Lecture # 22

Last time

Surface tension - free energy cost of creating new surface

\[ y = \frac{2A}{r} \, \text{r}_1r_2 \]

\[ y = \frac{2g}{r} \, \text{r}_1r_2 \]

\[ y = -\frac{\text{water}}{2a} \]

How much energy does it take for water drop \[ \bigcirc \rightarrow \bigcirc \]

1 mL \[ \text{.5mm drops} \]

\[ \Delta G = y \Delta A = y (\pi) \left[ \frac{1.5 \times 10^{-5}}{0.25}^2 - \frac{0.62}{2}^2 \right] \]

\[ = 7.34 - 4.8 = 2.2 \, \text{cm}^2 = 0.23 \, \text{m}^2 \]

\[ y = 72.8 \, \text{dyn/cm} = 0.0728 \, \text{kg/m}^2 \]

\[ \Delta G = (0.0728)(0.073) = 5.3 \times 10^{-3} \, \text{J} \]

Getting to be the time of year - what temp does sea water freeze? Why put salt on ice?

Dirty water freezes at a lower temp than pure water. (boils higher, also)

Let's now predict "colligative property"
Using the lattice model, we derived the relationship

\[
M_A = kT \left[ \frac{2}{\omega A} \left( \frac{F}{kT} \right) \right] N_A, T
\]

\[
= kT \left[ \ln x_A + \frac{\omega M_A}{kT} + \chi_{AB} (1-x_A)^2 \right]
\]

**Microscopic**

\[
M_A = \frac{\omega M_A}{2} + kT \left[ \ln (x_A) + \chi_{AB} (1-x_A)^2 \right]
\]

We could rewrite as

**Microscopic**

\[
M_A = \frac{\omega M_A}{2} + kT \ln \left( \frac{\chi_{AB} (1-x_A)^2}{x_A} \right)
\]

leads to an obvious definition of macroscopic \( M_A \)

**Macroscopic**

\[
M_A = M_A^0 + kT \ln \frac{x_A}{x_A}
\]

↑

pure \( A \)

activity coeff captures nonidealities

\( x_A \rightarrow 1 \) as \( x_A \rightarrow 0 \)

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Book analyzes boiling \( \Rightarrow \) that is for summer version of course.

Now lets analyze freezing salt water

similar approach to other phase transitions.

water = B

salt = A
pure

\[ M_B (\text{ice}, T) = M_B (\text{liq}, T, x_B) \]
\[ M_B^0 (\text{ice}) = M_B^0 (\text{liq}) + KT \ln \gamma_B x_B \]

dirty

\[ \ln \gamma_B x_B = \frac{1}{KT} \left[ M_B^0 (\text{ice}, T) - M_B^0 (\text{liq}, T) \right] \]

Eqn 16.16

Recall

\[ M_j = \frac{2G}{a N_j} \]

\[ M_j = \frac{\Delta H_j}{a N_j} - T \frac{\Delta S_j}{a N_j} = h_j - T s_j \quad \text{eqn 9.25} \]

Sub in

\[ \ln \gamma_B x_B = \frac{1}{KT} \left[ (h_{\text{ice}} - h_{\text{liq}}) - T \Delta s_{\text{ice}} - \Delta s_{\text{liq}} \right] \]

Now for pure H2O @ \( T = T_f \) freezing temp

\[ \ln \gamma = \frac{1}{K_{T_f}} \left( h_{\text{ice}} - h_{\text{liq}} \right) - \frac{1}{K} (s_{\text{ice}} - s_{\text{liq}}) \]

Subtract

\[ \ln \gamma_B x_B = 0 = \left( \frac{1}{KT} - \frac{1}{K_{T_f}} \right) (h_{\text{ice}} - h_{\text{liq}}) - \phi \]

\[ \Delta h_f \]

\[ \ln \gamma_B x_B = \frac{\Delta h_f (T_f - T)}{KT_f} \]

\[ \frac{T - T_f}{T_f} = \frac{T_f - T}{T_f^2} \]
Simplify
For small solute concentrations

\[
\ln \frac{Y_B}{X_B} = \ln \left[ \frac{Y_B}{1-x_A}\right] = \ln Y_B - \ln \left(1-x_A\right)
\]

From micro def

\[= x_A Y_B X_A^2 + \left(-x_A - \frac{x_A^2}{2} - \frac{x_A^3}{3} \ldots \right)\]

\[= -\left(x_A + \left(\frac{1}{2} - Y_{AB}\right)x_A^2 + \frac{x_A^3}{3} \ldots \right)\]

2nd order approx

\[\Delta T = T - T_F = \frac{kT_F^2}{\Delta h_f^0} \left[x_A + \left(\frac{1}{2} - Y_{AB}\right)x_A^2 + \frac{x_A^3}{3} \ldots \right]\]

and for \(x_A < 1\)

\[\Delta T = \frac{RT_F^2 x_A}{\Delta h_f^0} \text{ per mol} \text{ Does not depend on nature of the solute!}\]

For seawater

\(x_A = 0.035\)

\(T_F = 273 K\)

\(\Delta h_f = 6001 \text{ J/mol}\)

\(R = 8.315 \text{ J/mol K}\)

\[\Delta T_F = \frac{8.315 \times (273)^2 \times (0.035)}{6001} = 3.6 K\]

Can use FPD to get \(M_w\) of an unknown dilute:

\[x_A = \frac{M_w}{M_B} \text{ molar mass of solvent}\]