

Properties of Solutions

Raoult's Law

Raoult's Law

The presence of a nonvolatile solute lowers the vapor pressure of the solvent.

$$P_{\text{solution}} = \chi_{\text{solvent}} P_{\text{solvent}}^0$$

P_{solution} = Observed Vapor pressure of the solution

χ_{solvent} = Mole fraction of the solvent

P_{solvent}^0 = Vapor pressure of the pure solvent

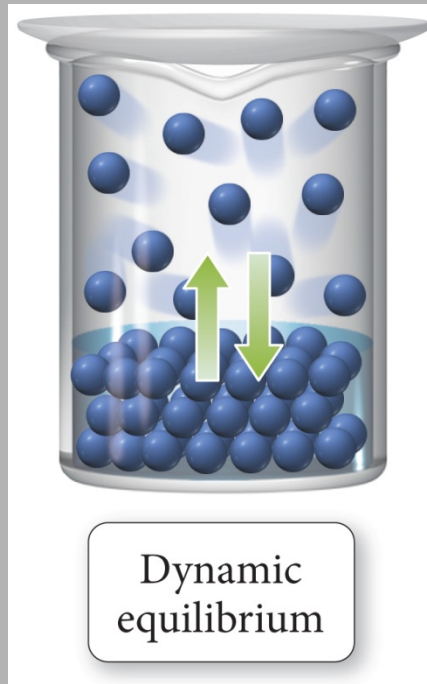
Vapor Pressure Lowering

- The vapor pressure of a solvent in a solution is always lower than the vapor pressure of the pure solvent.
- The vapor pressure of the solution is directly proportional to the amount of the solvent in the solution.
- The difference between the vapor pressure of the pure solvent and the vapor pressure of the solvent in solution is called the **vapor pressure lowering**.

$$\Delta P = P^{\circ}_{\text{solvent}} - P_{\text{solution}} = \chi_{\text{solute}} \cdot P^{\circ}_{\text{solvent}}$$

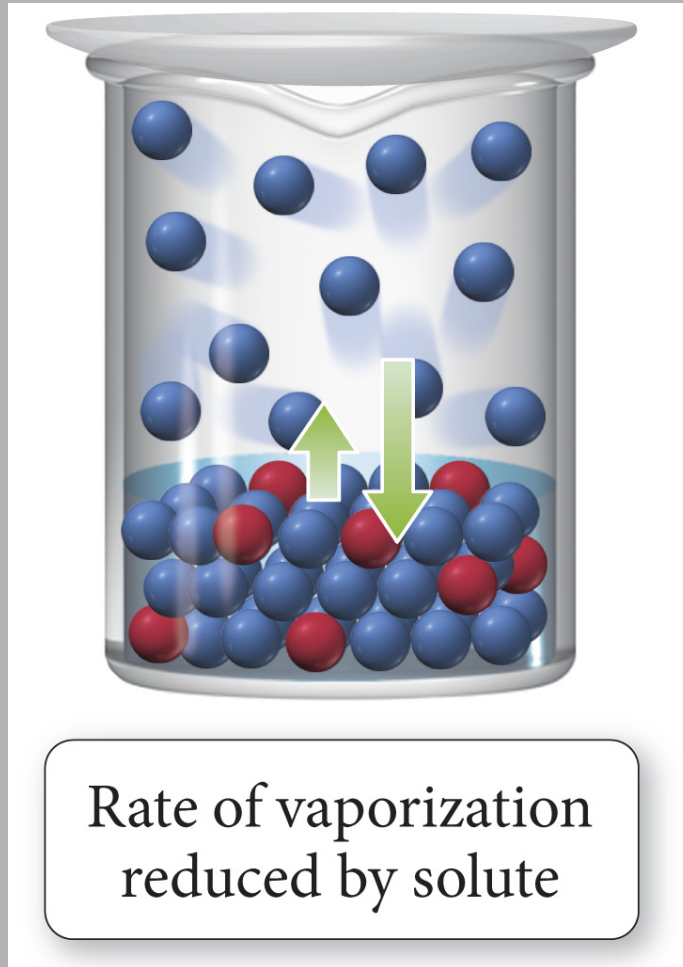
Vapor Pressure of Solutions

- The vapor pressure of a solvent above a solution is lower than the vapor pressure of the pure solvent.
 - The solute particles replace some of the solvent molecules at the surface.
 - The pure solvent establishes a liquid vapor equilibrium.



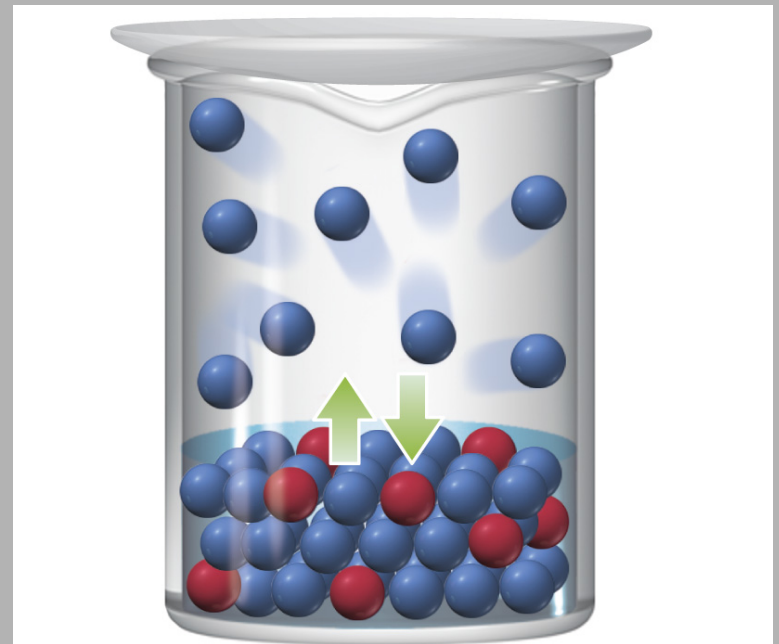
Vapor Pressure of Solutions

- Addition of a nonvolatile solute reduces the rate of vaporization, decreasing the amount of vapor.



Vapor Pressure of Solutions

- Eventually, equilibrium is re-established, but with a smaller number of vapor molecules; therefore, the vapor pressure will be lower.



Equilibrium reestablished
but with fewer molecules
in gas phase

Liquid-liquid solutions in which both components are volatile (Non-Ideal)

Modified Raoult's Law:

$$P_{TOTAL} = P_A + P_B = \chi_A P_A^0 + \chi_B P_B^0$$

P^0 is the vapor pressure of the pure solvent

P_A and P_B are the partial pressures

Ideal Sol'n

- 1. **Liquid-liquid** solution that obeys Raoult's law
 - a. No solution is perfectly ideal, though some are close
- 2. **Negative deviations** from Raoult's law (lower than predicted vapor pressure for the solution)
 - a. Solute and solvent are similar, with strong forces of attraction
 - b. $\Delta H_{\text{sol'n}}$ is large and negative
- 3. **Positive deviations** from Raoult's law (higher than predicted vapor pressure for the solution)
 - a. Solute and solvent are dissimilar, with only weak forces of attraction
 - b. Particles easily escape attractions in solution to enter the vapor phase

Ideal versus Nonideal Solution

- In ideal solutions, the made solute–solvent interactions are equal to the sum of the broken solute–solute and solvent–solvent interactions.
 - Ideal solutions follow Raoult's law
- Effectively, the solute is diluting the solvent.
- If the solute–solvent interactions are stronger or weaker than the broken interactions the solution is nonideal.

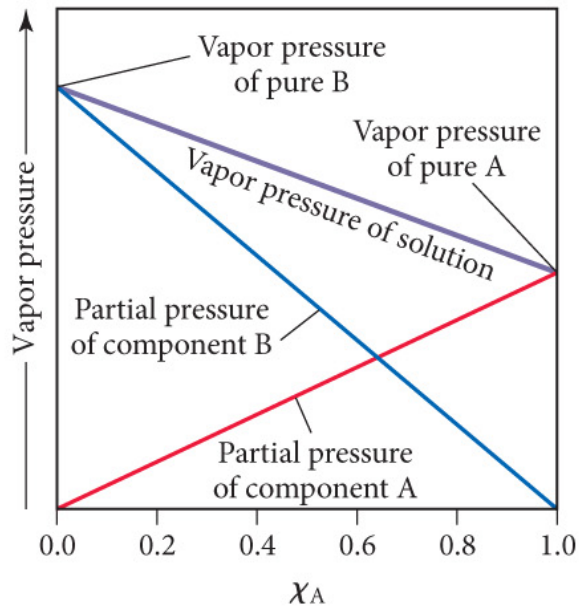
Vapor Pressure of a Non-ideal Solution

- When the solute–solvent interactions are stronger than the solute–solute + solvent–solvent, the total vapor pressure of the solution will be less than predicted by Raoult's law, because the vapor pressures of the solute and solvent are lower than ideal.
- When the solute–solvent interactions are weaker than the solute–solute + solvent–solvent, the total vapor pressure of the solution will be more than predicted by Raoult's Law.

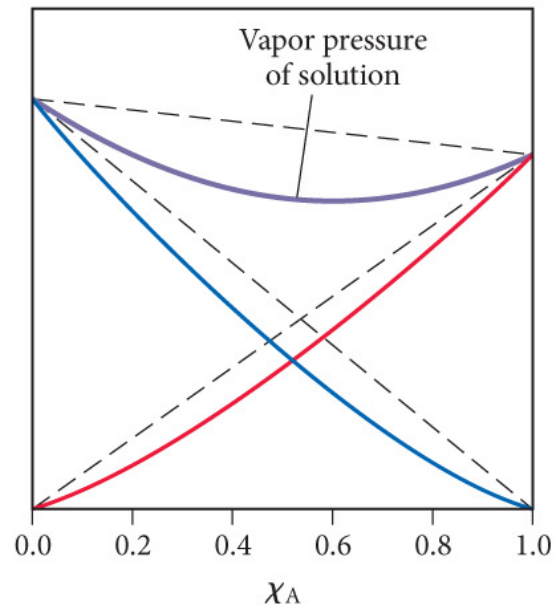
Deviations from Raoult's Law

Deviations from Raoult's Law

(a) Ideal solution



(b) Strong solute-solvent interactions



(c) Weak solute-solvent interactions

