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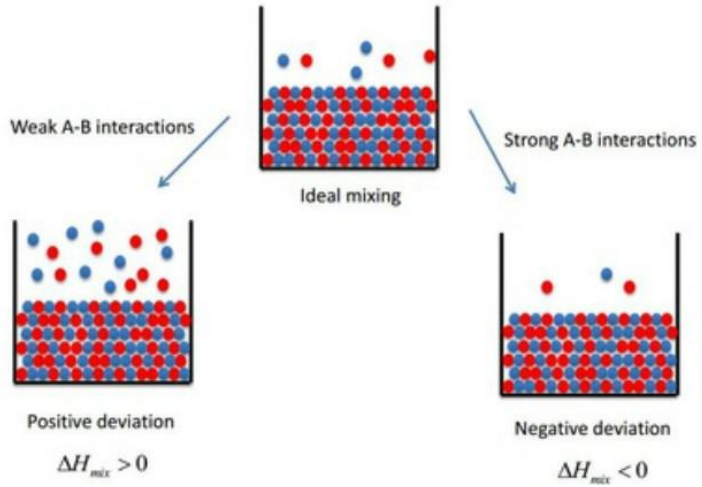
Physical Pharmacy

Non-electrolytes 2

Nonelectrolytes

Ideal and Real Solutions: Ideality

- Ideality in a gas implies the complete absence of attractive forces, and ideality in a solution means complete uniformity of attractive forces
- Because a liquid is a highly condensed state, it cannot be expected to be devoid of attractive forces.
- That is mean, in a mixture of A and B molecules, the forces between A and A, B and B, and A and B are all of the same order, the solution is considered to be ideal according to the definition just given



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Ideal and Real Solutions: Ideality

- **Ideal solution has the following properties :**

1)

a. There is no change in the properties of the components, other than dilution, when they are mixed to form the solution.

2)

a. No heat is evolved or absorbed during the mixing process, and the final volume of the solution represents an additive property of the individual constituents.

b. Stated another way, no shrinkage or expansion occurs when the substances are mixed.

c. Mixing substances with similar properties forms ideal solutions.

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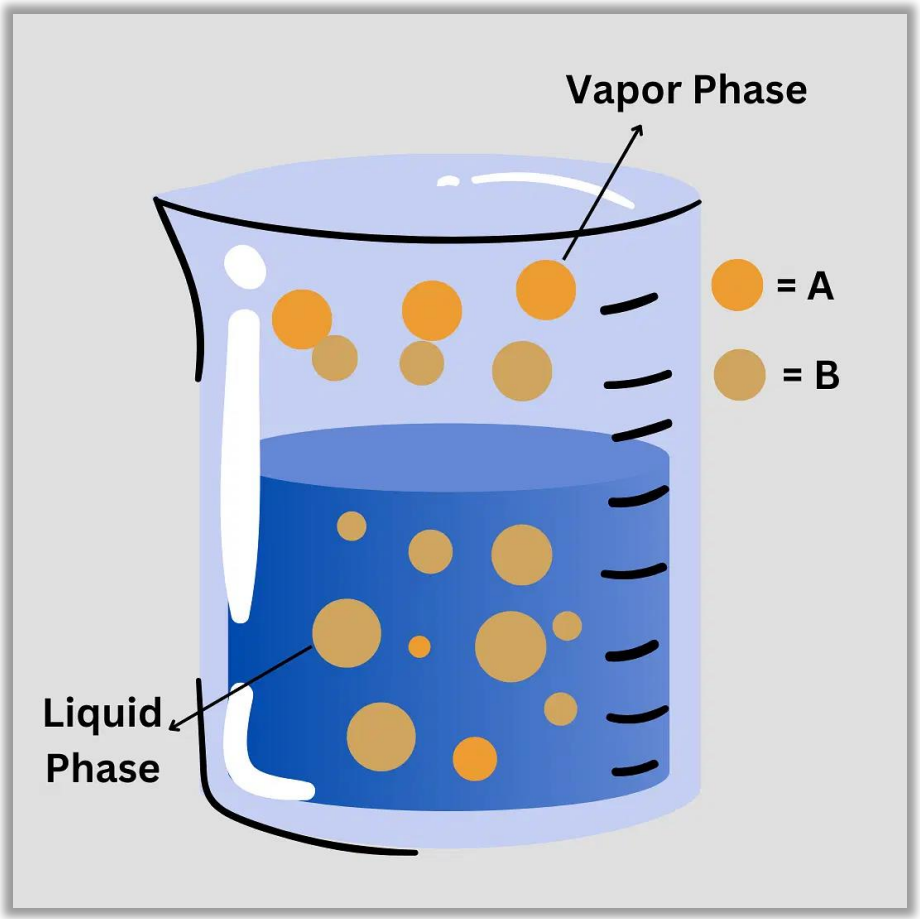
Ideal and Real Solutions: Ideality



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Ideal and Real Solutions: For example,

- when 100 mL of methanol is mixed with 100 mL of ethanol, the final volume of the solution is 200 ml, and no heat is evolved or absorbed, **The solution is nearly ideal.**
- When 100 mL of sulfuric acid is combined with 100 ml of water, however, the volume of the solution is about 180 ml at room temperature, and the mixing is attended by a considerable evolution of heat; the solution is said to be **non -ideal (real)**
- When 100 mL of water is mixed with 100 ml of ethanol, the final volume of thesolution is less than 200 ml ; the solution is said to be **non ideal**

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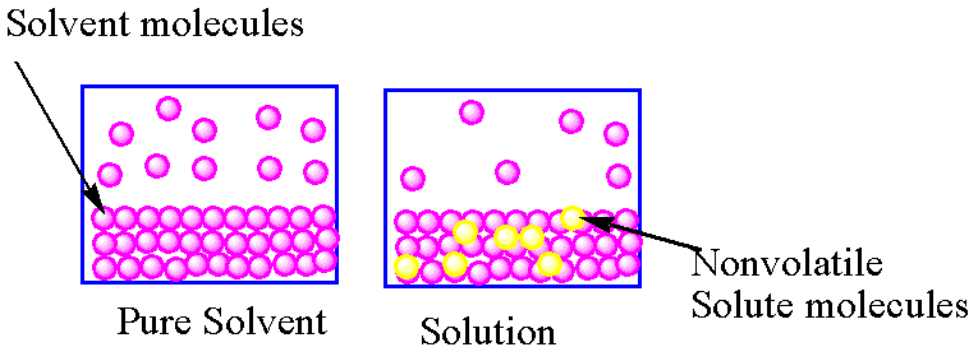
Ideal Solutions and Raoult's Law

- The vapor pressure of a solution is a particularly important property because it serves as a quantitative expression of escaping tendency.

- **Raoult's Law:-** In an ideal solution, the partial vapor pressure of each volatile constituent is equal to the vapor pressure of the pure constituent multiplied by its mole fraction in the solution.



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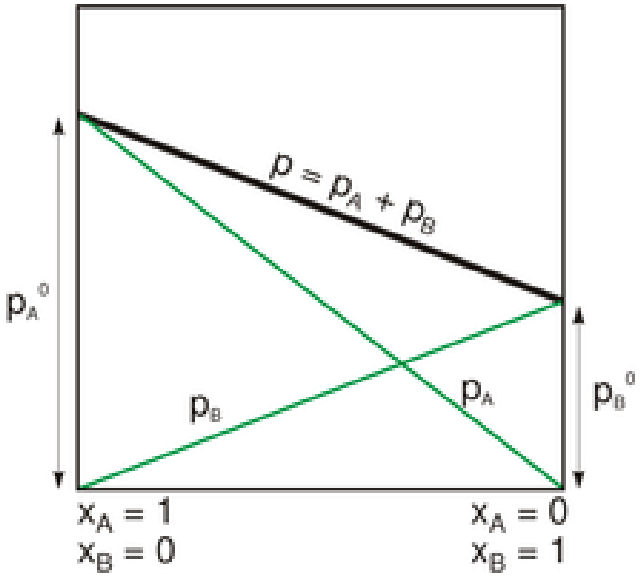
Ideal Solutions and Raoult's Law

- Thus, for two constituents **A** and **B**:-

$$P_A = p_A^\circ \cdot X_A \qquad P_B = p_B^\circ \cdot X_B \qquad P_{Total} = P_A + P_B$$

- Where pA and pB are the partial vapor pressures of the constituents over the solution when the mole fraction concentrations are XA and XB, respectively.

- The vapor pressures of the pure components are **pA°** and **pB°**, respectively.



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Ideal Solutions and Raoult's Law : Example

What is the partial vapor pressure of benzene and of ethylene chloride in a solution at a mole fraction of benzene of 0.6? ,The vapor pressure of pure benzene at 50°C is 268 mm, and the corresponding pA° for ethylene chloride is 236 mm, and what will be the total vapor pressure?

$P_B = P_B^\circ \cdot X_B \longrightarrow\longrightarrow$ 268 x 0.6 = 160.8mmHg (for benzene

XA = 1-0.6 =0.4

$P_A = P_A^\circ \cdot X_A \longrightarrow\longrightarrow$ 236 x 0.4 = 94.4 mmHg (for benzene

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Ideal Solutions and Raoult's Law

- Thus, in an ideal solution, when liquid A is mixed with liquid B, the vapor pressure of A is reduced by dilution with B in a manner depending on the mole fractions of A and B present in the final solution, **Why?**

- This because mixing will diminish the escaping tendency of each constituent, leading to a reduction in the rate of escape of the molecules of A and B from the surface of the liquid

- The vapor pressure–composition curve for the binary system (for example benzene and ethylene chloride at 50°C)is shown in the following Figure.

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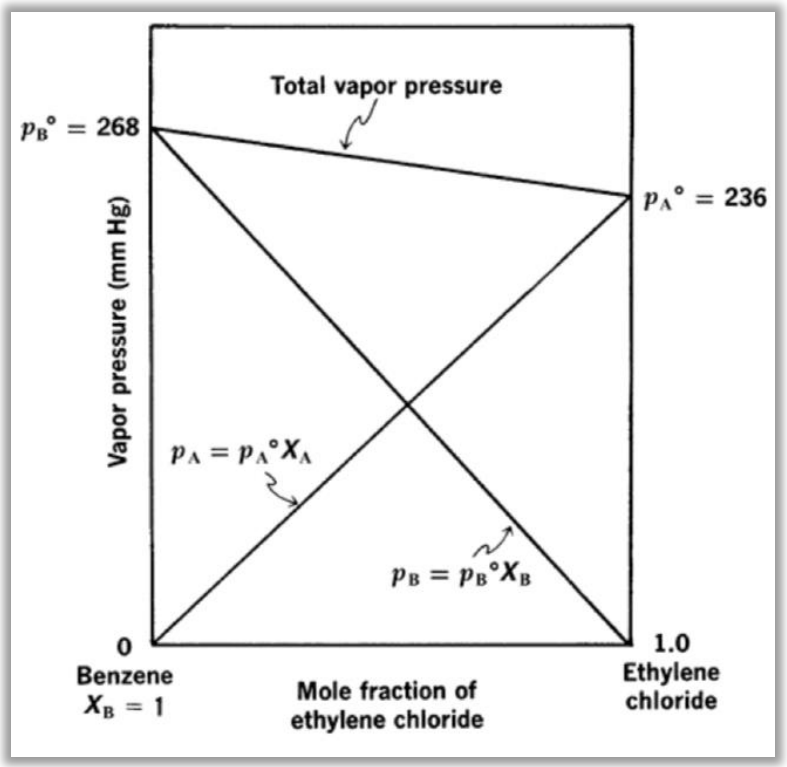
Fig. 5-1. Vapor pressure-composition curve for an ideal binary system

- The three lines represent the partial pressure of ethylene chloride, the partial pressure of benzene, and the total pressure of the solution as a function of the mole fraction of the constituents.



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Ideal Solutions and Raoult's Law : Example

The vapor pressure of pure Butane PB°= 2.3966 atm. At 25oC and that of n-pentane Pp°= 0.6999atm. At 25 oC. Using Raoult's Law:- Calculate the partial vapor pressure of Butane (Mwt= 58.12) and n-pentane (Mwt= 72. 15) in a mixture of 50 g. of each of these two vapors at 25oC and the total vapor pressure

Answer:

$P_B = P_B^\circ \cdot X_B$

$$XB = \frac{nB}{nB + nP}$$

$$nB = \frac{WtB}{MwtB}$$

$$nB = \frac{50}{58.12} = 0.86$$

$$XB = \frac{0.86}{0.86+0.693} = \frac{0.86}{1.553} = 0.554$$

$$PB = 2.3966 \text{ x } 0.554 = 1.328 \text{ atm (reduced)}$$

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Ideal Solutions and Raoult's Law : Example

The vapor pressure of pure Butane pB°= 2.3966 atm. At 25oC and that of n-pentane pP°= 0.6999atm. At 25 oC. Using Raoult's Law:- Calculate the partial vapor pressure of Butane (Mwt= 58.12) and n-pentane (Mwt= 72. 15) in a mixture of 50 g. of each of these two vapors at 25oC and the total vapor pressure

$P_P = P_P^\circ \cdot X_P$

$$XA = \frac{np}{nB + nP}$$

$$nP = \frac{Wtp}{Mwtp}$$

$$nP = \frac{50}{72.15} = 0.693$$

$$Xp = 1 - 0.554 = 0.446$$

$$Pp = 0.6999x\ 0.4461 = 0.312atm\ (\text{reduced})$$

$$P\ total = 1.328 + 0.312 = 1.640atm$$

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Real Solutions (Most solution) :

- **In a mixture of A and B:-**

A-A (Cohesive forces) , B-B(Cohesive forces), A-B(Adhesive forces)

- If the Cohesive forces = Adhesive forces ⟶ No change in the physical properties
  ⟶ Ideal solution

- But if Adhesive forces More than Cohesive forces OR Cohesive forces More than Adhesive forces

  ⟶ ⟶ Change in physical properties

  ⟶ ⟶ Non- Ideal Or Real solution

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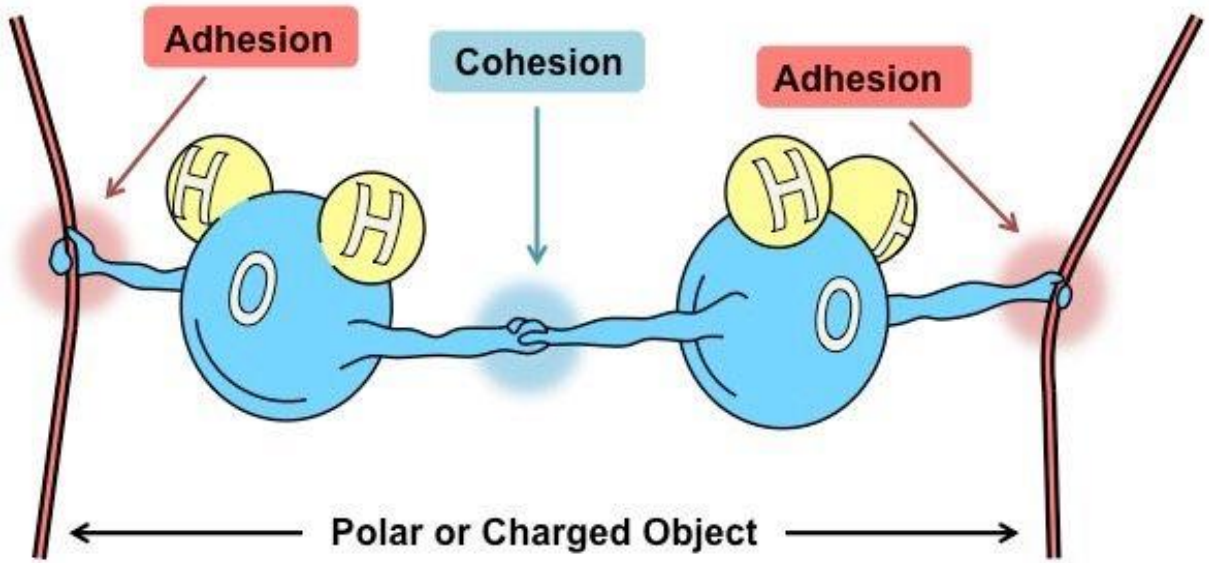
Adhesive forces More than Cohesive forces

- The components will stick to each other, and this will reduce the escaping tendency ofeach constituent, so they will not easily vaporize and the vapor pressure of the solution is less than that expected from Raoult's ideal solution law, and Negative Deviation occurs.



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1-Adhesive forces More than Cohesive forces

- This may occur whene the liquids are miscible in all proportion.
- (**Ex**. water and alcohol)
- This can be observed in the following Figure:-

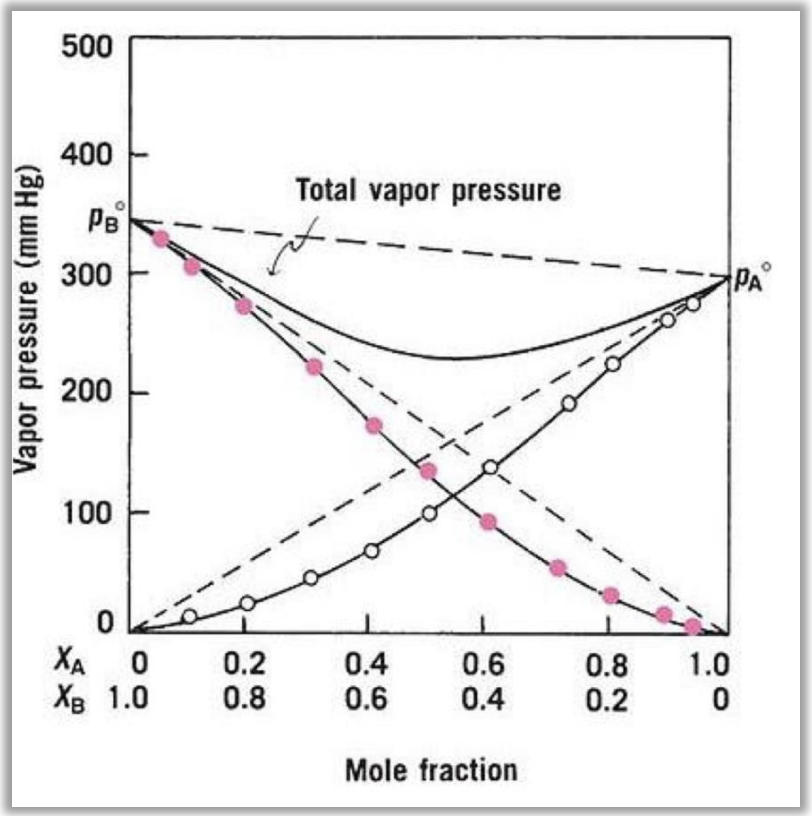

Fig. 5-2. Vapor pressure of a system showing negative deviation from Raoult's law.

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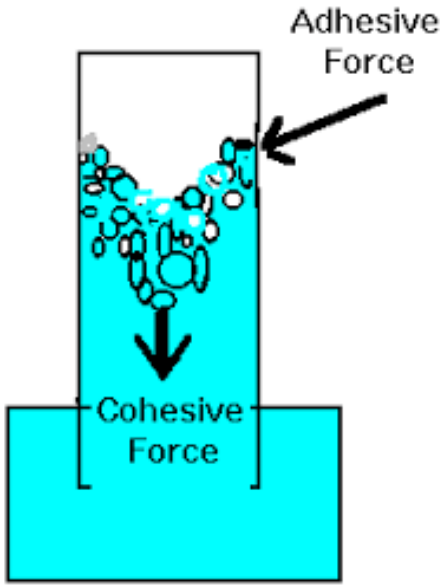
2- Cohesive forces More than Adhesive forces

- The components will repeal each other, this will results in a greater escaping tendency of each constituents, so they will easily vaporize and the partial vapor pressure of the constituents is greater than that expected from Raoult's law, and the system is said to exhibit positive deviation



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2- Cohesive forces More than Adhesive forces

- So in system of A and B the presence of B molecules reduces the interaction of the A molecules, and A molecules correspondingly reduce the B—B interaction

- This may occur whene the constituents have different polarities and immiscible with each other

- **Ex:** benzene and ethyl alcohol and chloroform and ethyl alcohol.

- This can be observed in the following Figure:-

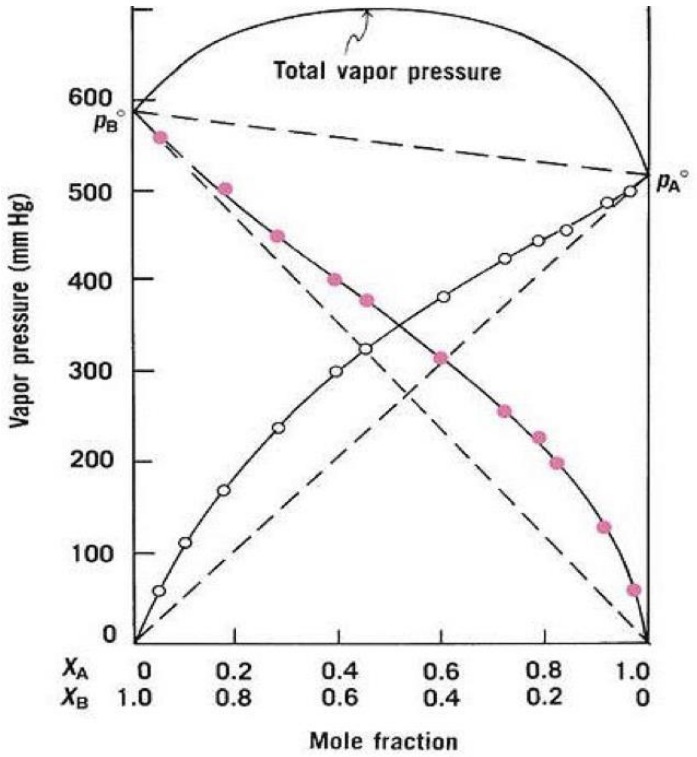

Fig. 5-3. Vapor pressure of a system showing positive deviation from Raoult's

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2- Cohesive forces More than Adhesive forces : Note:-

- Comparing actual measured vapor pressure to the predicted values from Raoult's law allows information about the relative strength of bonding between liquids to be obtained.

- If the measured value of the vapor pressure is less than expected value , this mean there is fewer molecules left the solution because the strength between the liquids molecules is greater than the bonding within the individual liquid and visa versa

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Thank You !

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