

11/4/05

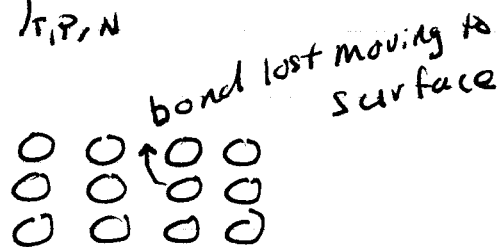
Last time

Surface tension - free energy cost of creating new surface

$$\gamma = \left. \frac{\partial A}{\partial A} \right|_{T, V, N}$$

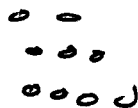
$$\gamma = \left. \frac{\partial G}{\partial A} \right|_{T, P, N}$$

$$\gamma = - \frac{w_{AA}}{2a}$$



How much energy does it take for

water drop



1 mL

.5 mm drops  
1.5 x 10<sup>5</sup>

$$\Delta G = \gamma \Delta A = \gamma (4\pi) [1.5 \times 10^5 (0.025)^2 - 0.62]^2$$

$$= 734 - 4.8 = 729 \text{ cm}^2 = .073 \text{ m}^2$$

$$\gamma = 72.8 \text{ dyne/cm} = 0.0728 \text{ kg/s}^2$$

$$\Delta G = (.0728)(.073) = 5.3 \times 10^{-3} \text{ J}$$

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 <sup>for</sup> regular solutions, this relationship

$$\mu_A = kT \left[ \frac{z}{2N_A} (F/kT) \right]_{N_A, T}$$

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

Microscopic  $\mu_A = \frac{zW_{AA}}{2} + kT \left[ \ln [x_A] + \chi_{AB} (1-x_A)^2 \right]$

We could rewrite as

Microscopic  $\mu_A = \frac{zW_{AA}}{2} + kT \ln \left[ \left( e^{\chi_{AB} (1-x_A)^2} \right) x_A \right]$

leads to an obvious definition of macroscopic  $\mu_A$

Macroscopic  $\mu_A = \mu_A^0 + kT \ln \gamma_A x_A$  Eq<sup>n</sup> 15.17

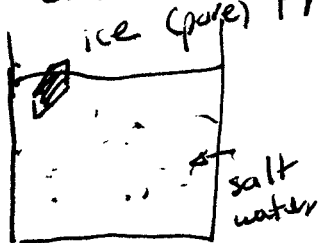
↑  
pure A

└  
activity coeff captures nonidealities

$\gamma_A \rightarrow 1$  as  $x_A \rightarrow \phi$

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

Now lets analyze freezing salt water  $\Rightarrow$  similar approach to other phase transitions.



water = B  
salt = A

$$\begin{array}{ccc}
 \text{pure} & & \text{dirty} \\
 \mu_B(\text{ice}, T) & = & \mu_B(\text{liq}, T, x_B) \\
 \downarrow & & \downarrow \\
 \mu_B^\circ(\text{ice}) & = & \mu_B^\circ(\text{liq}) + RT \ln x_B x_B \\
 & & \text{pure B}
 \end{array}$$

Eq<sup>n</sup> 16.16  
for boiling

$$\ln x_B x_B = \frac{1}{RT} [\mu_B^\circ(\text{ice}, T) - \mu_B^\circ(\text{liq}, T)]$$

Recall  $\mu_j = \frac{\partial G}{\partial N_j} \Big|_{T, P, N_{i \neq j}}$

$$\mu_j = \frac{\partial H_j}{\partial N_j} - T \frac{\partial S}{\partial N_j} = h_j - TS_j \quad \text{eq<sup>n</sup> 9.25}$$

sub in

$$\ln x_B x_B = \frac{1}{RT} [(h_{\text{ice}}^\circ - h_{\text{liq}}^\circ)] - \frac{1}{R} [(S_{\text{ice}}^\circ - S_{\text{liq}}^\circ)]$$

Now for pure H<sub>2</sub>O @ T = T<sub>f</sub> ← freezing temp

$$\ln(1) = \frac{1}{RT_f} (h_{\text{ice}}^\circ - h_{\text{liq}}^\circ) - \frac{1}{R} (S_{\text{ice}}^\circ - S_{\text{liq}}^\circ)$$

subtract  $\ln x_B x_B - 0 = \left( \frac{1}{RT} - \frac{1}{RT_f} \right) \underbrace{(h_{\text{ice}}^\circ - h_{\text{liq}}^\circ)}_{\Delta h_f} - \phi$

$$\ln x_B x_B = \frac{\Delta h_f (T_f - T)}{RT_f}$$

$$\begin{array}{l}
 T \sim T_f \\
 \frac{1}{T} - \frac{1}{T_f} = \frac{T_f - T}{T_f T} \sim \frac{T_f - T}{T_f^2}
 \end{array}$$

Simplify

For small solute concentrations

$$\begin{aligned} \ln Y_B X_B &= \ln [Y_B (1-x_A)] = \ln Y_B + \ln (1-x_A) \\ &\quad \swarrow \text{from micro def} \\ &= \chi_{AB} x_A^2 + (-x_A - \frac{x_A^2}{2} - \frac{x_A^3}{3} \dots) \\ &= -[x_A + (\frac{1}{2} - \chi_{AB})x_A^2 + \frac{x_A^3}{3} \dots] \end{aligned}$$

2nd order approx

$$\Delta T = T - T_F = \frac{K T_F^2}{\Delta h_f^\circ} [x_A + (\frac{1}{2} - \chi_{AB})x_A^2]$$

and for  $x_A \ll 1$

$$\Delta T = \frac{R T_F^2}{\Delta h_f^\circ} x_A \quad \text{per mol}$$

Does not depend on nature of the solute? only  $x_A$

For seawater

$$x_A \sim 0.035$$

$$T_F = 273 \text{ K}$$

$$\Delta h_f = 6001 \text{ J/mol}$$

$$R = 8.315 \text{ J/mol K}$$

$$\Delta T_F = \frac{8.315 (273)^2}{6001} (0.035) = 3.6 \text{ K}$$

Can use FPD to get Mw of an unknown dilute:

$$x_A = \frac{m_A}{M_A} M_B \leftarrow \text{molar mass of solvent}$$

↑  
moles A / 1000 kg solvent

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