

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 : $\Delta G_1^\circ = \Delta H^\circ - T_1 \Delta S^\circ = -RT_1 \ln K_1$

Solve for ΔS° : $\Delta S^\circ = R \ln K_1 + \Delta H^\circ / T_1$

At T_2 : $\Delta S^\circ = R \ln K_2 + \Delta H^\circ / T_2$

Combine, collect terms, rearrange:

$$\ln(K_2/K_1) = -(\Delta H^\circ/R)(1/T_2 - 1/T_1)$$

Van't Hoff
Equation

Endothermic: K *increases* with increasing temp

Exothermic: K **decreases** with increasing temp

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Clausius-Clapeyron *Revisited*

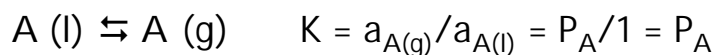
Recall, at any temperature T:

$$\Delta H^\circ - T\Delta S^\circ = -RT\ln K$$

Now, solve for $\ln K$:

$$\ln K = (-\Delta H^\circ/R)(1/T) + \Delta S^\circ$$

For the vaporization of a liquid:



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

$$\ln P_A = (-\Delta H^\circ_{\text{vap}}/R)(1/T) + \Delta S^\circ$$

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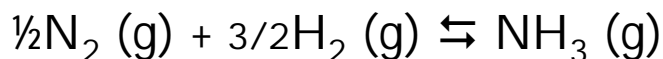
Fun with Van't Hoff

- Use to measure ΔH°
 - ✓ Measure K at different temperatures
 - ✓ Plot $\ln K$ versus $1/T$
 - ✓ Straight line plot with *slope* = $-\Delta H^\circ/R$
- Can calculate ΔG° from K
- Can calculate ΔS° (from ΔH° & ΔG°)

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Big Example Problem

Let's look at this process to make ammonia:



Some thermodynamic constants:

$$\mathbf{DG}_f^{\circ}: \quad 0 \quad 0 \quad -16.48 \text{ kJ/mol}$$

$$\mathbf{DH}_f^{\circ}: \quad 0 \quad 0 \quad -46.11 \text{ kJ/mol}$$

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Spontaneous at 25 °C?

■ Calculate $\mathbf{DG}_{\text{rxn}}^{\circ}$:

$$\Delta G^{\circ} = \sum \Delta G_f^{\circ} (\text{products}) - \sum \Delta G_f^{\circ} (\text{reactants})$$

$$= \Delta G_f^{\circ} (\text{NH}_3) - [\frac{1}{2}\Delta G_f^{\circ} (\text{N}_2) + \frac{3}{2}\Delta G_f^{\circ} (\text{H}_2)]$$

$$= -16.48 \text{ kJ} - 0$$

$$\Delta G^{\circ} = \underline{\underline{-16.48 \text{ kJ}}} \quad \text{Yes, reaction is spontaneous}$$

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What is the value of K?

■ From: $\Delta G^\circ = -RT \ln K$

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

Solving for K:

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

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What is ΔS° ?

We need ΔH° first:

$$\begin{aligned}\Delta H^\circ &= \sum \Delta H^\circ_f (\text{products}) - \sum \Delta H^\circ_f (\text{reactants}) \\ &= \Delta H^\circ_f (\text{NH}_3) - [\frac{1}{2}\Delta H^\circ_f (\text{N}_2) + 3/2\Delta H^\circ_f (\text{H}_2)] \\ &= -46.11 \text{ kJ} - 0\end{aligned}$$

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

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Now, on to ΔS° !

- Rearranging Gibbs-Helmholtz:

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

Substituting:

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

$$\Delta S^\circ = -99.37951 \text{ J/K}$$

$$\Delta S^\circ = \underline{\underline{-99.38 \text{ J/K}}}$$

Why *negative*?

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At What Temperature Will NH_3 Decompose?

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

negative *negative*

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

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

$$T > \underline{\underline{464.0 \text{ K}}}$$

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