

Colligative Properties

- ☞ Colligative properties are solution properties whose values depend upon solute concentration.

Some Colligative Properties

vapor pressure

boiling point

melting (freezing) point

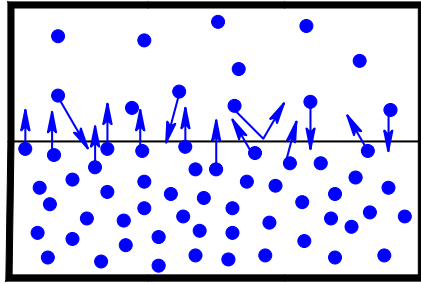
osmotic pressure

Molality

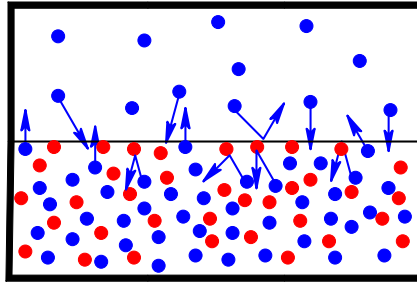
- ☞ For discussions of colligative properties, it is often convenient to express concentration in terms of *molality*.

$$\text{molality} = m \equiv \frac{\text{moles of solute}}{\text{kg of solvent}}$$

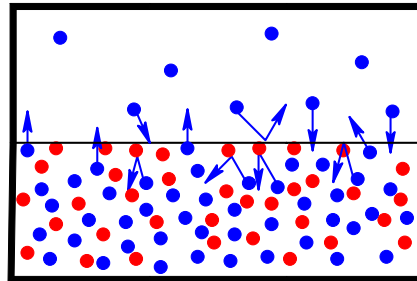
**Vapor Pressure Lowering
by
Adding a Non-Volatile Solute**



Pure Solvent

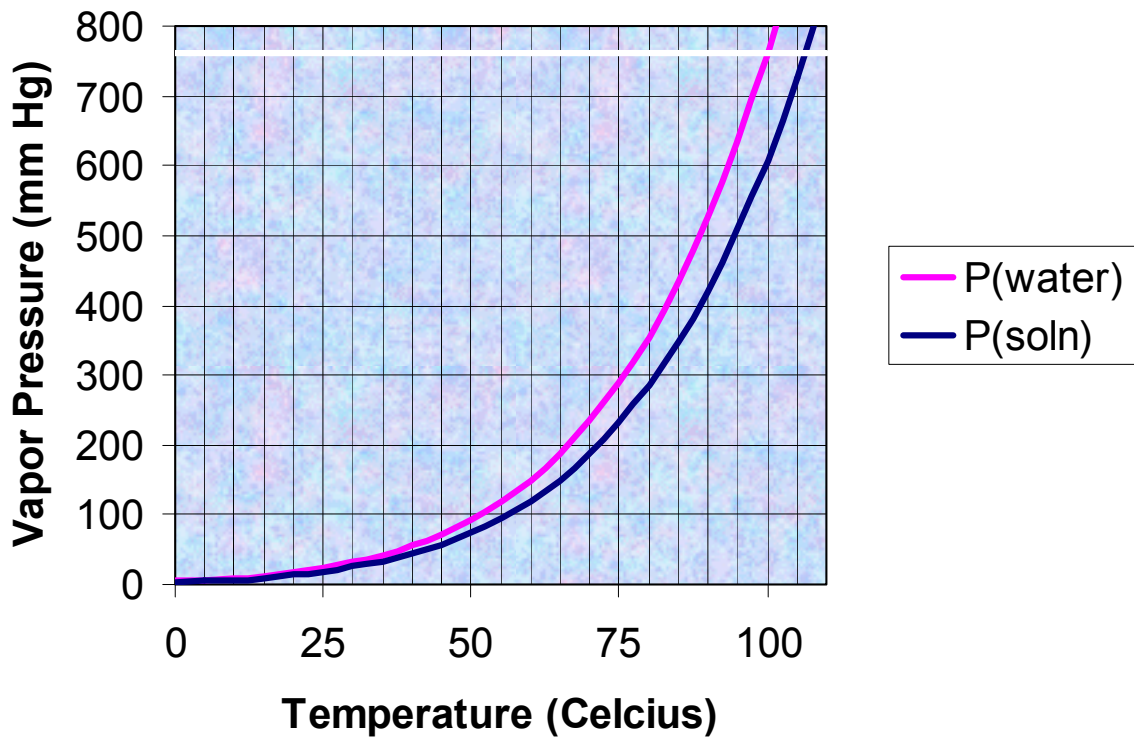


Solute Added



New Equilibrium at
Lower Vapor Pressure

Vapor Pressure of Pure Water and a Solution of a Non-Volatile Solute at Various Temperatures

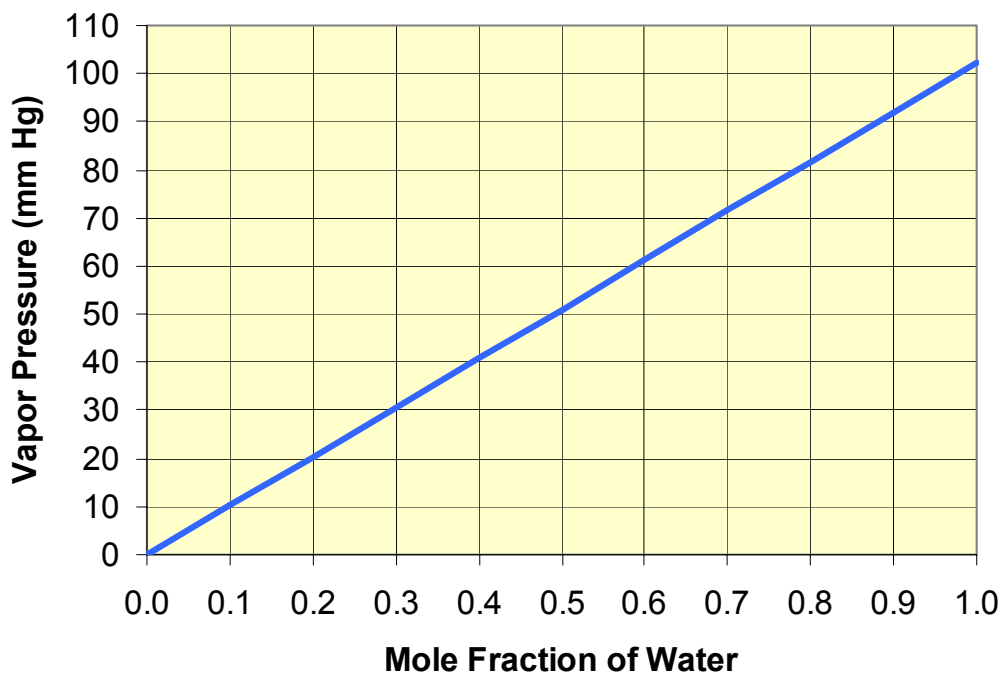


Raoult's Law

Special Case for a Non-Volatile Solute

$$P_{\text{soln}} = \chi_{\text{solv}} P_{\text{solv}}^{\circ}$$

**Predicted Vapor Pressure of Aqueous
Solutions of a Non-Volatile Solute at
325 K**

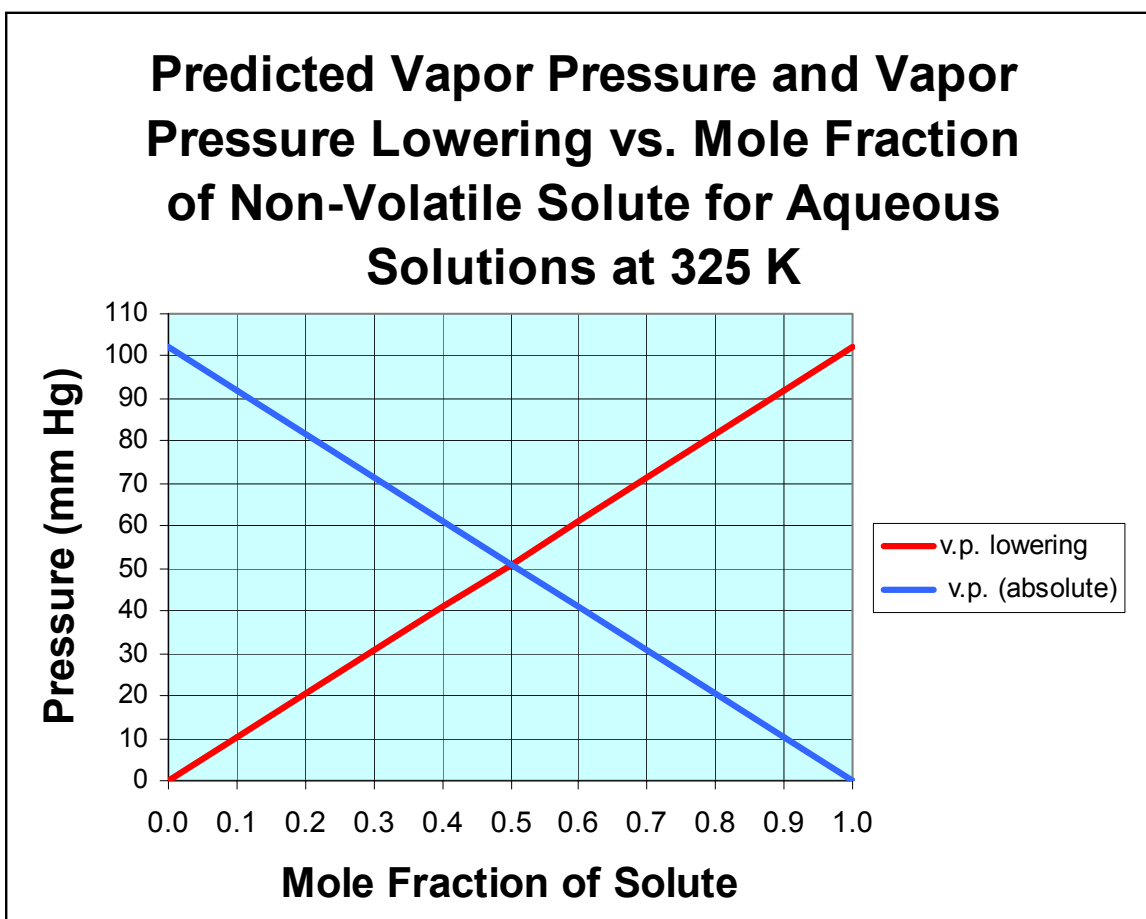


Vapor Pressure Lowering (ΔP) by a Non-Volatile Solute Special Case of Raoult's Law

$$\Delta P = P_{\text{soln}}^{\circ} - P_{\text{soln}} = P_{\text{soln}}^{\circ} - \chi_{\text{soln}} P_{\text{soln}}^{\circ} = (1 - \chi_{\text{soln}}) P_{\text{soln}}^{\circ}$$

But $\chi_{\text{solute}} = 1 - \chi_{\text{soln}}$, so

$$\Delta P = \chi_{\text{solute}} P_{\text{soln}}^{\circ}$$



Raoult's Law for Two or More Volatile Components General Case

☞ The total vapor pressure above a solution of two or more volatile liquids will be the sum of the vapor pressures (partial pressures) arising from each of the components in the mixture. (Dalton's Law of Partial Pressures)

- Each component's vapor pressure is given by

$$P_i = \chi_i^{\text{soln}} P_i^{\circ}$$

P_i = vapor pressure from an individual component

χ_i^{soln} = mole fraction of the component in the solution

P_i° = vapor pressure the pure liquid would have at the given temperature.

Thus, the general form of Raoult's Law can be stated as

$$\begin{aligned} P_t &= \sum \chi_i^{\text{soln}} P_i^{\circ} \\ &= \chi_1^{\text{soln}} P_1^{\circ} + \chi_2^{\text{soln}} P_2^{\circ} + \dots + \chi_n^{\text{soln}} P_n^{\circ} \end{aligned}$$

Raoult's Law for Two Volatile Components

$$P_t = \chi_A^{\text{soln}} P_A^\circ + \chi_B^{\text{soln}} P_B^\circ$$

- ☞ Raoult's Law applies to *ideal solutions*, in which interaction between solvent and solute molecules are virtually identical to those in the neat liquids.
- ☹ Virtually no real solution shows this behavior over a significant range of concentrations.
- ☺ A few carefully chosen mixtures, particularly with one component in very small mole fraction, *approximate* Raoult's Law.
- ☞ Raoult's Law is "more honour'd in the breach than the observance." [Shakespeare, *Hamlet*, IV, 14]

Mole Fraction in the Vapor vs. Mole Fraction in the Solution

☞ The more volatile component will have a higher mole fraction in the vapor than in solution.

☞ In the vapor, by Dalton's Law, the mole fractions are given by

$$P_A = \chi_A^{\text{vap}} P_t \qquad P_B = \chi_B^{\text{vap}} P_t$$

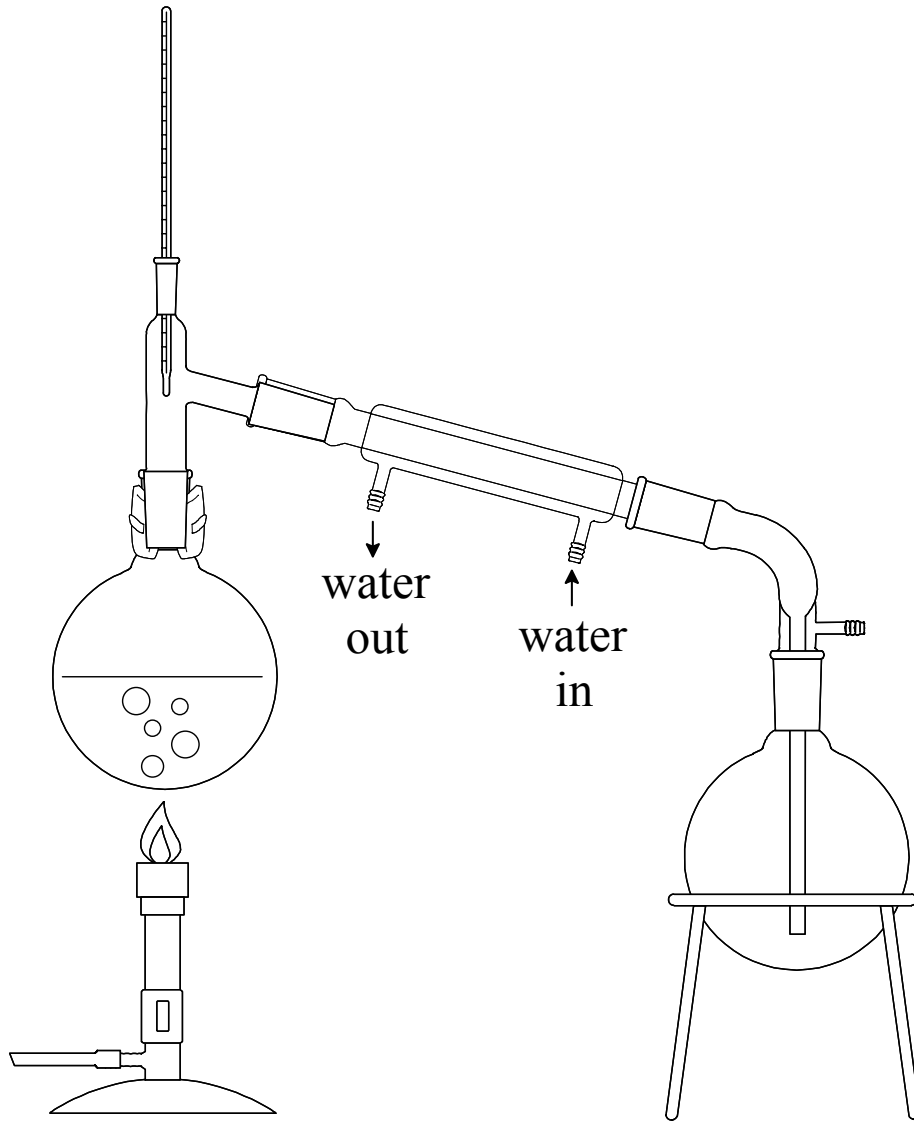
$$\chi_A^{\text{vap}} = P_A/P_t \qquad \chi_B^{\text{vap}} = P_B/P_t$$

☞ In the solution, by Raoult's Law, the mole fractions are given by

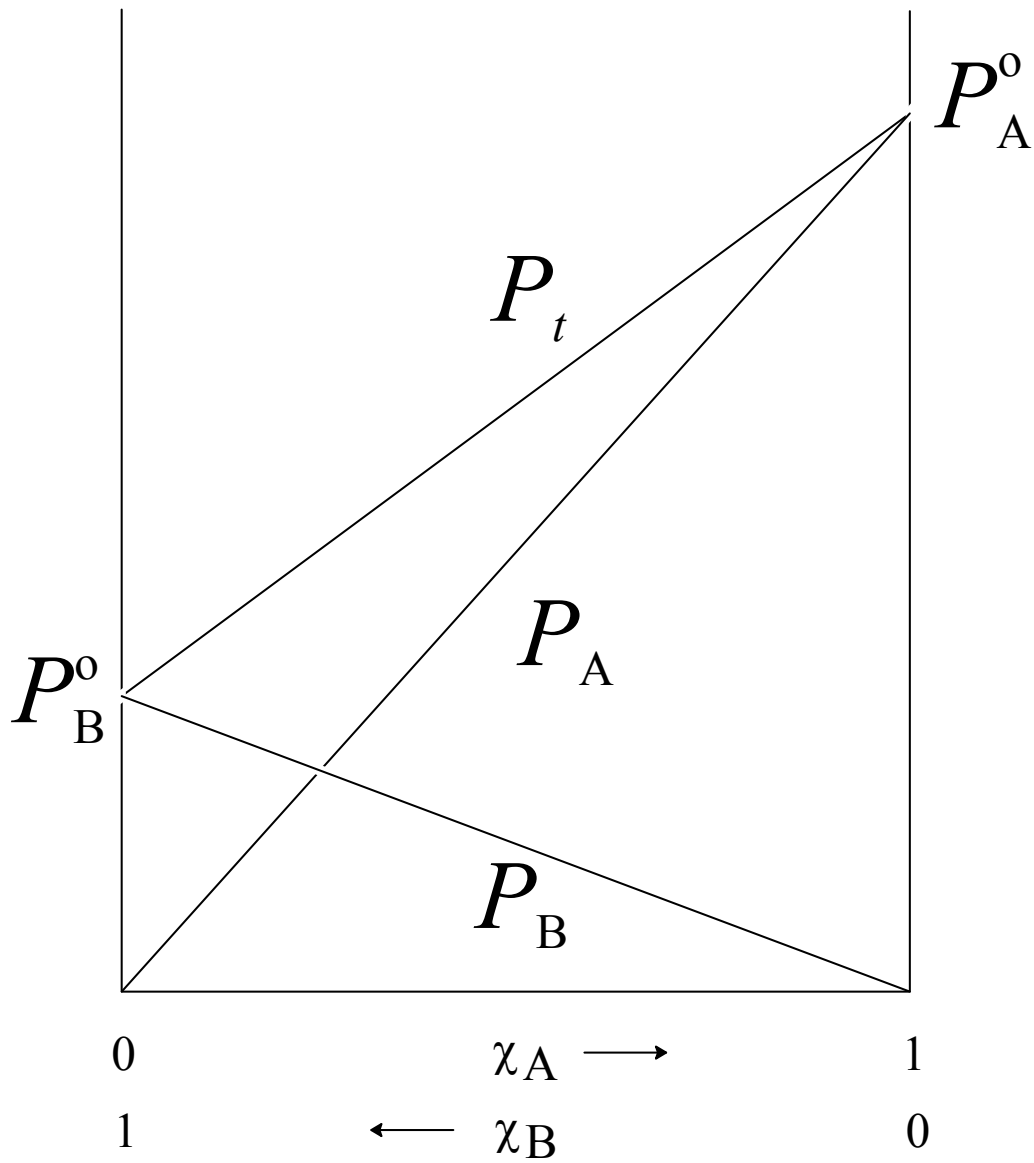
$$P_A = \chi_A^{\text{soln}} P_A^{\circ} \qquad P_B = \chi_B^{\text{soln}} P_B^{\circ}$$

$$\chi_A^{\text{soln}} = P_A/P_A^{\circ} \qquad \chi_B^{\text{soln}} = P_B/P_B^{\circ}$$

Distillation



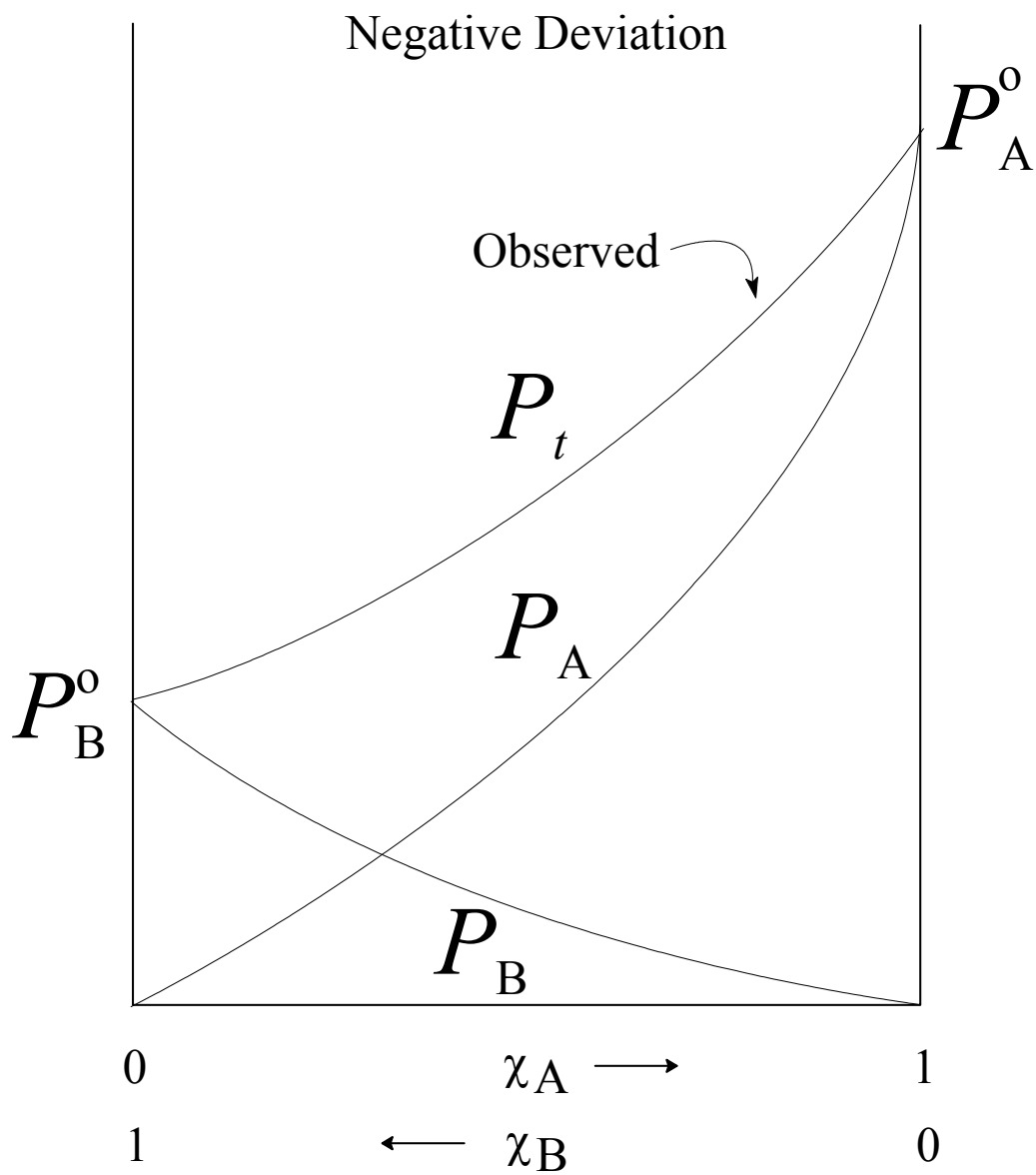
Ideal Raoult's Law Behavior



Intermolecular forces A-A \approx B-B \approx A-B

$$\Delta H_{\text{soln}} = 0$$

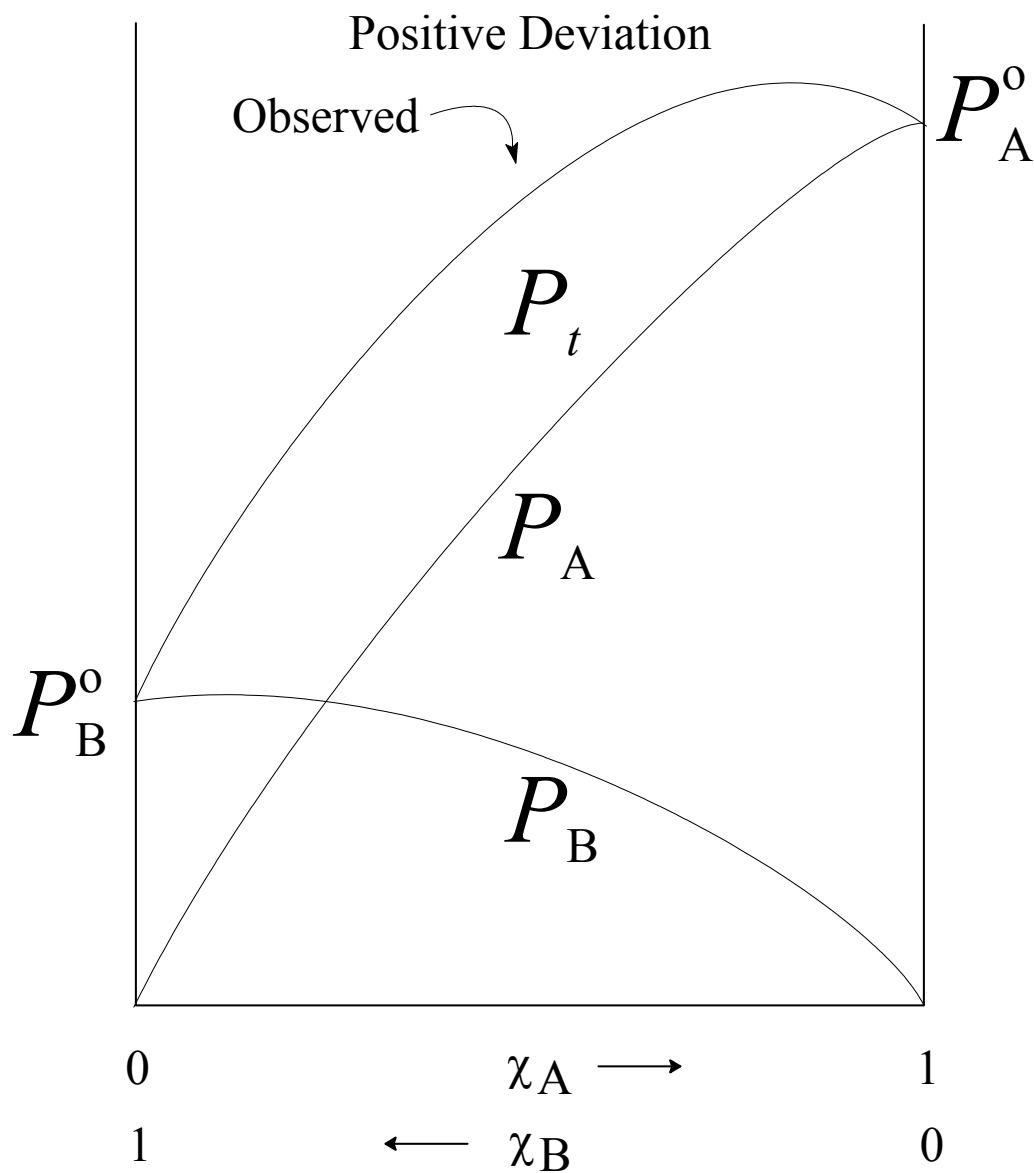
Non-Ideal Behavior



Intermolecular Forces A-A < A-B, B-B < A-B

$$\Delta H_{\text{soln}} < 0$$

Non-Ideal Behavior



Intermolecular forces $A-A > A-B, B-B > A-B$
 $\Delta H_{\text{soln}} > 0$