

# **N33 - SOLUTIONS**

## **Raoult's Law**

# Raoult's Law

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

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

$P_{\text{solution}}$  = Observed Vapor pressure of the solution

$\chi_{\text{solvent}}$  = Mole fraction of the solvent

$P_{\text{solvent}}^0$  = 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.

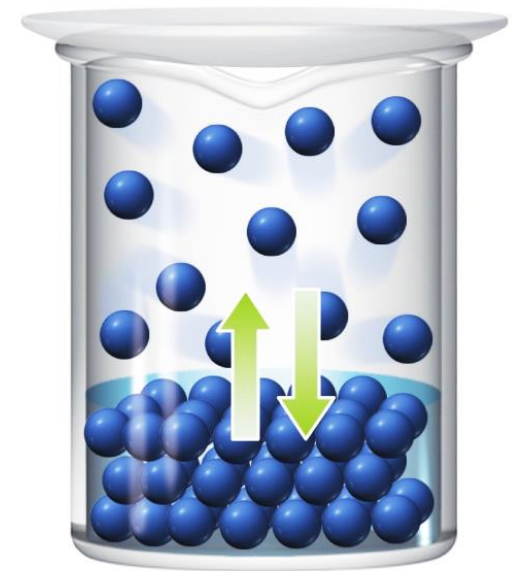
**Vapor Pressure Lowering** - The difference between the VP of the pure solvent and the VP of the solvent in solution

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

# Vapor Pressure of Solutions

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

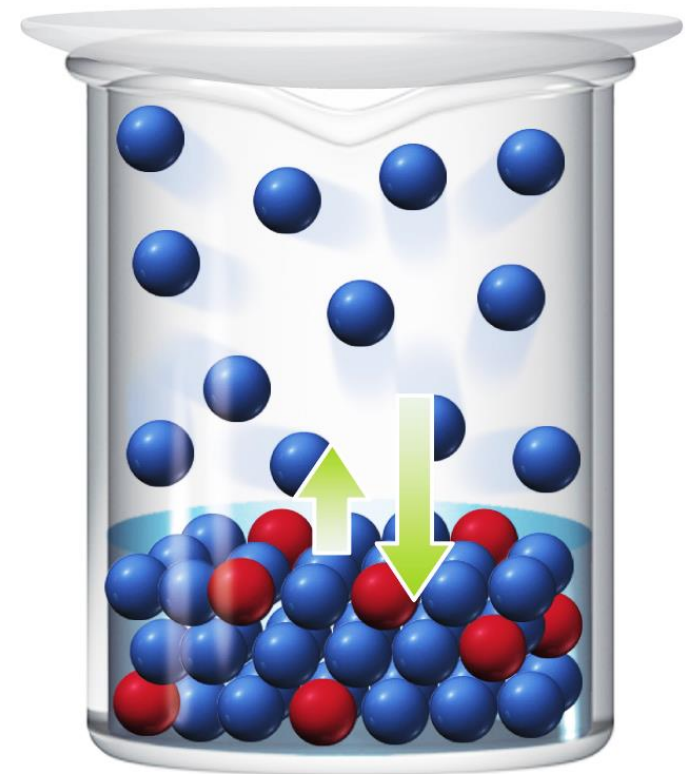
- The solute particles replace some of the solvent molecules at the surface.
- The pure solvent establishes a **dynamic liquid vapor equilibrium.**



Dynamic  
equilibrium

# Vapor Pressure of Solutions

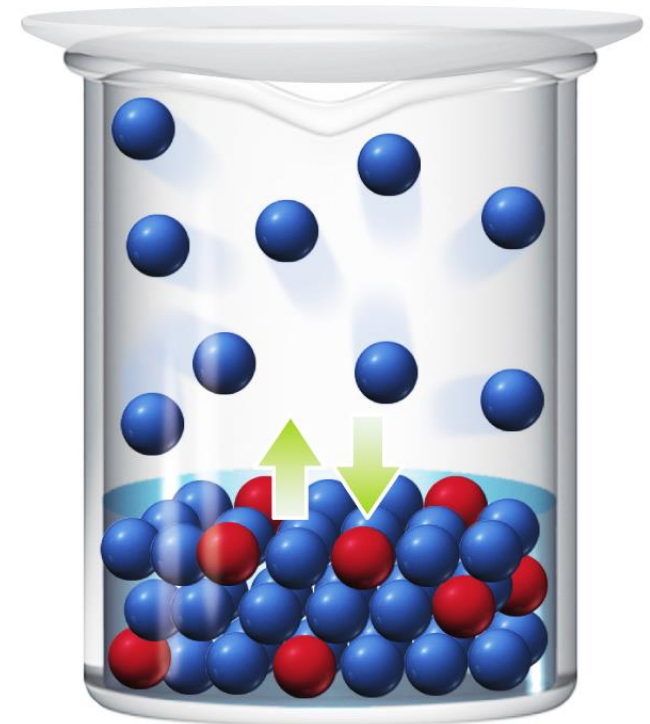
**Addition of a nonvolatile solute reduces the rate of vaporization, decreasing the amount of vapor.**



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:

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

$P^\circ$  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
  - $\Delta H_{sol'n}$  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

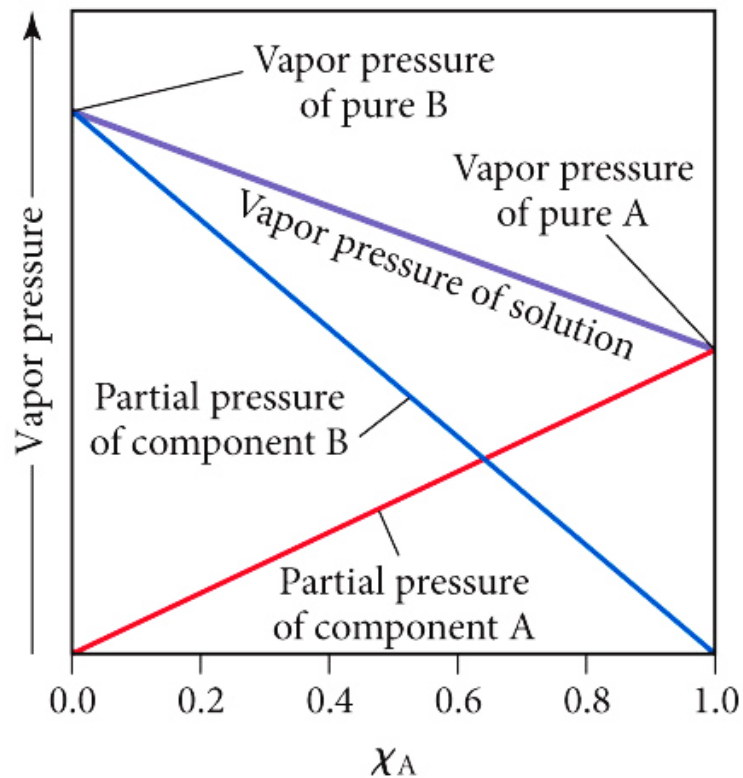
Solute–Solvent interactions are stronger than the Solute–Solute + Solvent–Solvent, **Total VP of the solution will be less than predicted** by Raoult's law, because the VP of the solute and solvent are lower than ideal.

## Positive Deviations

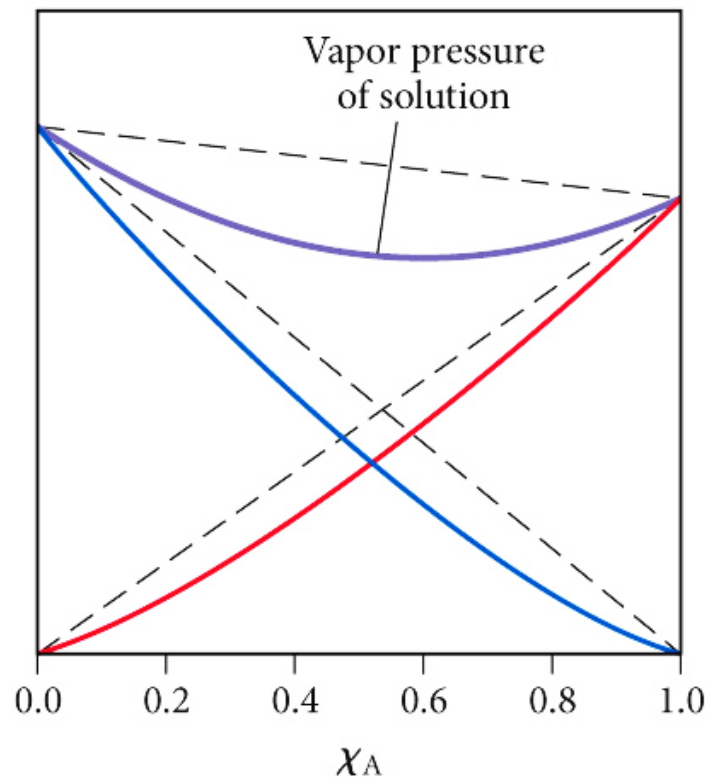
Solute–Solvent interactions are weaker than the Solute–Solute + Solvent–Solvent. **Total VP of the solution will be more than predicted** by Raoult's Law.

# Deviations from Raoult's Law

**IDEAL SOL'N  
NO DEVEATION**



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



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

