

# 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: 'kä-lə-<sub>I</sub>gā-tiv, kə-<sup>I</sup>li-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

# 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:

$$\gamma_{B}X_{B} = \exp \left[ -\frac{\Delta \overline{H}_{melining}}{R} \left[ \frac{1}{T_{f}} - \frac{1}{T_{f}} \right] \right] \qquad T_{f} = \frac{T_{f}\Delta \overline{H}_{B \ melining}}{\Delta \overline{H}_{B \ melining} - RT_{f} \ln \left( \gamma_{B}X_{B} \right)}$$

boiling point elevation:

boiling point elevation: 
$$\gamma_{B}X_{B} = \exp\left[\frac{\Delta \overline{H}_{vaportzation}}{R}\left[\frac{1}{T_{bp}} - \frac{1}{T_{bp}^{\bullet}}\right]\right] \qquad T_{bp} = \frac{T_{bp}^{\bullet}\Delta \overline{H}_{B \, vaportzation}}{\Delta \overline{H}_{B \, vaportzation} + RT_{bp}^{\bullet} \ln\left(\gamma_{B}X_{B}\right)}$$

• osmotic pressure: 
$$\pi = \frac{-RT \ln \left( \gamma_B X_B \right)}{\overline{V}_B} \qquad \pi \approx \frac{n_A RT}{V_B} = \frac{n_{solute} RT}{V_{solvent}} \quad for \ dilute \ solution$$

(hopefully) reassuring ??

#### 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<sub>A</sub> or X<sub>B</sub> and change in T or P.

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

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#### freezing point depression (solid ≥ liquid [solution])

I. pure solvent is originally in equilibrium in the two phases

solid is pure "solvent" B

X<sub>B</sub> = mole fraction solvent B in solution

 $X_A = mole fraction solute A in liquid$ 

 $pure\ solid_{B}^{\bullet} \rightleftharpoons pure\ \ell iquid_{B}^{\bullet} \quad at\ T_{f}^{\bullet} \equiv \text{the normal melting point} \left(T_{fusion}^{\bullet}\right)$ 

$$\mu_B^{s\bullet}(T_f^{\bullet}) = \mu_B^{\ell\bullet}(X_B = I, T_f^{\bullet})$$

$$\Delta \mu_B(T_f^{\bullet}) = \mu_B^{\ell \bullet}(T_f^{\bullet}) - \mu_B^{s \bullet}(T_f^{\bullet}) = 0$$

$$\Delta \overline{H}(T_{_f}^{ullet}) = \Delta \overline{H}_{B\ melting} > 0$$
 for solid  $\rightleftarrows$  liquid

#### freezing point depression (solid ≥ liquid [solution])

II. Still at  $T_f^{ullet}$  , add solute A to solvent with resulting mole fractions  ${\bf X_A}$  and  ${\bf X_B}$ 

 $\mu_{B}^{soln}$ lowers

 $\mu_{B}^{\ell}\left(X_{B},T_{f}^{\bullet}\right)$  is now chemical potential of solvent (B) in solution

At  $T_f$  the original freezing

$$\Delta\mu_{B}^{s\to\ell}\left(T_{f}^{\bullet}\right)=\mu_{B}^{\ell}\left(X_{B},T_{f}^{\bullet}\right)-\mu_{B}^{s}\left(T_{f}^{\bullet}\right)$$
original freezing temperature 
$$\Delta\mu_{B}^{s\to\ell}\left(T_{f}^{\bullet}\right)=RT_{f}^{\bullet}\ln\left(\gamma_{B}X_{B}\right) \text{ "proof "}$$



so at  $T^{\bullet}$  the forward reacton (melting of the solid) would now occur spontaneously

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#### freezing point depression (solid *₹ liquid [solution]*)

III. Alter temperature to restore equilibrium  $T_f^{ullet} o T_f \ \left[ rac{\partial rac{\Delta \mu}{T}}{\partial T} 
ight] = -rac{\Delta ar{H}}{T^2}$ 

solvent at new  $T_f$  solvent at  $T_f$  $\begin{array}{ccc} \text{calculate } \Delta \pmb{\mu} \text{:} & \left( \frac{\Delta \mu_{\scriptscriptstyle B}(T_{\scriptscriptstyle f})}{T_{\scriptscriptstyle f}} \right)_{\scriptscriptstyle P} = & \left( \frac{\Delta \mu_{\scriptscriptstyle B}(T_{\scriptscriptstyle f}^{\, \bullet})}{T_{\scriptscriptstyle f}^{\, \bullet}} \right)_{\scriptscriptstyle P} & -\int\limits_{\tau_{\scriptscriptstyle f}^{\, \bullet}}^{\tau_{\scriptscriptstyle f}} \frac{\Delta \overline{H}_{\scriptscriptstyle B\, melting}}{T^2} dT \end{array}$ 

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

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

extra:

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



change in  $\Delta\mu_{\rm B}$  due to adding solute

change in  $\Delta\mu_{\rm B}$  due to temperature change

#### freezing point lowering

# IV. Obtain relationships between X<sub>B</sub> and change in T

$$R\ln\left(\gamma_{_{B}}X_{_{B}}\right) = \int_{T_{_{f}}^{*}}^{T_{_{f}}} \frac{\Delta \overline{H}_{_{B \, melting}}}{T^{2}} dT \quad \text{from III}$$

$$R\ln\left(\gamma_{\scriptscriptstyle B}X_{\scriptscriptstyle B}\right) = -\Delta \overline{H}_{\scriptscriptstyle B\ melting} \left[\frac{1}{T_{\scriptscriptstyle f}} - \frac{1}{T_{\scriptscriptstyle f}^{\bullet}}\right]$$

since lhs < 0 and 
$$\Delta H_{\text{melting}} > 0$$

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

$$T_{f} = \frac{T_{f}^{\bullet} \Delta \overline{H}_{B \text{ melting}}}{\Delta \overline{H}_{B \text{ melting}} - R T_{f}^{\bullet} \ln(\gamma_{B} X_{B})} \quad (\sim \text{eqn } 9.32 \text{ E\&R}_{4th})$$

extra:



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

Colligative properties:

• freezing point lowering: 
$$\gamma_{g}X_{g} = \exp\left[-\frac{\Delta \overline{H}_{melting}}{R}\left[\frac{1}{T_{f}} - \frac{1}{T_{f}}\right]\right] \qquad T_{f} = \frac{T_{f}^{*}\Delta \overline{H}_{B \ melting}}{\Delta \overline{H}_{B \ melting} - RT_{f} \ln\left(\gamma_{B}X_{B}\right)}$$

boiling point elevation

$$\gamma_{\mathcal{B}} X_{\mathcal{B}} = \exp \left[ \frac{\Delta \overline{H}_{\text{vaportzation}}}{R} \left[ \frac{1}{T_{bp}} - \frac{1}{T_{bp}^{\bullet}} \right] \right] \qquad T_{bp} = \frac{T_{bp}^{\bullet} \Delta \overline{H}_{\mathcal{B} \text{ vaportzation}}}{\Delta \overline{H}_{\mathcal{B} \text{ vaportzation}} + RT_{bp}^{\bullet} \ln \left( \gamma_{\mathcal{B}} X_{\mathcal{B}} \right)} \right]$$

- · boiling point elevation and freezing point depression similar except for sign change (due to  $X_B^{\ell}$  product in melting, reactant in vaporization)
- $\gamma_{_{B}}X_{_{B}}$  < 1 and  $\Delta \overline{H}_{_{vaporization}}$  > 0 implies that so  $T_{bp} > T_{bp}^{\bullet}$  HIGHER BOILING POINT with salt

HANDOUT #53



# non-volatile ionic solutes in vapor pressure and colligative properties

for X<sub>B</sub>, mole fraction solvent,

$$X_{B} = X_{solvent} = \frac{n_{solvent}}{n_{solvent} + n_{(total solute particles)}}$$

 $NaCl \rightarrow Na^{\scriptscriptstyle +} + Cl^{\scriptscriptstyle -}$ 

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

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

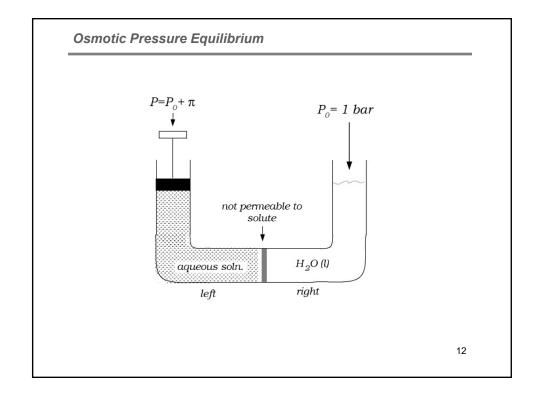
molality =m= (moles solute)/(1000 g solvent) molarity =M= (moles solute)/(1L solution)

HW8 #58

$$A_x B_y(s) \rightleftharpoons x A^{(\text{soln})} + y B^{(\text{soln})}$$

'K<sub>sp</sub> molality reference'

$$K_{sp} = \frac{\left(a_{A\text{solin}}\right)^{x} \left(a_{B\text{solin}}\right)^{y}}{\left(a_{AB\text{solid}}\right)} = \frac{\left(\gamma_{\pm} \begin{bmatrix} m_{A} \end{bmatrix} / \sum_{l \text{ m}} x \begin{bmatrix} \gamma_{\pm} \begin{bmatrix} m_{B} \end{bmatrix} / \sum_{l \text{ m}} y \end{bmatrix}}{1}$$
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# osmotic pressure (solution [solvent + solute] ≠ pure solvent)

 pure solvent at P<sub>left</sub> is originally in equilibrium with pure solvent at P<sub>right</sub>; i.e. P<sub>left</sub>=P<sub>right</sub>=P<sub>0</sub>

pure  $\ell$ iquid $_{_B}^{\bullet}(P_0, left) \rightleftarrows pure \ell$ iquid $_{_B}^{\bullet}(P_0, right)$  at T 'left' and 'right' refer to compartments separated by solute impermeable membrane  $\mu_{_B}^{\bullet}(P_0, left) = \mu_{_B}^{\bullet}(P_0, right)$ 

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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  $\mathbf{X}_{\mathbf{A}}$  and  $\mathbf{X}_{\mathbf{B}}$ 

 $\begin{array}{c} \text{add } X_{\scriptscriptstyle A} \text{ solute to liquid in 'left' compatment resulting in } X_{\scriptscriptstyle B} \text{ for solvent} \\ \text{lectures 20-21} \\ \text{slide #20} \end{array} \\ \mu_{\scriptscriptstyle B}^{\ell}(P_{\scriptscriptstyle 0}, left) = \mu_{\scriptscriptstyle B}^{\ell \bullet}(P_{\scriptscriptstyle 0}, left) + RT \ln \left(\gamma_{\scriptscriptstyle B} X_{\scriptscriptstyle B}\right) < \quad \mu_{\scriptscriptstyle B}^{\ell \bullet}(P_{\scriptscriptstyle 0}, right) \\ \end{array}$ 

 $\mu_B^{\ell}(P_0, left) < \mu_B^{\bullet \bullet}(P_0, right)$ so the solvent B moves spontaneously left  $\leftarrow$  right (i.e. diluting solution on left)

#### osmotic pressure (III, alter pressure)

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

how does 
$$\mu$$
 change  $\left[\frac{\partial \mu_B^{left}}{\partial z}\right] = \overline{V}_B$   $\int_{-R_0+\pi}^{R_0+\pi} d\mu_B^{left}(X_B) = \int_{-R_0+\pi}^{R_0+\pi} \overline{V}_B dP$ 

$$\begin{array}{|c|c|} \hline \text{how does } \pmb{\mu} \text{ change} \\ \hline \text{with pressure?} \end{array} \left( \frac{\partial \mu_{B}^{\text{left}}}{\partial P_{\text{left}}} \right)_{T} = \overline{V}_{B} \qquad \int\limits_{P_{0}}^{P_{0}+\pi} d\, \mu_{B}^{\text{left}} \left( X_{B} \right) = \int\limits_{P_{0}}^{P_{0}+\pi} \overline{V}_{B} dP$$

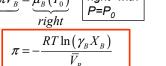
$$\begin{array}{c} \mu_{\scriptscriptstyle B}^{\rm left}\left(X_{\scriptscriptstyle B},P_{\scriptscriptstyle 0}+\pi\right) = \mu_{\scriptscriptstyle B}^{\rm left}\left(X_{\scriptscriptstyle B},P_{\scriptscriptstyle 0}\right) + \left[P_{\scriptscriptstyle 0}+\pi-P_{\scriptscriptstyle 0}\right] \overline{V}_{\scriptscriptstyle B} \\ \mu_{\scriptscriptstyle B}^{\rm left}\left(X_{\scriptscriptstyle B},P_{\scriptscriptstyle 0}+\pi\right) = \mu_{\scriptscriptstyle B}^{\rm left}\left(X_{\scriptscriptstyle B},P_{\scriptscriptstyle 0}\right) + \pi \overline{V}_{\scriptscriptstyle B} \end{array}$$

integrate 
$$\mu_{B}^{left}\left(X_{B},P_{0}+\pi\right)=\underbrace{\mu_{B}^{left}\left(X_{B},P_{0}\right)+\pi\overline{V}_{B}}_{left}$$

$$\mu_{B}^{left}\left(X_{B},P_{0}+\pi\right)=\underbrace{\mu_{B}^{\bullet}\left(P_{0}\right)+RT\ln\left(\gamma_{B}X_{B}\right)+\pi\overline{V}_{B}}_{left}$$

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

$$\underbrace{\mu_B^{\bullet}(P_0) + RT \ln(\gamma_B X_B) + \pi \overline{V}_B}_{left} = \underbrace{\mu_B^{\bullet}(P_0)}_{right} \qquad \underbrace{\begin{array}{c} right \ with \\ P=P_0 \end{array}}_{RT \ln(\gamma_B X_B)}$$





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#### osmotic pressure (a little more manipulation)

IV. Obtain relationships between  $X_A$  and  $\pi$ , change in P

$$\pi = -\frac{RT\ln\left(\gamma_{B}X_{B}\right)}{\overline{V}_{R}}$$

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

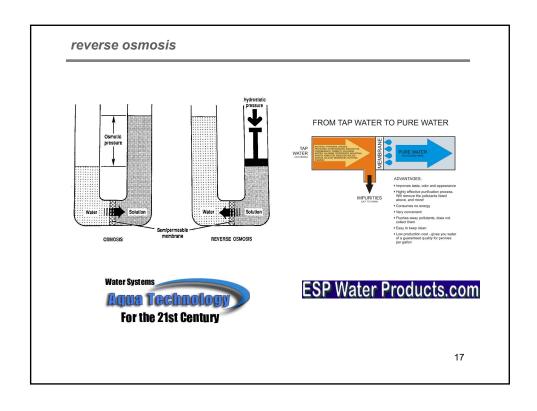
$$\pi = -\frac{RT \ln(1 - X_A)}{\overline{V}_B}$$

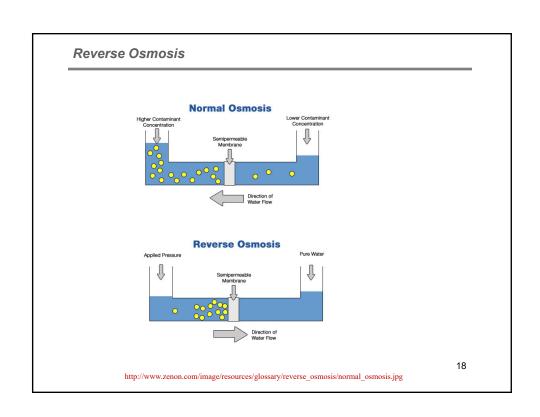
further manipulations

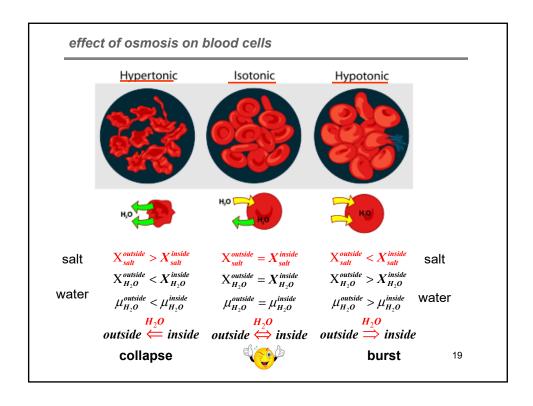
$$\pi V_B = \underline{n_A} RT$$



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









quantitative treatment of colligative properties

#### **Handout #53** Colligative Properties

from relationships for Chem 163B final:

Colligative properties:

· freezing point lowering:

• freezing point lowering: 
$$\gamma_{\mathcal{B}} X_{\mathcal{B}} = \exp \left[ -\frac{\Delta \overline{H}_{\text{melting}}}{R} \left[ \frac{1}{T_f} - \frac{1}{T_f^{\star}} \right] \right] \qquad T_f = \frac{T_f^{\star} \Delta \overline{H}_{\mathcal{B} \, \text{melting}}}{\Delta \overline{H}_{\mathcal{B} \, \text{melting}} - R T_f^{\star} \ln \left( \gamma_{\mathcal{B}} X_{\mathcal{B}} \right)}$$
• boiling point elevation:

$$\gamma_{B}X_{B} = \exp\left[\frac{\Delta \overline{H}_{vaportzation}}{R} \left[\frac{1}{T_{bp}} - \frac{1}{T_{bp}^{\bullet}}\right]\right] \qquad T_{bp} = \frac{T_{bp}^{\bullet} \Delta \overline{H}_{B \, vaportzation}}{\Delta \overline{H}_{B \, vaportzation} + RT_{bp}^{\bullet} \ln\left(\gamma_{B}X_{B}\right)}$$

$$\pi = \frac{-RT\ln\left(\gamma_{B}X_{B}\right)}{\overline{V}_{B}} \qquad \quad \pi \approx \frac{n_{A}RT}{V_{B}} = \frac{n_{solute}RT}{V_{solvent}} \quad for \ dilute \ solution$$

(hopefully) reassuring ??

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# End of Lectures 22.23

freezing point depression (solid ≥ solution)

II. Still at  $T_f^{ullet}$  , add solute A to solvent with resulting mole fractions  ${\bf X_A}$  and  ${\bf X_B}$ 

for solid phase of B there is no change:

$$\mu_B^{s\bullet}(T_f^{\bullet}) = \mu_B^{solid}(T_f^{\bullet})$$

for the solvent (B) in solution: see lect 20-21 slide #20

$$\boldsymbol{\mu}_{B}^{\ell}(\boldsymbol{T}_{f}^{\bullet}) \equiv \boldsymbol{\mu}_{B}^{solvent} \equiv \boldsymbol{\mu}_{B}^{\ell \, (in \, soln)}(\boldsymbol{T}_{f}^{\bullet}) = \boldsymbol{\mu}_{B}^{\ell \bullet}(\boldsymbol{T}_{f}^{\bullet}) + R\boldsymbol{T}_{f}^{\bullet} \ln \left(\boldsymbol{\gamma}_{B} \boldsymbol{X}_{B}\right)$$

so now 
$$\Delta \mu_B(T_f^{\bullet}) = \mu_B^{\ell}(T_f^{\bullet}) - \mu_B^{s\bullet}(T_f^{\bullet}) = \mu_B^{\ell\bullet}(T_f^{\bullet}) + RT_f^{\bullet} \ln(\gamma_B X_B) - \mu_B^{s\bullet}(T_f^{\bullet})$$

but  $\mu_B^{\ell \bullet}(T_f^{\bullet}) - \mu_B^{s \bullet}(T_f^{\bullet}) = 0$  since pure liquid and solid are in equilibrium at  $T_f^{\bullet}$ 

thus 
$$\Delta \mu_B(T_e^{\bullet}) = RT_e^{\bullet} \ln(\gamma_B X_B) < 0$$



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freezing point depression (solid ≥ solution)

III. Alter temperature to restore equilibrium  $T_f^{ullet} o T_f$ 

$$\left(\frac{\partial \frac{\Delta \mu}{T}}{\partial T}\right)_{P} = -\frac{\Delta \overline{H}}{T^{2}}$$

$$\int_{T_{f}^{*}}^{T_{f}} d\left(\frac{\Delta \mu_{B}}{T}\right)_{P} = -\int_{T_{f}^{*}}^{T_{f}} \frac{\Delta \overline{H}_{B \text{ melting}}}{T^{2}} dT$$

$$\left(\frac{\Delta \mu_{B}(T_{f})}{T_{f}}\right)_{P} - \left(\frac{\Delta \mu_{B}(T_{f}^{*})}{T_{f}^{*}}\right)_{P} = -\int_{T_{f}^{*}}^{T_{f}} \frac{\Delta \overline{H}_{B \text{ melting}}}{T^{2}} dT$$
old stuff

#### freezing point depression (solid 2 solution)

III. Alter temperature to restore equilibrium (continued)

$$\left(\frac{\Delta\mu_{B}^{s}(T_{f})}{T_{f}}\right)_{p} - \left(\frac{\Delta\mu_{B}^{s}(T_{f}^{\bullet})}{T_{f}^{\bullet}}\right)_{p} = -\int_{T_{f}^{\bullet}}^{T_{f}} \frac{\Delta\overline{H}_{B \text{ melting}}}{T^{2}} dT$$

$$\left(\frac{\Delta\mu_{B}(T_{f})}{T_{f}}\right)_{p} = 0 \text{ since at 'new' equilibrium } T_{f}, \Delta\mu_{B}(T_{f}) = 0$$

$$and \quad \left(\frac{\Delta\mu_{B}(T_{f}^{\bullet})}{T_{f}^{\bullet}}\right)_{p} = R \ln\left(\gamma_{B}X_{B}\right) \quad \text{from eqn in } II.$$

$$-R \ln\left(\gamma_{B}X_{B}\right) = -\int_{T_{f}^{\bullet}}^{T_{f}} \frac{\Delta\overline{H}_{B \text{ melting}}}{T^{2}} dT$$

$$R \ln\left(\gamma_{B}X_{B}\right) + \left[-\int_{T_{f}^{\bullet}}^{T_{f}} \frac{\Delta\overline{H}_{B \text{ melting}}}{T^{2}} dT\right] = 0$$

change in  $\Delta\mu_{\rm B}$  due to adding solute

change in  $\Delta\mu_{\rm B}$  due to temperature change

#### freezing point lowering

IV. Obtain relationships between X<sub>B</sub> and change in T

$$R\ln\left(\gamma_{B}X_{B}\right) = \int_{T_{f}^{+}}^{T_{f}} \frac{\Delta \overline{H}_{B \text{ melting}}}{T^{2}} dT$$

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

$$R\ln\left(\gamma_{_{B}}X_{_{B}}\right) = -\Delta \overline{H}_{_{B \ melting}} \left[\frac{1}{T_{_{f}}} - \frac{1}{T_{_{f}}^{\bullet}}\right]$$

since  $lhs < 0 \implies T_f < T_f^{\bullet}$  (freezing point **depression**)

$$\gamma_{\scriptscriptstyle B} X_{\scriptscriptstyle B} = \exp \left[ -\frac{\Delta \overline{H}_{\scriptscriptstyle B \, melting}}{R} \left[ \frac{1}{T_f} - \frac{1}{T_f^{\bullet}} \right] \right]$$
 (integration of eqn 9.31 E&R)

# freezing point lowering

IV. Obtain relationships between X<sub>B</sub> and change in T (cont)

$$\gamma_{\scriptscriptstyle B} X_{\scriptscriptstyle B} = \exp \left[ -\frac{\Delta \overline{H}_{\scriptscriptstyle B \, melting}}{R} \left[ \frac{1}{T_f} - \frac{1}{T_f^{\bullet}} \right] \right]$$

$$-\frac{R}{\Delta \overline{H}_{B melting}} \ln (\gamma_B X_B) + \frac{1}{T_f^{\bullet}} = \frac{1}{T_f}$$

$$T_f = \frac{T_f^{\bullet} \Delta \overline{H}_{B melting}}{\Delta \overline{H}_{B melting} - R T_f^{\bullet} \ln (\gamma_B X_B)} \quad (\sim \text{eqn } 9.32 \text{ E&R}_{4th})$$



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#### osmotic pressure (III, alter pressure)

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

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

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

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

assuming solvent is incompressible

 $(\overline{V}_{B} \text{ doesn't change with pressure at constant T})$ 

$$\mu_{\scriptscriptstyle B}^{\scriptscriptstyle left}\left(X_{\scriptscriptstyle B},P_{\scriptscriptstyle 0}+\pi\right)=\mu_{\scriptscriptstyle B}^{\scriptscriptstyle left}\left(X_{\scriptscriptstyle B},P_{\scriptscriptstyle 0}\right)+\left[P_{\scriptscriptstyle 0}+\pi-P_{\scriptscriptstyle 0}\right]\overline{V}_{\scriptscriptstyle B}$$

$$\mu_{B}^{left}\left(X_{B},P_{0}+\pi\right)=\mu_{B}^{left}\left(X_{B},P_{0}\right)+\pi\overline{V}_{B}$$

# osmotic pressure (III, alter pressure, continued)

$$\mu_{B}^{left}(X_{B}, P_{0} + \pi) = \mu_{B}^{left}(X_{B}, P_{0}) + \pi \overline{V}_{B}$$

$$\mu_{B}^{left}(X_{B}, P_{0} + \pi) = \mu_{B}^{\bullet}(P_{0}) + RT \ln(\gamma_{B}X_{B}) + \pi \overline{V}_{B}$$

want  $\pi$  to restore equilibrium such that

$$\mu_B^{left}\left(\boldsymbol{X}_B,\boldsymbol{P}_0+\boldsymbol{\pi}\right) = \mu_B^{\bullet \ right}\left(\boldsymbol{P}_0\right)$$

$$\begin{split} \underbrace{\mu_{B}^{\bullet}\left(P_{0}\right) + RT\ln\left(\gamma_{B}X_{B}\right) + \pi\overline{V_{B}}}_{left} &= \underbrace{\mu_{B}^{\bullet}\left(P_{0}\right)}_{right} \\ \pi &= -\frac{RT\ln\left(\gamma_{B}X_{B}\right)}{\overline{V_{B}}} \end{split}$$



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#### osmotic pressure (a little more manipulation)

$$\pi = -\frac{RT \ln \left(\gamma_B X_B\right)}{\overline{V}_B} \qquad \text{A=solute} \\ for \ \gamma_B \approx 1 \quad and \ X_B = 1 - X_A \qquad \text{B=solvent} \\ \pi = -\frac{RT \ln \left(1 - X_A\right)}{\overline{V}_B} \\ \ln (1 + x) \approx x \quad for \ small \ x \quad (i.e. \ dilute \ solution, \ X_A \ small) \\ \pi = \frac{X_A RT}{\overline{V}_B} \\ X_A = \frac{n_A}{n_A + n_B} \quad and \ n_A + n_B \approx n_B \quad for \ dilute \ solution \\ \pi \approx \frac{n_A RT}{n_B \overline{V}_B} \\ \pi V_B = n_A RT \\ \pi V_{solution} = n_{solute} RT$$

### colligative properties and nonvolatile solutes

- mole fraction solvent  $X_B = n_B/n_{total}$
- for non-volatile solute A P\*<sub>A</sub>=0
- concentrations frequently given in molality
   M=molarity=(moles solute)/(L solution)
   †m=molality=(moles solute)/(1000g solvent)
   moles H<sub>2</sub>O/1000g solvent≈55.55 moles
   aqueous soln: X<sub>solvent</sub>=55.55/(m+55.55)
- for ionic solvent (moles solute)=(total moles of ions)
- example: 2 m aqueous solution of CaCl<sub>2</sub> (complete dissociation)

$$X_{H_2O} = \frac{55.55\,\mathrm{moles\,/\,kgH,O}}{(2\mathrm{moles\,solute/kgH,O} \times 3\mathrm{moles\,ions/moles\,solute}) + 55.55\mathrm{moles\,/\,kgH,O})} = .9025$$

\* however when referring to the molality of a specific ion, e.g. [Cl<sup>-</sup>] from CaCl<sub>2</sub>, the number of ions per mole of solute is already factored in