

N33 - 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.

VP of the solution is directly proportional to the amount of the solvent in the solution.

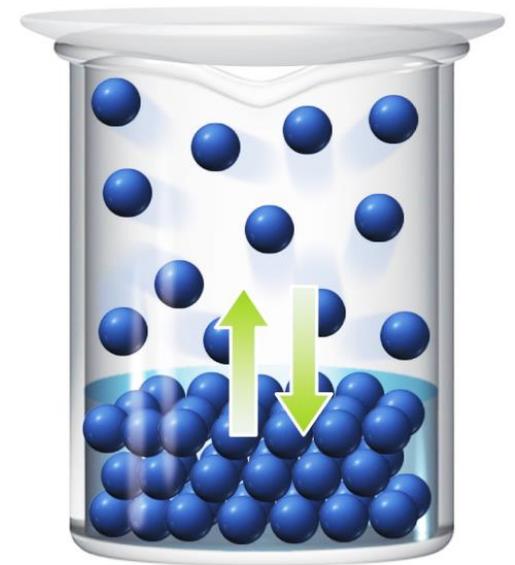
Vapor Pressure Lowering - The difference between the VP of the pure solvent and the VP of the solvent in solution

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

Vapor Pressure of Solutions

The VP of a solvent above a solution is lower than the VP of the pure solvent.

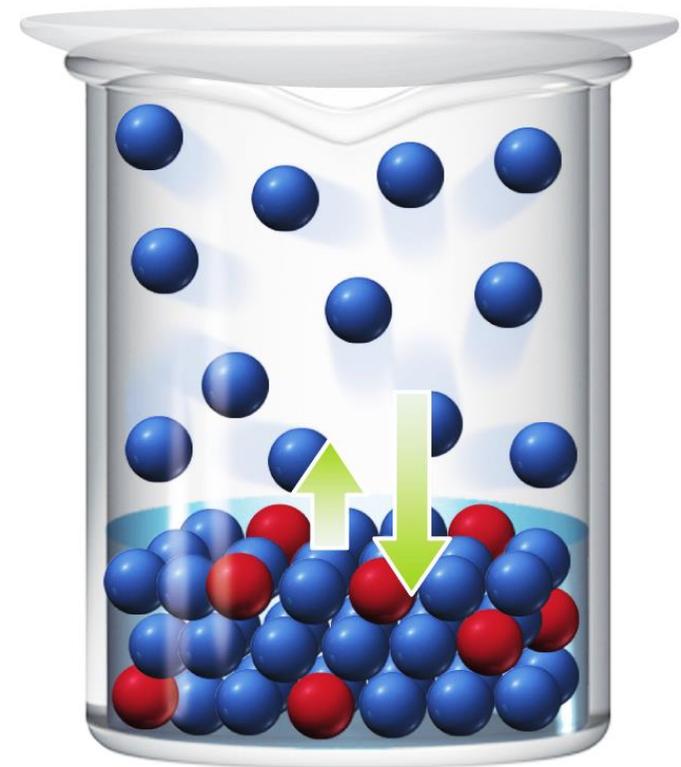
- The solute particles replace some of the solvent molecules at the surface.
- The pure solvent establishes a **dynamic liquid vapor equilibrium.**



Dynamic
equilibrium

Vapor Pressure of Solutions

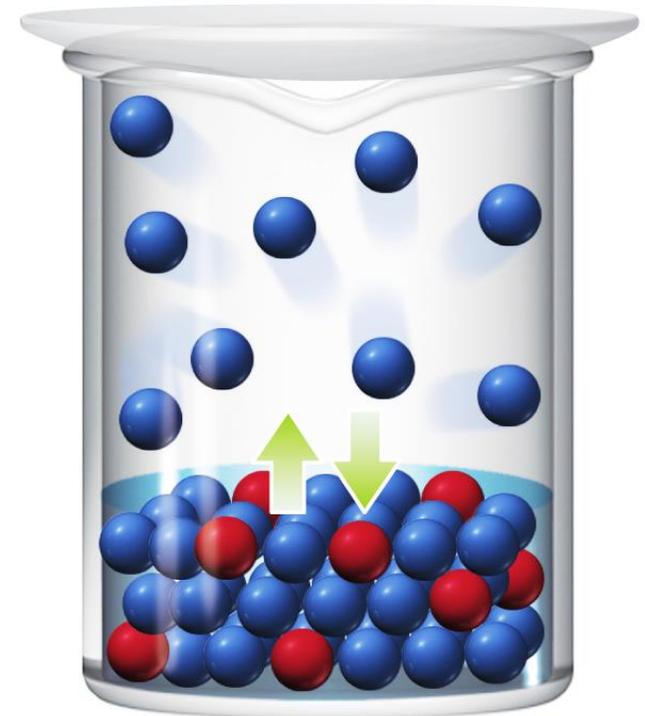
Addition of a nonvolatile solute reduces the rate of vaporization, decreasing the amount of vapor.



Rate of vaporization
reduced by solute

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

Non-Ideal Liquid-Liquid Solutions

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

Modified Raoult's Law:

$$P_{total} = P_A + P_B = \chi_A P_A^\circ + \chi_B P_B^\circ$$

P° is the vapor pressure of the pure solvent

P_A and P_B are the partial pressures

Ideal Solutions

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

Ideal versus Non-Ideal Solutions

- **Ideal solutions**
 - **Solute–Solvent interactions being made 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 Non-Ideal Solutions

Negative Deviations

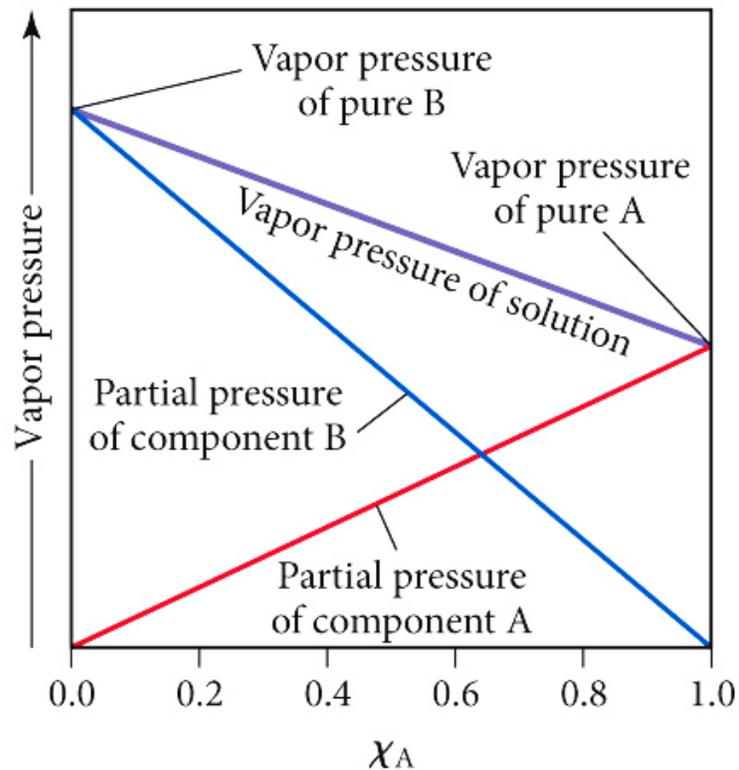
Solute–Solvent interactions are stronger than the Solute–Solute + Solvent–Solvent, **Total VP of the solution will be less than predicted** by Raoult's law, because the VP of the solute and solvent are lower than ideal.

Positive Deviations

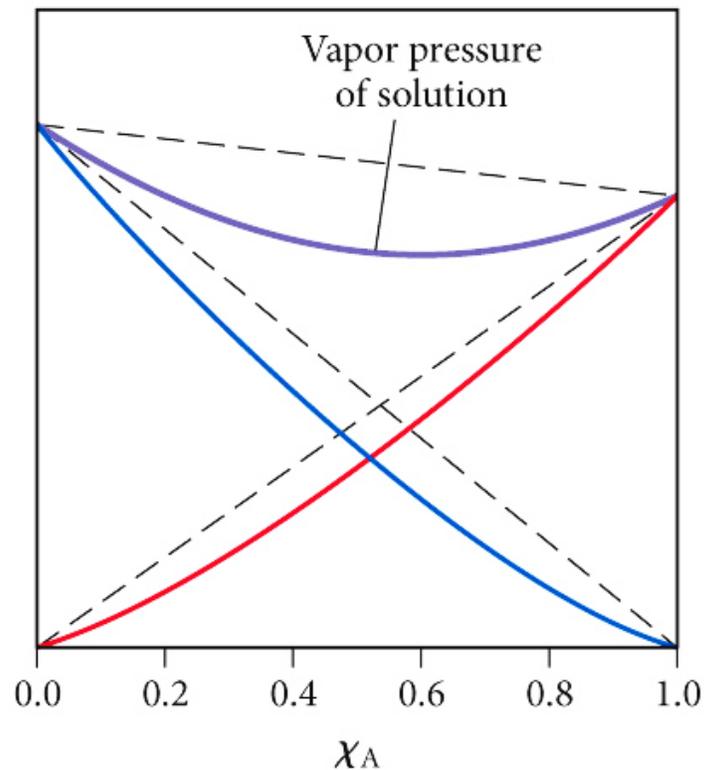
Solute–Solvent interactions are weaker than the Solute–Solute + Solvent–Solvent. **Total VP of the solution will be more than predicted** by Raoult's Law.

Deviations from Raoult's Law

**IDEAL SOL'N
NO DEVEATION**



**STRONG
SOLUTE-SOLVENT
ATTRACTIONS
NEGATIVE DEV.**



**WEAK
SOLUTE-SOLVENT
ATTRACTIONS
POSITIVE DEV.**

