February 15, 2002

- **Exam #1:** Solutions key will be online this weekend
- **Chapter 12**: Assigned problems will appear online later today
- ***University Holiday:*** Monday, 2/18
  (Happy Presidents' Day!)

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Effect of Temperature on K

- ΔG is temperature dependent, so:

At T_1: $\Delta G^o_1 = \Delta H^o - T_1\Delta S^o = -RT_1 LnK_1$

Solve for ΔS^o: $\Delta S^o = RLnK_1 + \Delta H^o/T_1$

At T_2: $\Delta S^o = RLnK_2 + \Delta H^o/T_2$

Combine, collect terms, rearrange:

$$\boxed{\mathbf{Ln(K_2/K_1) = -(\Delta H^o/R)(1/T_2 - 1/T_1)}}$$

Van't Hoff Equation

Endothermic: K *increases* with increasing temp

Exothermic: K **decreases** with increasing temp

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Clausius-Clapeyron *Revisited*

Recall, at any temperature T:

$$\Delta H^o - T\Delta S^o = -RTLnK$$

Now, solve for **LnK**:

$$\mathbf{LnK = (-DH^o/R)(1/T) + DS^o}$$

For the vaporization of a liquid:

$A\ (l) \leftrightarrows A\ (g) \qquad K = a_{A(g)}/a_{A(l)} = P_A/1 = P_A$

Just substitute and, voila, we have C-C:

$$\boxed{\mathbf{LnP_A = (-DH^o_{vap}/R)(1/T) + DS^o}}$$

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Fun with Van’t Hoff

- Use to measure ΔH^o
  - ✓*Measure K* at different temperatures
  - ✓*Plot* LnK versus 1/T
  - ✓Straight line plot with ***slope*** $\mathbf{= -DH^o/R}$
- Can calculate ΔG^o from K
- Can calculate ΔS^o (from ΔH^o & ΔG^o)

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Big Example Problem

Let's look at this process to make ammonia:

$$\frac{1}{2}N_2\ (g) + 3/2 H_2\ (g) \leftrightarrows NH_3\ (g)$$

Some thermodynamic constants:

ΔG^o_f:	0	0	-16.48 kJ/mol
ΔH^o_f:	0	0	-46.11 kJ/mol

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Spontaneous at 25 ^{o}C?

- Calculate **ΔG^o_{rxn}**:

$\Delta G^o = \Sigma\ \Delta G^o_f$ (products) - $\Sigma\ \Delta G^o_f$ (reactants)

$= \Delta G^o_f\ (NH_3) - [\frac{1}{2}\Delta G^o_f\ (N_2) + 3/2\Delta G^o_f\ (H_2)]$

$= -16.48$ kJ - 0

$\Delta G^o =$ ***-16.48 kJ*** Yes, reaction is spontaneous

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What is the value of K?

- From: **DGº = -RTLnK**

$$\ln K = \frac{\Delta G^o}{-RT} = \frac{-16.48 \times 10^3 \text{ J}}{-(8.3145 \text{ J/mol-K})(298.15 \text{ K})} = 6.6479$$

Solving for K:

$$K = e^{6.6479} = 7.7118 \times 10^2 = \underline{\boldsymbol{7.71 \times 10^2}}$$

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What is ΔS^o?

We need ΔH^o first:

$$\Delta H^o = \Sigma\, \Delta H^o_f \text{ (products)} - \Sigma\, \Delta H^o_f \text{ (reactants)}$$

$$= \Delta H^o_f\,(NH_3) - [\tfrac{1}{2}\Delta H^o_f\,(N_2) + 3/2\,\Delta H^o_f\,(H_2)]$$

$$= -46.11 \text{ kJ} - 0$$

$$\Delta H^o = \underline{\boldsymbol{-46.11 \text{ kJ}}}$$

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Now, on to ΔS^o!

- Rearranging Gibbs-Helmholtz:

$$\Delta S^o = (\Delta H^o - \Delta G^o)/T$$

Substituting:

$\Delta S^o = [(-46{,}110\ J - (-16{,}480\ J))]/298.15\ K$

$\Delta S^o = -99.37951\ J/K$

$\Delta S^o =$ ***-99.38 J/K***

Why *negative?*

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At What Temperature Will NH_3 *Decompose*?

$$\Delta G^o = \underbrace{\Delta H^o}_{negative} - T\underbrace{\Delta S^o}_{negative}$$

- At a high enough temperature, ΔG^o will be *positive* and the reverse rxn will be spontaneous:

$T > \Delta H^o/\Delta S^o = -46{,}110\ J/-99.38\ J/K$

$T >$ *464.0 K*

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