

# Lecture 22-23

## Chemistry 163B W2020

### Colligative Properties

### Challenged Penpersonship

### Notes



# *colligative properties of solutions*

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## **colligative**



One entry found.

Main Entry: col·li·ga·tive

Pronunciation: ˈkɑ-lə-gā-tiv, kə-ˈli-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*>

## *quantitative treatment of colligative properties*

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***A. Freezing point depression***

***B. Boiling Point Elevation***

***C. Osmotic Pressure***

## Handout #53 Colligative Properties

from relationships for Chem 163B final:

Colligative properties:

- freezing point lowering:

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

- boiling point elevation:

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

- osmotic pressure:

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

*(hopefully) reassuring ??*

## *quantitative treatment of colligative properties*

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- 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.

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

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

*solid is pure "solvent" B*

$X_B$  = mole fraction solvent B in solution

$X_A$  = mole fraction solute A in liquid

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

$$\mu_B^{s^\bullet}(T_f^\bullet) = \mu_B^{\ell^\bullet}(X_B = 1, T_f^\bullet)$$

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

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

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

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

$\mu_B^{\text{soln}}$   
lowers

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

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

$$\Delta\mu_B^{s \rightarrow \ell}(T_f^\bullet) = RT_f^\bullet \ln(\gamma_B X_B) \quad \text{“proof”}$$

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



so at  $T_f^\bullet$  the forward reaction (melting of the solid) would now occur spontaneously

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

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

calculate  $\Delta\mu$ :  $T_f^\bullet \rightarrow T_f$

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

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

but at new  $T_f$ :  
want

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

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

one gets:

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

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

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

extra:





## freezing point lowering

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### IV. Obtain relationships between $X_B$ and change in $T$

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

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

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

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

freezing point **depression**

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

extra:



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

Colligative properties:

- freezing point lowering:

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

- boiling point elevation:

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

- boiling point elevation and freezing point depression similar except for sign change  
(due to  $X_B$  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

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

for  $X_B$ , mole fraction solvent,

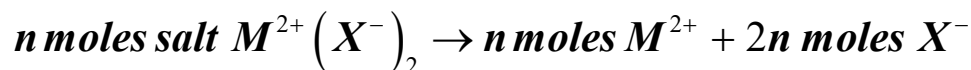
$$X_B = X_{\text{solvent}} = \frac{n_{\text{solvent}}}{n_{\text{solvent}} + n_{\text{(total solute particles)}}}$$



1 mole  $\rightarrow$  2 moles 'particles'

*in mole fraction : moles solute = total moles ions*

HW7 #52b



*3n moles solute*

$$X_{\text{H}_2\text{O}} = \frac{\text{moles H}_2\text{O}}{(\text{moles H}_2\text{O} + 3 \times \text{moles salt})}$$

molality = **m** = (moles solute)/(1000 g solvent)

molarity = **M** = (moles solute)/(1L solution)

HW8 #58

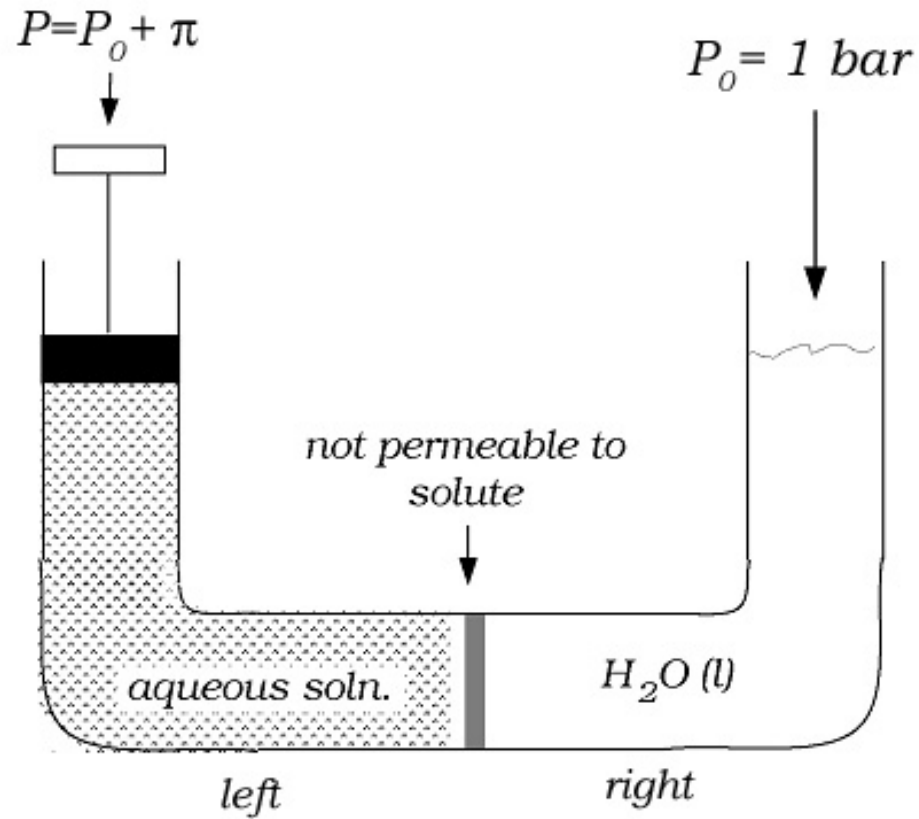


' $K_{sp}$  molality reference'

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

# Osmotic Pressure Equilibrium

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## *osmotic pressure (solution [solvent + solute] ⇌ pure solvent)*

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



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

$$\mu_B^{\bullet}(P_0, \text{left}) = \mu_B^{\bullet}(P_0, \text{right})$$

## osmotic pressure (II add solute to left compartment)

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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

$$\mu_B^l(P_0, \text{left}) = \mu_B^{l\bullet}(P_0, \text{left}) + RT \ln(\gamma_B X_B) < \mu_B^{l\bullet}(P_0, \text{right})$$

---

$$\mu_B^l(P_0, \text{left}) < \mu_B^{l\bullet}(P_0, \text{right})$$

so the solvent B moves spontaneously left ← 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  $(X_B, P_0 + \pi, \text{left}) \rightleftharpoons \text{pure solvent}(P_0, \text{right})$

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

how does  $\mu$  change with pressure?

$$\left( \frac{\partial \mu_B^{\text{left}}}{\partial P_{\text{left}}} \right)_T = \bar{V}_B \quad \int_{P_0}^{P_0 + \pi} d\mu_B^{\text{left}}(X_B) = \int_{P_0}^{P_0 + \pi} \bar{V}_B dP$$

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.

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

left with  $P = P_0 + \pi$

$$\underbrace{\mu_B^\bullet(P_0) + RT \ln(\gamma_B X_B) + \pi \bar{V}_B}_{\text{left}} = \underbrace{\mu_B^\bullet(P_0)}_{\text{right}}$$

right with  $P = P_0$

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

extra:



## osmotic pressure (a little more manipulation)

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

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

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

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

further manipulations

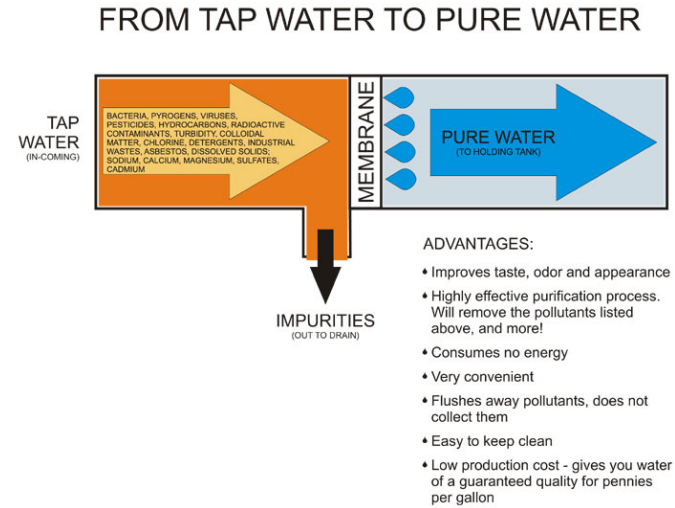
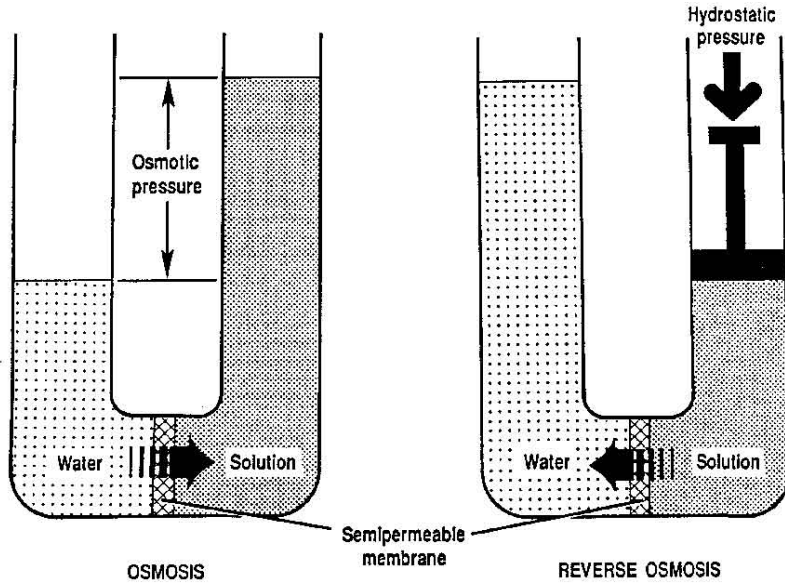
$$\pi V_B = n_A RT$$



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



# reverse osmosis



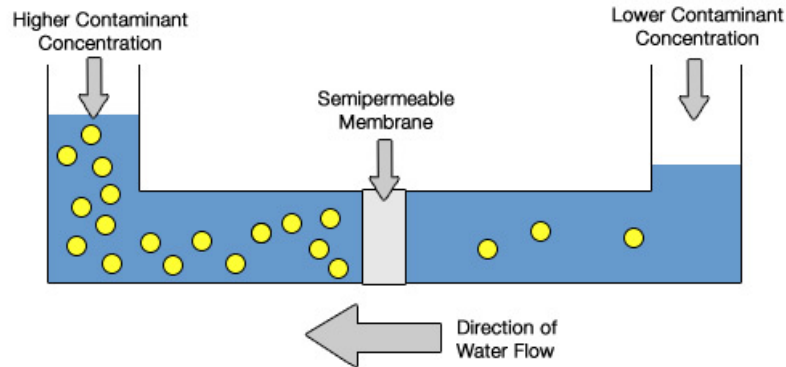
Water Systems  
**Aqua Technology**  
 For the 21st Century

[ESP Water Products.com](http://ESP Water Products.com)

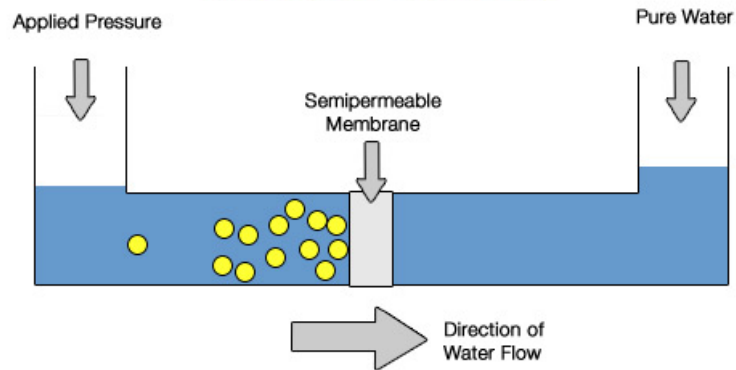
# Reverse Osmosis

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## Normal Osmosis



## Reverse Osmosis

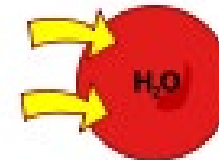
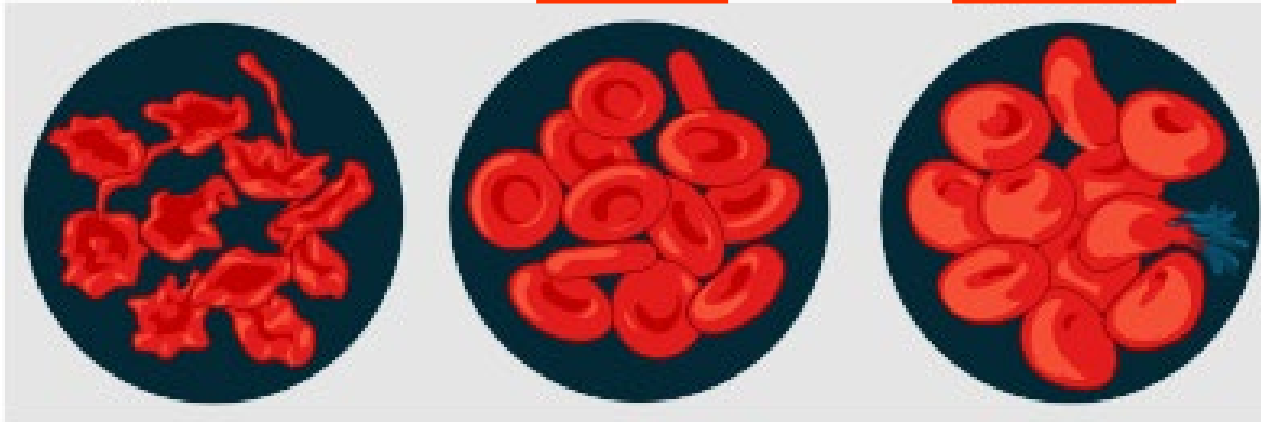


# effect of osmosis on blood cells

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

$$\mu_{\text{H}_2\text{O}}^{\text{outside}} < \mu_{\text{H}_2\text{O}}^{\text{inside}}$$

$$\mu_{\text{H}_2\text{O}}^{\text{outside}} = \mu_{\text{H}_2\text{O}}^{\text{inside}}$$

$$\mu_{\text{H}_2\text{O}}^{\text{outside}} > \mu_{\text{H}_2\text{O}}^{\text{inside}}$$

$\text{H}_2\text{O}$   
outside  $\leftarrow$  inside

$\text{H}_2\text{O}$   
outside  $\leftrightarrow$  inside

$\text{H}_2\text{O}$   
outside  $\Rightarrow$  inside

**collapse**



**burst**

## Woman dies after water-drinking contest

Water intoxication eyed in 'Hold Your Wee for a Wii' contest death

**AP** 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, 28, 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 KDND 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."

 NBC VIDEO



Launch

### **Woman in water drinking contest dies**

Jan. 15: Sacramento Bee reporter Christina Jewett talks to MSNBC-TV's Contessa Brewer about the death of a woman who had competed in a radio station contest.

MSNBC

## Handout #53 Colligative Properties

from relationships for Chem 163B final:

Colligative properties:

- freezing point lowering:

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

- boiling point elevation:

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

- osmotic pressure:

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

*(hopefully) reassuring??*

**End of Lectures 22-23**

## freezing point depression (solid $\rightleftharpoons$ solution)

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

for solid phase of B there is no change :

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

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

$$\mu_B^l(T_f^\bullet) \equiv \mu_B^{solvent} \equiv \mu_B^{l(in\ soln)}(T_f^\bullet) = \mu_B^{l^\bullet}(T_f^\bullet) + RT_f^\bullet \ln(\gamma_B X_B)$$

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

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

$$\text{thus } \Delta\mu_B(T_f^\bullet) = RT_f^\bullet \ln(\gamma_B X_B) < 0$$



## freezing point depression (solid $\rightleftharpoons$ solution)

---

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

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

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

*old stuff*

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



## freezing point depression (solid $\rightleftharpoons$ solution)

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### III. Alter temperature to restore equilibrium (continued)

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

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

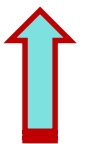
$$\text{and } \left( \frac{\Delta\mu_B(T_f^\bullet)}{T_f^\bullet} \right)_P = R \ln(\gamma_B X_B) \text{ from eqn in II.}$$

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

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

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

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



IV. Obtain relationships between  $X_B$  and change in T

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

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

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

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

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

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

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

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

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



## osmotic pressure (III, alter pressure)

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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* ( $P_0, \text{right}$ )

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

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

assuming solvent is incompressible

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

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

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

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

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

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

want  $\pi$  to restore equilibrium such that

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

$$\underbrace{\mu_B^\bullet(P_0) + RT \ln(\gamma_B X_B) + \pi \bar{V}_B}_{\text{left}} = \underbrace{\mu_B^\bullet(P_0)}_{\text{right}}$$

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



## osmotic pressure (a little more manipulation)

---

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

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

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

A=solute  
B=solvent

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

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

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

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

$$\pi V_B = n_A RT$$

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



## colligative properties and nonvolatile solutes

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- mole fraction solvent  $X_B = n_B/n_{\text{total}}$
- for non-volatile solute A  $P_A^* = 0$
- 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:  $X_{\text{solvent}} = 55.55/(m+55.55)$
- for ionic solvent (moles solute)=(total moles of ions)
- example: 2 m aqueous solution of CaCl<sub>2</sub> (complete dissociation)

$$X_{H_2O} = \frac{55.55 \text{ moles / kgH}_2\text{O}}{(2 \text{ moles solute/kgH}_2\text{O} \times 3 \text{ moles ions/moles solute}) + 55.55 \text{ moles / kgH}_2\text{O}} = .9025$$

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