**Chemistry 163B
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-gā-tiv, kə-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

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quantitative treatment of colligative properties

Handout #55

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

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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.

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freezing point depression (solid ⇌ solution)

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

$pure\ solid_B^{\bullet} \rightleftarrows pure\ (liquid_B^{\bullet}\quad at\ T_f^{\bullet}\quad the\ normal\ melting\ T_{fusion}$

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

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

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

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freezing point depression (solid ⇌ solution)

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

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

where $\Delta\mu_s^{\bullet}(T_f^{\bullet}) = \mu_B^{l\bullet}(T_f^{\bullet}) - \mu_B^{s\bullet}(T_f^{\bullet})$

and $\Delta\mu_s^{\bullet}(T_f^{\bullet}) = 0$ since pure liquid and solid are in equilibrium at $T_f^{\bullet}$

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

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

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freezing point depression (solid ⇌ solution)

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

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

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

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

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freezing point depression (solid ⇌ solution)

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

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

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

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

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

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

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

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

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

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

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

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

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freezing point lowering

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

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

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

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

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Osmotic Pressure Equilibrium

$P = P_0 + \pi$ $P_0 = 1 \, bar$

not permeable to solute

aqueous soln. H_2O (l)

left   right

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

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

$$pure\ liquid_B^{\bullet}(P_0, left) \rightleftharpoons pure\ liquid_B^{\bullet}(P_0, right) \quad at\ T$$

'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 X_A and X_B

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

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

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

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osmotic pressure (III, alter pressure)

III. alter Pressure: $P_{left} \longrightarrow P_0 + \pi$ to restore equilibrium

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

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

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

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

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

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

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osmotic pressure (III, alter pressure, continued)

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

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

want π to restore equilibrium such that

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

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

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

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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)

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

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

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

$$\pi V_B = n_A RT$$

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

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quantitative treatment of colligative properties

Handout #55 Colligative Properties

from relationships for Chem 163B final:

Colligative properties:

• freezing point lowering: $\gamma_B X_B = \exp\left[-\frac{\Delta\bar{H}_{fusion}}{R}\left[\frac{1}{T_f} - \frac{1}{T_f^*}\right]\right]$

• boiling point elevation: $\gamma_B X_B = \exp\left[\frac{\Delta\bar{H}_{vaporization}}{R}\left[\frac{1}{T_{bp}} - \frac{1}{T_{bp}^*}\right]\right]$

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

$\pi \approx \frac{n_A RT}{V_B} = \frac{n_{solute} RT}{V_{solvent}}$ for dilute solution

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reverse osmosis

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Reverse Osmosis

Normal Osmosis

Higher Contaminant Concentration — Lower Contaminant Concentration

Semipermeable Membrane

Direction of Water Flow

Reverse Osmosis

Applied Pressure — Pure Water

Semipermeable Membrane

Direction of Water Flow

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

H_2O H_2O H_2O

$\mu_{H_2O}^{outside} < \mu_{H_2O}^{inside}$ ⠀ $\mu_{H_2O}^{outside} = \mu_{H_2O}^{inside}$ ⠀ $\mu_{H_2O}^{outside} > \mu_{H_2O}^{inside}$

$X_{H_2O}^{outside} < X_{H_2O}^{inside}$ ⠀ $X_{H_2O}^{outside} = X_{H_2O}^{inside}$ ⠀ $X_{H_2O}^{outside} > X_{H_2O}^{inside}$

$X_{salt}^{outside} > X_{salt}^{inside}$ ⠀ $X_{salt}^{outside} = X_{salt}^{inside}$ ⠀ $X_{salt}^{outside} < X_{salt}^{inside}$

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hyponatremia

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

NBC VIDEO

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."

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

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End of Lecture

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