

Chemistry 163B, Winter 2020
Lecture 22-23 Colligative Properties




Lecture 22-23
Chemistry 163B W2020
Colligative Properties
Challenged Penpersonship
Notes



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colligative properties of solutions



colligative
One entry found.
Main Entry: col-li-ga-tive
Pronunciation: kə-lī-gā-tiv, kə-lī-gə-tiv
Function: adjective

: depending on the number of particles (as molecules) and not on the nature of the particles
<pressure is a *colligative property*>

<http://www.merriam-webster.com/dictionary/colligative>

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quantitative treatment of colligative properties

A. Freezing point depression
B. Boiling Point Elevation
C. Osmotic Pressure

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quantitative treatment of colligative properties

Handout #53 Colligative Properties

from relationships for Chem 163B final:

Colligative properties:

- freezing point lowering:

$$\gamma_B X_B = \exp\left[-\frac{\Delta\bar{H}_{\text{melting}}}{R} \left(\frac{1}{T_f} - \frac{1}{T_f^*}\right)\right] \quad T_f = \frac{T_f^* \Delta\bar{H}_{\text{melting}}}{\Delta\bar{H}_{\text{melting}} - RT_f \ln(\gamma_B X_B)}$$
- boiling point elevation:

$$\gamma_B X_B = \exp\left[\frac{\Delta\bar{H}_{\text{vaporization}}}{R} \left(\frac{1}{T_{bp}} - \frac{1}{T_{bp}^*}\right)\right] \quad T_{bp} = \frac{T_{bp}^* \Delta\bar{H}_{\text{vaporization}}}{\Delta\bar{H}_{\text{vaporization}} + RT_{bp} \ln(\gamma_B X_B)}$$
- osmotic pressure:

$$\pi = \frac{-RT \ln(\gamma_B X_B)}{V_B} \quad \pi \approx \frac{n_s RT}{V_s} = \frac{n_{\text{solute}} RT}{V_{\text{solvent}}} \quad \text{for dilute solution}$$

(hopefully) reassuring ??

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quantitative treatment of colligative properties

- I. The pure solvent (component B) is originally in equilibrium in the two phases.
- II. Addition of solute (component A) lowers the chemical potential of the solvent in the solution phase
- III. Temperature (freezing point depression, boiling point elevation) or pressure (osmotic pressure) must be altered to reestablish equilibrium between the solution and the pure solvent phase.
- IV. Obtain relationships between X_A or X_B and change in T or P.

It's as easy as I., II., III., IV.

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freezing point depression (solid \rightleftharpoons liquid [solution])

- I. pure solvent is originally in equilibrium in the two phases
 - solid is pure "solvent" B*
 - $X_B = \text{mole fraction solvent B in solution}$
 - $X_A = \text{mole fraction solute A in liquid}$

pure solid $_B^*$ \rightleftharpoons *pure liquid* $_B^*$ at $T_f^* \equiv$ the normal melting point (T_{fusion}^*)

$\mu_B^*(T_f^*) = \mu_B^*(X_B = 1, T_f^*)$

$\Delta\mu_B(T_f^*) = \mu_B^*(T_f^*) - \mu_B^*(T_f^*) = 0$

$\Delta\bar{H}(T_f^*) = \Delta\bar{H}_{\text{melting}} > 0 \quad \text{for solid} \rightleftharpoons \text{liquid}$

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freezing point depression (solid ⇌ liquid [solution])

II. Still at T_f^* , add solute A to solvent with resulting mole fractions X_A and X_B

μ_B^{soln} lowers


$\mu_B^l(X_B, T_f)$ is now chemical potential of solvent (B) in solution

At T_f , the original freezing temperature

$\Delta\mu_B^{s \rightarrow l}(T_f) = \mu_B^s(X_B, T_f) - \mu_B^l(X_B, T_f)$

$\Delta\mu_B^{s \rightarrow l}(T_f) = RT_f \ln(\gamma_B X_B)$ "proof"

$\Delta\mu_B^{s \rightarrow l}(T_f) < 0$



so at T_f the forward reaction (melting of the solid) would now occur spontaneously

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freezing point depression (solid ⇌ liquid [solution])

III. Alter temperature to restore equilibrium $T_f^* \rightarrow T_f$ $\left(\frac{\partial \Delta\mu}{\partial T}\right)_P = -\frac{\Delta\bar{H}}{T^2}$

solvent at new T_f solvent at T_f^* change $T_f^* \rightarrow T_f$

calculate $\Delta\mu$: $\left(\frac{\Delta\mu_B(T_f)}{T_f}\right)_P = \left(\frac{\Delta\mu_B(T_f^*)}{T_f^*}\right)_P - \int_{T_f^*}^{T_f} \frac{\Delta\bar{H}_{B \text{ melting}}}{T^2} dT$

but at new T_f : $\left(\frac{\Delta\mu_B(T_f)}{T_f}\right)_P = 0$ since at 'new' equilibrium T_f , $\Delta\mu_B(T_f, X_B^l) = 0$

want

with: $\Delta\mu_B(T_f^*) = RT_f^* \ln(\gamma_B X_B)$ from II

extra:

one gets: $0 = R \ln(\gamma_B X_B) + \left[-\int_{T_f^*}^{T_f} \frac{\Delta\bar{H}_{B \text{ melting}}}{T^2} dT \right]$

change in $\Delta\mu_B$ due to adding solute change in $\Delta\mu_B$ due to temperature change

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freezing point lowering

IV. Obtain relationships between X_B and change in T

$R \ln(\gamma_B X_B) = \int_{T_f^*}^{T_f} \frac{\Delta\bar{H}_{B \text{ melting}}}{T^2} dT$ from III

$R \ln(\gamma_B X_B) = -\Delta\bar{H}_{B \text{ melting}} \left[\frac{1}{T_f} - \frac{1}{T_f^*} \right]$

since lhs < 0 and $\Delta\bar{H}_{\text{melting}} > 0$

$\left[\frac{1}{T_f} - \frac{1}{T_f^*} \right] > 0 \Rightarrow T_f < T_f^*$

freezing point depression

$T_f = \frac{T_f^* \Delta\bar{H}_{B \text{ melting}}}{\Delta\bar{H}_{B \text{ melting}} - RT_f^* \ln(\gamma_B X_B)}$ (~ eqn 9.32 E&R₁₀)

extra:

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boiling point elevation (cooking veggies in salt water !!)


Colligative properties:

- freezing point lowering: $\gamma_B X_B = \exp\left[-\frac{\Delta\bar{H}_{\text{melting}}}{R} \left[\frac{1}{T_f} - \frac{1}{T_f^*}\right]\right]$ $T_f = \frac{T_f^* \Delta\bar{H}_{B \text{ melting}}}{\Delta\bar{H}_{B \text{ melting}} - RT_f^* \ln(\gamma_B X_B)}$
- boiling point elevation: $\gamma_B X_B = \exp\left[\frac{\Delta\bar{H}_{\text{vaporization}}}{R} \left[\frac{1}{T_{bp}} - \frac{1}{T_{bp}^*}\right]\right]$ $T_{bp} = \frac{T_{bp}^* \Delta\bar{H}_{B \text{ vaporization}}}{\Delta\bar{H}_{B \text{ vaporization}} + RT_{bp}^* \ln(\gamma_B X_B)}$

- boiling point elevation and freezing point depression similar except for sign change (due to X_B^l product in melting, reactant in vaporization)
- $\gamma_B X_B < 1$ and $\Delta\bar{H}_{\text{vaporization}} > 0$ implies that $\left[\frac{1}{T_{bp}} - \frac{1}{T_{bp}^*}\right] < 0$

so $T_{bp} > T_{bp}^*$ **HIGHER BOILING POINT with salt**

HANDOUT #53



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non-volatile ionic solutes in vapor pressure and colligative properties

for X_B , mole fraction solvent, $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$

$X_B = X_{\text{solvent}} = \frac{n_{\text{solvent}}}{n_{\text{solvent}} + n_{\text{total solute particles}}}$ 1 mole \rightarrow 2 moles 'particles'

in mole fraction: moles solute = total moles ions

HW7 #52b n moles salt $M^{2+}(X^-)_2 \rightarrow n$ moles $M^{2+} + 2n$ moles X^-

$3n$ moles solute

$X_{H_2O} = \frac{\text{moles } H_2O}{(\text{moles } H_2O + 3 \times \text{moles salt})}$

molality = $m = (\text{moles solute}) / (1000 \text{ g solvent})$

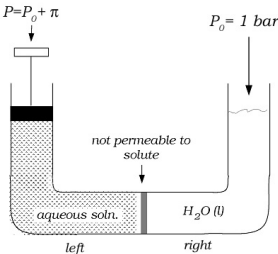
molality = $M = (\text{moles solute}) / (1 \text{ L solution})$

HW8 #58 $A_x B_y (s) \rightleftharpoons x A^{(\text{soln})} + y B^{(\text{soln})}$ 'K_{sp} molality reference'

$K_{sp} = \frac{(a_{A \text{ soln}})^x (a_{B \text{ soln}})^y}{(a_{AB \text{ solid}})} = \frac{(\gamma_{\pm} [m_{\pm}] / 1m)^x (\gamma_{\pm} [m_{\pm}] / 1m)^y}{1}$

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Osmotic Pressure Equilibrium



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osmotic pressure (solution [solvent + solute] \rightleftharpoons pure solvent)

I. pure solvent at P_{left} is originally in equilibrium with pure solvent at P_{right} ; i.e. $P_{\text{left}} = P_{\text{right}} = P_0$

pure liquid $^*(P_0, \text{left}) \rightleftharpoons$ *pure liquid* $^*(P_0, \text{right})$ at T

'left' and 'right' refer to compartments separated by solute impermeable membrane

$\mu_b^*(P_0, \text{left}) = \mu_b^*(P_0, \text{right})$

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osmotic pressure (II add solute to left compartment)

II. in left hand compartment add solute A to solvent with resulting mole fractions X_A and X_B

add X_A solute to liquid in 'left' compartment resulting in X_B for solvent

lectures 20-21 slide #20 $\mu_b^*(P_0, \text{left}) = \mu_b^*(P_0, \text{left}) + RT \ln(\gamma_B X_B) < \mu_b^*(P_0, \text{right})$

$\mu_b^*(P_0, \text{left}) < \mu_b^*(P_0, \text{right})$

so the solvent B moves spontaneously left \leftarrow right (i.e. diluting solution on left)

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osmotic pressure (III, alter pressure)

III. alter Pressure: $P_{\text{left}} \rightarrow (P_0 + \pi)_{\text{left}}$ to restore equilibrium solution $(X_B, P_0 + \pi, \text{left}) \rightleftharpoons$ pure solvent (P_0, right)

want: $\mu_{\text{solution}}(X_B, P_0 + \pi, \text{left}) = \mu_{\text{pure solvent}}(P_0, \text{right})$

how does μ change with pressure? $\left(\frac{\partial \mu_B^{\text{left}}}{\partial P}\right)_T = \bar{V}_B \int_{P_0}^{P_0 + \pi} d\mu_B^{\text{left}}(X_B) = \int_{P_0}^{P_0 + \pi} \bar{V}_B dP$

integrate

$\mu_B^{\text{left}}(X_B, P_0 + \pi) = \mu_B^{\text{left}}(X_B, P_0) + [P_0 + \pi - P_0] \bar{V}_B$

$\mu_B^{\text{left}}(X_B, P_0 + \pi) = \mu_B^{\text{left}}(X_B, P_0) + \pi \bar{V}_B$

from II.

$\mu_B^{\text{left}}(X_B, P_0 + \pi) = \mu_b^*(P_0) + RT \ln(\gamma_B X_B) + \pi \bar{V}_B$

left with $P = P_0 + \pi$ **right with $P = P_0$**

$\mu_b^*(P_0) + RT \ln(\gamma_B X_B) + \pi \bar{V}_B = \mu_b^*(P_0)$

$\pi = - \frac{RT \ln(\gamma_B X_B)}{\bar{V}_B}$

extra:

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osmotic pressure (a little more manipulation)

IV. Obtain relationships between X_A and π , change in P

$\pi = - \frac{RT \ln(\gamma_B X_B)}{\bar{V}_B}$

for $\gamma_B = 1$ and $X_B = 1 - X_A$

$\pi = - \frac{RT \ln(1 - X_A)}{\bar{V}_B}$

further manipulations $\pi \bar{V}_B = n_A RT$

$\pi V_{\text{solution}} = n_{\text{solute}} RT$

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reverse osmosis

Water Systems
Aqua Technology
For the 21st Century

ESP Water Products.com

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Reverse Osmosis

http://www.zenon.com/image/resources/glossary/reverse_osmosis/normal_osmosis.jpg

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effect of osmosis on blood cells

	Hypertonic	Isotonic	Hypotonic	
salt	$X_{\text{salt}}^{\text{outside}} > X_{\text{salt}}^{\text{inside}}$	$X_{\text{salt}}^{\text{outside}} = X_{\text{salt}}^{\text{inside}}$	$X_{\text{salt}}^{\text{outside}} < X_{\text{salt}}^{\text{inside}}$	salt
water	$X_{\text{H}_2\text{O}}^{\text{outside}} < X_{\text{H}_2\text{O}}^{\text{inside}}$	$X_{\text{H}_2\text{O}}^{\text{outside}} = X_{\text{H}_2\text{O}}^{\text{inside}}$	$X_{\text{H}_2\text{O}}^{\text{outside}} > X_{\text{H}_2\text{O}}^{\text{inside}}$	water
	$\mu_{\text{H}_2\text{O}}^{\text{outside}} < \mu_{\text{H}_2\text{O}}^{\text{inside}}$	$\mu_{\text{H}_2\text{O}}^{\text{outside}} = \mu_{\text{H}_2\text{O}}^{\text{inside}}$	$\mu_{\text{H}_2\text{O}}^{\text{outside}} > \mu_{\text{H}_2\text{O}}^{\text{inside}}$	
	H_2O outside \leftarrow inside	outside \rightleftharpoons inside	outside \rightarrow inside	
	collapse		burst	19

hyponatremia

Woman dies after water-drinking contest
Water intoxication eyed in 'Hold Your Wee for a Wii' contest death

Associated Press
updated 7:24 p.m. PT, Sat., Jan. 13, 2007

SACRAMENTO, Calif. - A woman who competed in a radio station's contest to see how much water she could drink without going to the bathroom died of water intoxication, the coroner's office said Saturday.

Jennifer Strange, 20, was found dead Friday in her suburban Rancho Cordova home hours after taking part in the "Hold Your Wee for a Wii" contest in which KQMD 107.9 promised a Nintendo Wii video game system for the winner.

"She said to one of our supervisors that she was on her way home and her head was hurting her real bad," said Laura Rios, one of Strange's co-workers at Radiological Associates of Sacramento. "She was crying and that was the last that anyone had heard from her."

Woman in water drinking contest dies
Jan. 13: Sacramento file reporter Christine Jewett talks to KQMD-TV's Confessa Brewer about the death of a woman who had competed in a radio station contest. JEWETT

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quantitative treatment of colligative properties

Handout #53 Colligative Properties

from relationships for Chem 163B final:

Colligative properties:

- freezing point lowering:

$$\gamma_B X_B = \exp\left[\frac{\Delta\bar{H}_{\text{fusion}}}{R} \left(\frac{1}{T_f} - \frac{1}{T_f^*}\right)\right] \quad T_f = \frac{T_f^* \Delta\bar{H}_{\text{fusion}}}{\Delta\bar{H}_{\text{fusion}} - RT_f^* \ln(\gamma_B X_B)}$$
- boiling point elevation:

$$\gamma_B X_B = \exp\left[\frac{\Delta\bar{H}_{\text{vaporization}}}{R} \left(\frac{1}{T_b} - \frac{1}{T_b^*}\right)\right] \quad T_b = \frac{T_b^* \Delta\bar{H}_{\text{vaporization}}}{\Delta\bar{H}_{\text{vaporization}} + RT_b^* \ln(\gamma_B X_B)}$$
- osmotic pressure:

$$\pi = \frac{-RT \ln(\gamma_B X_B)}{V_B} \quad \pi \approx \frac{n_s RT}{V_{\text{solvent}}} = \frac{n_{\text{solute}} RT}{V_{\text{solvent}}} \text{ for dilute solution}$$

(hopefully) reassuring??

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End of Lectures 22-23

freezing point depression (solid \rightleftharpoons solution)

II. Still at T_f^* , add solute A to solvent with resulting mole fractions X_A and X_B

for solid phase of B there is no change:
 $\mu_B^*(T_f^*) = \mu_B^{\text{solid}}(T_f^*)$

for the solvent (B) in solution: see lect 20-21 slide #20
 $\mu_B(T_f^*) \equiv \mu_B^{\text{solvent}} \equiv \mu_B^{\text{(in soln)}}(T_f^*) = \mu_B^*(T_f^*) + RT_f^* \ln(\gamma_B X_B)$

so now $\Delta\mu_B(T_f^*) = \mu_B^{\text{solid}}(T_f^*) - \mu_B^{\text{(in soln)}}(T_f^*) = \mu_B^*(T_f^*) + RT_f^* \ln(\gamma_B X_B) - \mu_B^*(T_f^*)$
 but $\mu_B^{\text{solid}}(T_f^*) - \mu_B^{\text{(in soln)}}(T_f^*) = 0$ since pure liquid and solid are in equilibrium at T_f^*

thus $\Delta\mu_B(T_f^*) = RT_f^* \ln(\gamma_B X_B) < 0$

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freezing point depression (solid \rightleftharpoons solution)

III. Alter temperature to restore equilibrium $T_f^* \rightarrow T_f$

$$\left(\frac{\partial \Delta\mu}{\partial T}\right)_P = -\frac{\Delta\bar{H}}{T^2}$$

$$\int_{T_f^*}^{T_f} d\left(\frac{\Delta\mu_B}{T}\right)_P = -\int_{T_f^*}^{T_f} \frac{\Delta\bar{H}_{B, \text{melting}}}{T^2} dT$$

$$\left(\frac{\Delta\mu_B(T_f)}{T_f}\right)_P - \left(\frac{\Delta\mu_B(T_f^*)}{T_f^*}\right)_P = -\int_{T_f^*}^{T_f} \frac{\Delta\bar{H}_{B, \text{melting}}}{T^2} dT$$

old stuff

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freezing point depression (solid in solution)

III. Alter temperature to restore equilibrium (continued)

$$\left(\frac{\Delta\mu_B^s(T_f)}{T_f}\right)_p - \left(\frac{\Delta\mu_B^s(T_f^*)}{T_f^*}\right)_p = -\int_{T_f^*}^{T_f} \frac{\Delta\bar{H}_{B, \text{melting}}}{T^2} dT$$

$$\left(\frac{\Delta\mu_B(T_f)}{T_f}\right)_p = 0 \text{ since at 'new' equilibrium } T_f, \Delta\mu_B(T_f) = 0$$

$$\text{and } \left(\frac{\Delta\mu_B(T_f^*)}{T_f^*}\right)_p = R \ln(\gamma_B X_B) \text{ from eqn in II.}$$

$$-R \ln(\gamma_B X_B) = -\int_{T_f^*}^{T_f} \frac{\Delta\bar{H}_{B, \text{melting}}}{T^2} dT$$

$$R \ln(\gamma_B X_B) + \left[-\int_{T_f^*}^{T_f} \frac{\Delta\bar{H}_{B, \text{melting}}}{T^2} dT\right] = 0$$

change in $\Delta\mu_B$ due to adding solute

change in $\Delta\mu_B$ due to temperature change

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freezing point lowering

IV. Obtain relationships between X_B and change in T

$$R \ln(\gamma_B X_B) = \int_{T_f^*}^{T_f} \frac{\Delta\bar{H}_{B, \text{melting}}}{T^2} dT$$

$$\Delta\bar{H}_{B, \text{melting}} \sim \text{independent of T}$$

$$R \ln(\gamma_B X_B) = -\Delta\bar{H}_{B, \text{melting}} \left[\frac{1}{T_f} - \frac{1}{T_f^*} \right]$$

since $lfs < 0 \Rightarrow T_f < T_f^*$ (freezing point depression)

$$\gamma_B X_B = \exp \left[-\frac{\Delta\bar{H}_{B, \text{melting}}}{R} \left[\frac{1}{T_f} - \frac{1}{T_f^*} \right] \right] \text{ (integration of eqn 9.31 E\&R)}$$

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freezing point lowering

IV. Obtain relationships between X_B and change in T (cont)

$$\gamma_B X_B = \exp \left[-\frac{\Delta\bar{H}_{B, \text{melting}}}{R} \left[\frac{1}{T_f} - \frac{1}{T_f^*} \right] \right]$$

$$-\frac{R}{\Delta\bar{H}_{B, \text{melting}}} \ln(\gamma_B X_B) + \frac{1}{T_f^*} = \frac{1}{T_f}$$

$$T_f = \frac{T_f^* \Delta\bar{H}_{B, \text{melting}}}{\Delta\bar{H}_{B, \text{melting}} - RT_f^* \ln(\gamma_B X_B)} \text{ (~ eqn 9.32 E\&R, 4th)}$$

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osmotic pressure (III, alter pressure)

III. alter Pressure: $P_{\text{left}} \rightarrow (P_0 + \pi)_{\text{left}}$ to restore equilibrium

solution ($X_B, P_0 + \pi, \text{left}$) \rightleftharpoons pure solvent (P_0, right)

$$\left(\frac{\partial \mu_B^{\text{left}}}{\partial P_{\text{left}}}\right)_T = \bar{V}_B$$

$$\int_{P_0}^{P_0 + \pi} d\mu_B^{\text{left}}(X_B) = \int_{P_0}^{P_0 + \pi} \bar{V}_B dP$$

assuming solvent is incompressible

(\bar{V}_B doesn't change with pressure at constant T)

$$\mu_B^{\text{left}}(X_B, P_0 + \pi) = \mu_B^{\text{left}}(X_B, P_0) + [P_0 + \pi - P_0] \bar{V}_B$$

$$\mu_B^{\text{left}}(X_B, P_0 + \pi) = \mu_B^{\text{left}}(X_B, P_0) + \pi \bar{V}_B$$

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osmotic pressure (III, alter pressure, continued)

$$\mu_B^{\text{left}}(X_B, P_0 + \pi) = \mu_B^{\text{left}}(X_B, P_0) + \pi \bar{V}_B$$

$$\mu_B^{\text{left}}(X_B, P_0 + \pi) = \mu_B^*(P_0) + RT \ln(\gamma_B X_B) + \pi \bar{V}_B$$

want π to restore equilibrium such that

$$\mu_B^{\text{left}}(X_B, P_0 + \pi) = \mu_B^*(P_0)$$

$$\mu_B^*(P_0) + RT \ln(\gamma_B X_B) + \pi \bar{V}_B = \mu_B^*(P_0)$$

$$\pi = -\frac{RT \ln(\gamma_B X_B)}{\bar{V}_B}$$

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osmotic pressure (a little more manipulation)

$$\pi = -\frac{RT \ln(\gamma_B X_B)}{\bar{V}_B}$$

for $\gamma_B \approx 1$ and $X_B = 1 - X_A$

$$\pi = -\frac{RT \ln(1 - X_A)}{\bar{V}_B}$$

$\ln(1+x) \approx x$ for small x (i.e. dilute solution, X_A small)

$$\pi = \frac{X_A RT}{\bar{V}_B}$$

$$X_A = \frac{n_A}{n_A + n_B} \text{ and } n_A + n_B = n_B \text{ for dilute solution}$$

$$\pi = \frac{n_A RT}{n_B \bar{V}_B}$$

$$\pi \bar{V}_B = n_A RT$$

$$\pi V_{\text{solution}} = n_{\text{solute}} RT$$

A=solute
B=solvent

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colligative properties and nonvolatile solutes

- mole fraction solvent $X_B = n_B/n_{\text{total}}$
- for non-volatile solute A $P_A^* = 0$
- concentrations frequently given in molality
 $M = \text{molality} = (\text{moles solute})/(\text{L solution})$
 $m = \text{molality} = (\text{moles solute})/(1000\text{g solvent})$
moles $\text{H}_2\text{O}/1000\text{g solvent} \approx 55.55$ moles
aqueous soln: $X_{\text{solvent}} = 55.55/(m+55.55)$
- for ionic solvent (moles solute) = (total moles of ions)
- example: 2 m aqueous solution of CaCl_2 (complete dissociation)

$$X_{\text{H}_2\text{O}} = \frac{55.55 \text{ moles / kgH}_2\text{O}}{(2 \text{ moles solute/kgH}_2\text{O} \times 3 \text{ moles ions/moles solute}) + 55.55 \text{ moles / kgH}_2\text{O}} = .9025$$

* however when referring to the molality of a specific ion, e.g. $[\text{Cl}^-]$ from CaCl_2 , the number of ions per mole of solute is already factored in

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