Ministry of Higher Education and Scientific Research

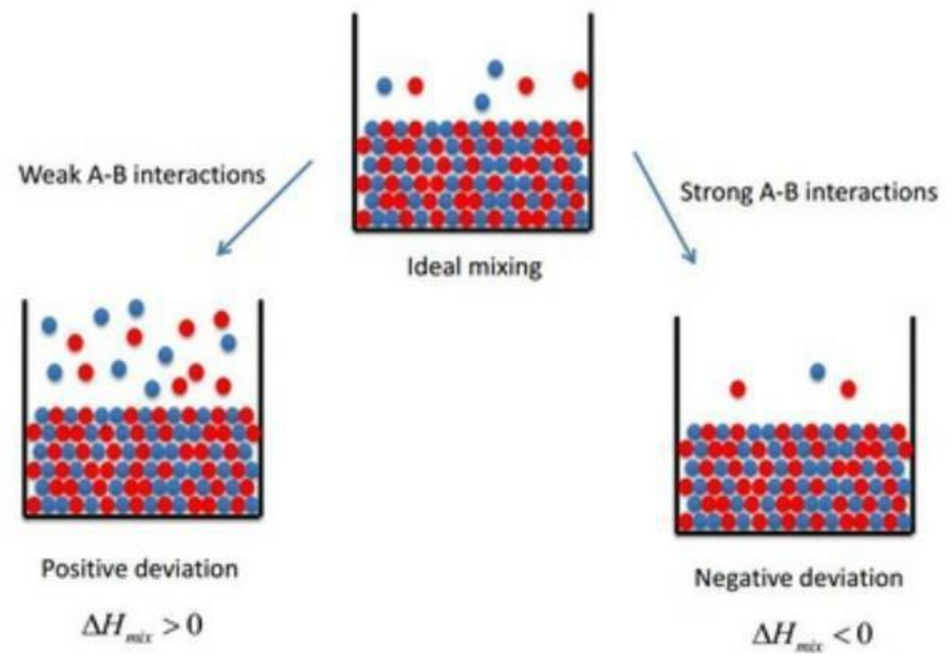
Al-Mustaqbal University College

Chemical engineering and petroleum industries

Physical chemistry

Ideal Solutions

The solutions which obey Raoult's Law at every range of concentration and at all temperatures are Ideal Solutions. We can obtain ideal solutions by mixing two ideal components that are, solute and a solvent having similar molecular size and structure.



For Example, consider two liquids A and B, and mix them. The formed solution will experience several intermolecular forces of attractions inside it, which will be:

- A – A intermolecular forces of attraction
- B – B intermolecular forces of attraction
- A – B intermolecular forces of attraction

The solution is said to be an ideal solution, only when the intermolecular forces of attraction between A – A, B – B and A – B are nearly equal.

Characteristics of Ideal Solutions

Ideal Solutions generally have characteristics as follows:

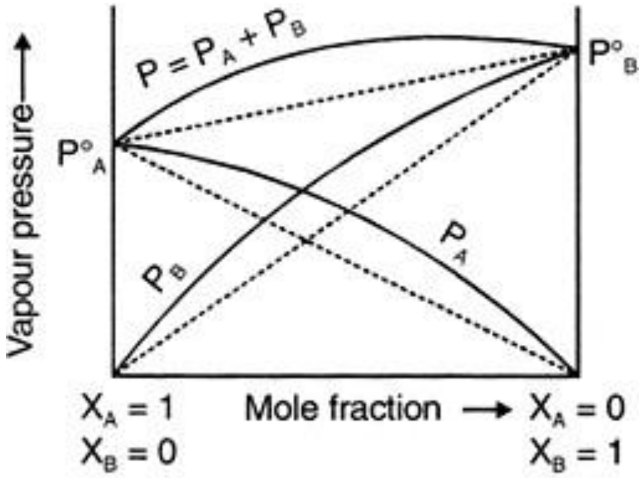
- They follow Raoult's Law. This implies that the partial pressure of components A and B in a solution will be $P_A = P_A^0 \; x_A$ and $P_B = P_B^0 \; x_B$. P_A^0 and P_B^0 are respective vapour pressure in pure form. On the other hand, x_A and x_B are respective mole fractions of components A and B.
- The enthalpy of mixing of two components should be zero, that is, $\Delta_{mix} H = 0$. 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

- n-hexane and n-heptane
- Bromoethane and Chloroethane
- Benzene and Toluene
- CCl4 and $SiCl_4$
- Chlorobenzene and Bromobenzene
- Ethyl Bromide and Ethyl Iodide
- n-Butyl Chloride and n-Butyl Bromide

Non-Ideal Solutions

The solutions which don't obey Raoult's law at every range of concentration and at all temperatures are Non-Ideal Solutions. Non-ideal solutions deviate from ideal solutions and are also known as Non-Ideal Solutions.



P-X graph for non-ideal solution showing +ve deviation

Characteristics of Non-ideal Solutions

Non-ideal solutions depict characteristics as follows:

- The solute-solute and solvent-solvent interaction is different from that of solute-solvent interaction.
- The enthalpy of mixing that is, $\Delta_{mix}H \neq 0$, which means that heat might have released if enthalpy of mixing is negative ($\Delta_{mix}H < 0$) or the heat might have observed if enthalpy of mixing is positive ($\Delta_{mix}H > 0$).
- The volume of mixing that is, $\Delta_{mix}V \neq 0$, which depicts that there will be some expansion or contraction in the dissolution of liquids.

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^0 and x_A respectively and that of component B be P_B , P_B^0 and x_B respectively. These liquids will show positive deviation hen Raoult's Law when:

- $P_A > P_A^0\, x_A$ and $P_B > P_B^0\, x_B$, as the total vapour pressure ($P_A^0\, x_A + P_B^0\, x_B$) 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

Following are examples of solutions showing positive deviation from Raoult's Law:

- Acetone and Carbon disulphide
- Acetone and Benzene
- Carbon Tetrachloride and Toluene or Chloroform
- Methyl Alcohol and Water
- Acetone and Ethanol
- 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:

- $P_A < P_A^0 x_A$ and $P_B < P^0{}_B x_B$ as the total vapour pressure ($P^0_A x_A + P^0_B x_B$) 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
- Chloroform and Diether
- Acetone and Aniline
- Nitric Acid (HNO_3) and water
- Acetic Acid and pyridine
- Hydrochloric Acid (HCl) and water