## Problem 8.11 from text

- The normal boiling point of iodomethane, $CH_3I$, is 42.43 ˚C and its vapor pressure at 0 ˚C is 140 torr. Calculate

(a) standard enthalpy of vaporization ($\Delta H^\circ_{vap}$) of iodomethane

(b) standard entropy of vaporization ($\Delta S^\circ_{vap}$) of iodomethane

(c) the vapor pressure of $CH_3I$ at 25 ˚C

## Solution to problem 8.11

(a) The data given in the problem actually supplies the vapor pressure of at two temperatures (0 and 42.43˚C, or 273.15 and 315.58 K), so the easiest equation to use is: $\ln (P_2/P_1) \approx - (\Delta H^\circ/R)(1/T_2 - 1/T_1)$

$$\ln\frac{760}{140} = \frac{\Delta H^\circ_{vap}}{8.314\ \text{J mol}^{-1}\text{K}^{-1}} \times \left(\frac{1}{315.58\ \text{K}} - \frac{1}{273.15\ \text{K}}\right)$$

$$\Delta H^\circ_{vap} = +28.6\ \text{kJ mol}^{-1}$$

## Solution to problem 8.11 cont.

(b) Now we can use the basic expression $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ to solve for $\Delta S^\circ$. Since $\Delta G$ at boiling point is zero,

$$\Delta S^\circ_{vap} = (\Delta H^\circ_{vap}/T_b)$$

$$\Delta S^\circ_{vap} = \left(\frac{28600\ \text{J}}{315.58\ \text{K}}\right) = +\ 90.6\ \text{J K}^{-1}$$

## Solution to problem 8.11

(c) Use again: $\ln (P_2/P_1) \approx -(\Delta H°/R)(1/T_2 - 1/T_1)$

$$\ln \frac{P_{298\ \mathrm{K}}}{1\ \mathrm{atm}} = -\frac{28600\ \mathrm{J}}{8.314\ \mathrm{J\ mol^{-1}K^{-1}}} \times \left( \frac{1}{298.15\ \mathrm{K}} - \frac{1}{315.58\ \mathrm{K}} \right)$$

$$P_{298\ \mathrm{K}} = 0.529\ \mathrm{atm}\ = 402\ \mathrm{torr}$$

## Sample Problem

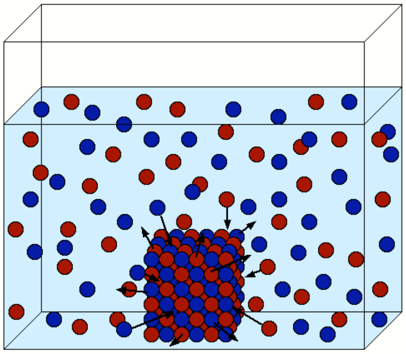
$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

limestone lime

- Given:
  $\Delta H° = +178$ kJ; at 25 ˚C, $K_P = 1.39 \times 10^{-23}$
- Give an estimate for $K_P$ at 800 ˚C.

## Solubility Equilibrium (Chap. 11)

The process is in equilibrium when rate of ions (or molecules) leaving the solid = rate returning to the solid. That is, when dissolution rate = precipitation rate



## Solubility Product, $K_{sp}$ (Sec. 11.10)

$$A_xX_y(s) \rightleftharpoons x\ X^{y+}(aq) + y\ X^{x-}(aq)$$

$$(\text{eg.,}\quad BaCl_2(s) \rightleftharpoons Ba^{2+}(aq) + 2\ Cl^{-}(aq))$$

- What is the form for the equilibrium constant?

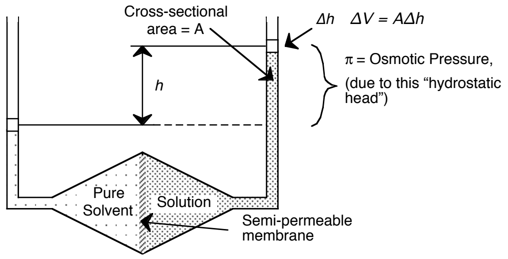
$$K_{eq} = \frac{\text{activities of products}}{\text{activities of reactants}} \quad \text{(at equilibrium)}$$

- Write the equilibrium constant expression.

## Colligative Properties

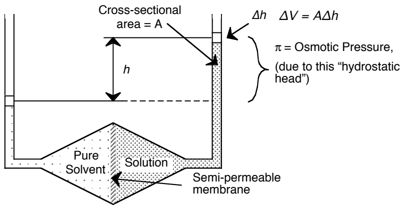
- Depend solely on relative numbers of solvent and solute molecules in solutions, not on their chemical identity.
- The specifics of intermolecular interactions are not important for determining these properties
- Typical examples:
  - Boiling point elevation and freezing point depression
  - Osmosis and osmotic pressure

## Osmosis - The process



$\pi$ = Osmotic Pressure,
(due to this “hydrostatic head”)

# Osmotic Pressure



$\rho$ = density of solvent ≈ density of solution (if very dilute)

$hA = V_{solution} - V_{solvent}$ = Volume of "hydrostatic head"

$\rho(V_{solution} - V_{solvent}) = \rho(hA)$

= mass of solvent in the "hydrostatic head"

π = Osmotic Pressure = Force/Area = (mass × $g$)/Area

($g$ = gravitational constant)

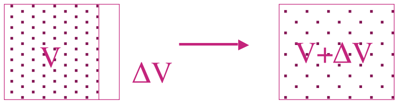
$$\pi = \frac{[\rho(hA)] \times g}{A} = \rho h g$$

# Osmosis

- Pure solvent "moves into" a solution when the solution and solvent are separated by a semipermeable membrane
- Why?

Entropy increases when solvent moves through the membrane into the solution because the solute molecules then have a greater volume to move in. (See sections 7.3 and 7.6).

# Entropy change when solution volume increases by ΔV



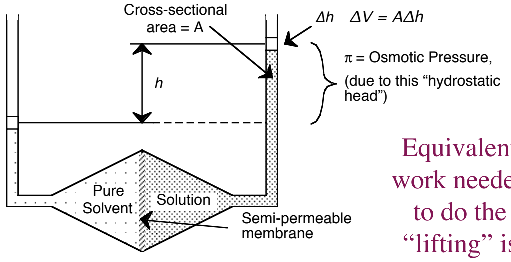
$n$ moles of solute molecules expand into available solvent like a gas expands into a vacuum.

$\Delta S = nR\ln[(V+\Delta V)/V] = nR\ln[1+(\Delta V/V)]$

Since $V >> \Delta V$, $\ln[1+(\Delta V/V)] \approx \Delta V/V$

$\Delta S = nR(\Delta V/V) \quad \Rightarrow \quad T\Delta S = (nRT/V)\Delta V$

The solvent in the $\Delta V$ element must be "lifted" by height $h$.



Equivalent work needed to do the "lifting" is $(\rho\Delta V)gh$.

## Entropy Gain vs Enthalpy Cost

No more solvent will move from the pure solvent into the solution when $\Delta G$ for that process is no longer negative: $\Delta G = \Delta H - T\Delta S$

The enthalpy cost from "lifting" the solvent" in the volume element $\Delta V$ is: $\Delta H = (\rho\Delta V)gh$,

But $\pi = \rho gh$, $\therefore$ $\Delta H = \pi\Delta V$

We already found $T\Delta S = (nRT/V)\Delta V$

So, when $\Delta G = 0$, $\pi = nRT/V$

## Other Useful Forms

$$\pi = nRT/V = [{}^{n}/_{V}]RT$$

$[{}^{n}/_{V}]$ = moles solute per liter solution

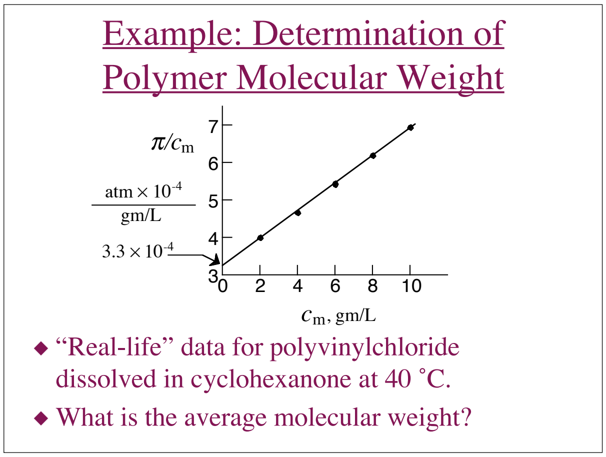
If we know mass (grams) of solute per liter, $c_m$, then we transform to

$$({}^{mol}/_{L}) \sim ({}^{g}/_{L})({}^{mol}/_{g})$$

$[{}^{n}/_{V}] = ({}^{c_m}/_{M})$ M = molar mass ("mol. weight")

$$\pi = ({}^{c_m}/_{M})RT$$

If the solute dissociates, a factor "$i$" accounts the actual number of particles: $\pi = i[{}^{n}/_{V}]RT$



# Example: Determination of Polymer Molecular Weight

- “Real-life” data for polyvinylchloride dissolved in cyclohexanone at 40 ˚C.
- What is the average molecular weight?