Chemistry 163B, Winter 2014

Lecture 23 Colligative Properties

Chemistry 163B

Colligative Properties

Challenged Penpersonship Notes

colligative properties of solutions

colligative
One entry found.
Main Entry: col·li·ga·tive
Pronunciation: ˈkä-lə-ˌgā-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*>

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

quantitative treatment of colligative properties

Handout #55

A. Freezing point depression

B. Boiling Point Elevation

C. Osmotic Pressure

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.

freezing point depression (solid ⇄ solution)

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

$$\textit{pure solid}_B^\bullet \rightleftarrows \textit{pure } \ell\textit{iquid}_B^\bullet \quad \textit{at } T_f^\bullet \quad \textit{the normal melting } T_{fusion}$$

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

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

$$\Delta\bar{H}(T_f^\bullet) = \Delta\bar{H}_{B\,melting} \quad > 0$$

for solid ⟶ liquid

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:

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

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

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

and $\Delta\mu_B^\bullet(T_f^\bullet) = 0$ 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 $T_f^\bullet$

freezing point depression (solid ⇄ solution)

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

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

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

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)*

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

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

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

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

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

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

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

$\Delta\bar{H}_{B\,melting}$ ~ 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**)

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

(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)*

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

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

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

(~ eqn 9.32 E&R)

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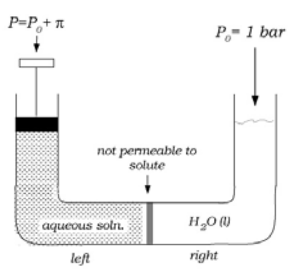
Osmotic Pressure Equilibrium



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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. $P_{left}=P_{right}=P_0$

$$pure\ \ell iquid_B^\bullet(P_0, left) \rightleftarrows pure\ \ell iquid_B^\bullet(P_0, right)\quad at\ T$$

'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*

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

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

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

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

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

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

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

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

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

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osmotic pressure (III, alter pressure, continued)

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

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

want π to restore equilibrium such that

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

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

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

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osmotic pressure (a little more manipulation)

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

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

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

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

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

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

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

$$\pi V_B = n_A RT$$

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

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quantitative treatment of colligative properties

Handout #55 **Colligative Properties**

from relationships for Chem 163B final:

Colligative properties:
:

- freezing point lowering: $\gamma_B X_B = \exp\left[-\frac{\Delta \overline{H}_{fusion}}{R}\left[\frac{1}{T_f} - \frac{1}{T_f^{\bullet}}\right]\right]$
- boiling point elevation: $\gamma_B X_B = \exp\left[\frac{\Delta \overline{H}_{vaporization}}{R}\left[\frac{1}{T_{bp}} - \frac{1}{T_{bp}^{\bullet}}\right]\right]$
- osmotic pressure: $\pi = \frac{-RT\ln(\gamma_B X_B)}{\overline{V}_B}$

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

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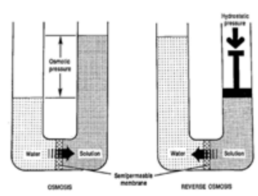
reverse osmosis



Water Systems Aqua Technology For the 21st Century

ESP Water Products.com

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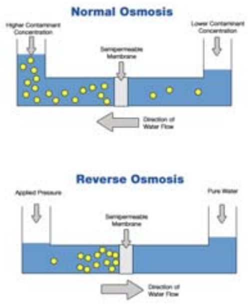
Reverse Osmosis



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

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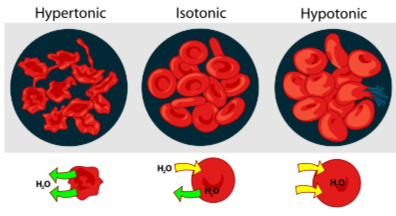
effect of osmosis on blood cells



Hypertonic	Isotonic	Hypotonic
$\mu_{H_2O}^{outside} < \mu_{H_2O}^{inside}$	$\mu_{H_2O}^{outside} = \mu_{H_2O}^{inside}$	$\mu_{H_2O}^{outside} > \mu_{H_2O}^{inside}$
$X_{H_2O}^{outside} < X_{H_2O}^{inside}$		$X_{H_2O}^{outside} > X_{H_2O}^{inside}$
$X_{salt}^{outside} > X_{salt}^{inside}$	$X_{salt}^{outside} = X_{salt}^{inside}$	$X_{salt}^{outside} < X_{salt}^{inside}$

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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

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

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End of Lecture