$) is less than what it should be with respect to Raoult's Law. The solute-solvent interaction is stronger than solute-solute and solvent-solvent interaction that is, $A - B > A - A$ or $B - B$. The enthalpy of mixing is negative that is, $\Delta_{mix}H < 0$ because more heat is released when new molecular interactions are formed. The volume of mixing is negative that is, $\Delta_{mix}V < 0$ as the volume decreases on the dissolution of components A and B.



Following are examples of solutions showing negative deviation from Raoult's Law.

- Chloroform and Benzene
- Acetone and Aniline
- Nitric Acid (HNO_3) and water
- Acetic Acid and pyridine
- Hydrochloric Acid (HCl) and water

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