January 30, 2002

- **Problem Set Solutions:**
  - Chapters 9, 11 and 15 now online
- **Revised Office Hours:**
  - Monday, 1:30 - 2:30
  - Tuesday, 2:00 - 3:00
  - Friday, 1:30 - 2:30 (*except 2/8)*
- **Lab starts TODAY!**

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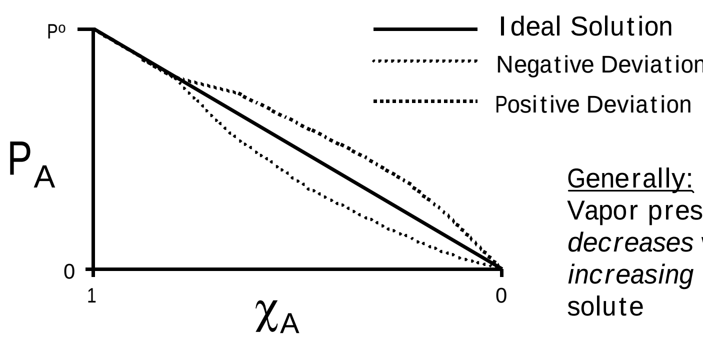
Effect on Vapor Pressure

- What happens to the vapor pressure of solvent A (P_A) as solute concentration increases?



Generally:
Vapor pressure *decreases* with *increasing* dissolved solute

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Raoult's Law

For an Ideal Solution:

$$\boxed{P_A = c_A\, P^o_A}$$

Solvent Vapor Pressure above solution

Mole Fraction of Solvent

Vapor Pressure of Pure Solvent

In an *ideal solution*: all IM forces are of a similar magnitude

• Negative Deviations: *solute-solvent* IM forces **too strong**

• Positive Deviations: *solute-solvent* IM forces **too weak**

What if both *solute* and *solvent* are **volatile liquids?**

➢ **Raoult's Law** applies to *both:*

$P_B = \chi_B\, P^o_B$ (for volatile solute B)

$\chi_A + \chi_B = 1$ (for a 2-component mix)

➢ **Now it gets interesting!**

Suppose we have a solution with a composition such that: $\mathbf{c_A = c_B = 0.5}$

Question: ***What are*** χ_A and χ_B *in the* ***vapor*** if **A** is 2x as volatile as **B** ($P^o_A = 2\, P^o_B$)?

The Solution (or is it the vapor?!)

$P_A = \chi_A P^o_A$

Substituting:

$P_A = (0.5)\ 2P^o_B$

Giving:

$\boxed{P_A = P^o_B}$

Also:

$P_B = \chi_B P^o_B$

So:

$\boxed{P_B = (0.5)\ P^o_B}$

So, in the *vapor:*

$\chi_A \text{ (vapor)} = P_A/(P_A + P_B)$

Substituting:

$\chi_A \text{ (vapor)} = P^o_B/(P^o_B + (0.5)\ P^o_B)$

$\boxed{\mathbf{c_A \text{ (vapor)} = 2/3}}$

And, since $\chi_A + \chi_B = 1$:

$\boxed{\mathbf{c_B \text{ (vapor)} = 1/3}}$

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Why so interesting?

- **Notice:** the *vapor is enriched in the more volatile component (A)*
- **So, to separate a mixture of *A* and *B:***
  - ✓ Collect and condense vapor above liquid
  - ✓ Repeat process with condensed vapor
  - ✓ The *new* vapor phase will be: $\chi_A = 0.80$
  - ✓ Repeat, repeat, repeat!
  - Perform at or near *boiling point* to maximize amounts of compounds in vapor phase (distillation)

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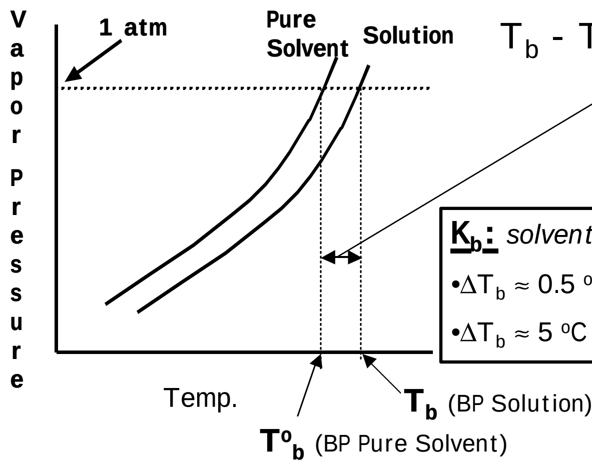
Boiling Point Elevation



$$T_b - T^o_b = \boxed{\Delta T_b = K_b\, m}$$

BP Elevation Constant
(*Ebulioscopic Constant*)

K_b: *solvent specific*

- $\Delta T_b \approx 0.5\ ^oC$ for 1 *m* sol'n in water
- $\Delta T_b \approx 5\ ^oC$ for 1 *m* sol'n in CCl_4

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Freezing Point Depression

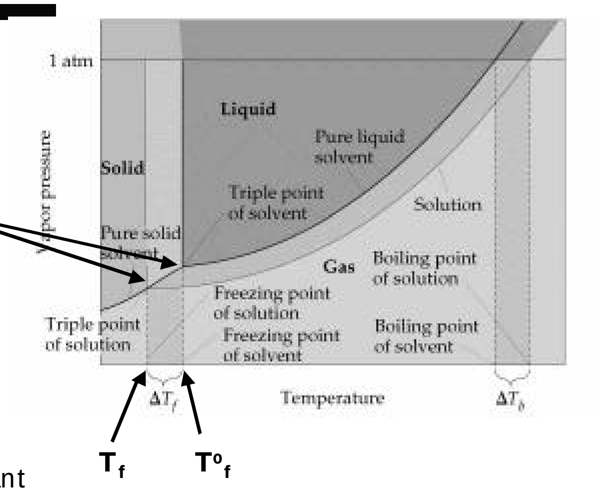
- **Freezing Point:** the temperature at which the VP of the *Liquid* and *Solid* phases are the same

So:

$$T^o_f - T_f = \mathrm{D}T_f$$

$$\boxed{\mathrm{D}T_f = K_f\, m}$$

FP Depression Constant
(Cryoscopic Constant)



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How Depressed?

- K_f is usually *larger* than K_b:
  - $\Delta T_f \approx 2\ ^oC$ for 1 *m* sol'n in water
  - $\Delta T_b \approx 32\ ^oC$ for 1 *m* sol'n in CCl_4
- **Uses for FP Depression:**
  - Melting Ice
  - Auto Antifreeze
  - Solvent Purification
  - Molecular Weight Determination

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MW Determination via FP Depression

- ✓ Add a *known amount* of compound to *known amount* of solvent
  - Weigh compound and solvent *accurately*
  - Use solvent with a **large** K_f
- ✓ Measure $\mathbf{DT_f}$
- ✓ Determine *molality*: $\mathbf{DT_f = K_f}\ \boldsymbol{m}$
- ✓ Use *m* to solve for n_{cmpd}: $\boldsymbol{m} = \mathbf{n_{cmpd}/kg\ solvent}$
- ✓ Finally, calculate MW: $\mathbf{MW = g\ cmpd/n_{cmpd}}$

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