Answers for Assignment XII
Due November 8, 2004

p. 513, #9

substance with higher entropy underlined

a. $1 \text{ mol } F_2 (g, 300K)$ or $1 \text{ mol } F (g, 300K)$
   more atoms

b. $1 \text{ mol } H_2O(g, 300K)$ or $1 \text{ mol } H_2O (l, 300K)$
   same substance in higher energy/entropy phase

c. $2 \text{ mol } O_2 (g, 300K)$ or $2 \text{ mol } O_2 (g, 400K)$
   higher temperature

d. $10 \text{ g } O_2 (g, 298.15 \text{ K})$ or $10 \text{ g } O_2 (g, 298.15 \text{ K})$
   more atoms

p. 513, #11

a. $\text{SF}_4 (g) + F_2 (g) \rightarrow \text{SF}_6 (g)$
   $\Delta S$ is negative
   $\Delta n_{\text{gas}} = -1$

b. $\text{H}_2\text{S} (g) + \text{NH}_3 (g) \rightarrow \text{NH}_4\text{HS} (g)$
   $\Delta S$ is negative
   $\Delta n_{\text{gas}} = -2$

c. $\text{O}_2 (g) \rightarrow 2 \text{O (g)}$
   $\Delta S$ is positive
   $\Delta n_{\text{gas}} = +1$

d. $\text{CH}_3\text{OH} (l) \rightarrow \text{CH}_3\text{OH (s)}$
   $\Delta S$ is negative
   substance going to lower energy/entropy phase

p. 513, #17

$\text{Ba}^{2+} (aq) + 2 \text{Cl}^- (aq) \rightarrow \text{BaCl}_2 (s)$

$\Delta S^\circ_r = 123.68 - (9.6 + 2(56.5)) = 1.08 \text{ J/(K mol)}$
CaCl$_2$ (s) $\rightarrow$ Ca$^{2+}$ (aq) + 2 Cl$^-$ (aq)  \[ \Delta S_\text{f}^\circ = -44.7 \text{ J/(K mol)} \]

Because the dissolution process is spontaneous, the value of $\Delta S_\text{surr}^\circ$ must be greater than 44.7 J/(K mol).

Carbon’s most stable form is graphite. $\Delta H_\text{f}^\circ = 0$ for graphite because it is the enthalpy change for the “non-reaction”, C (graphite) $\rightarrow$ C (graphite).

$S^\circ$ for graphite is not zero because C (graphite) is not a perfect crystal at absolute zero.

Tungsten (W); mp = 3410°C; $\Delta H_\text{fus}^\circ = 35.4$ kJ/mol

At the melting point, $\Delta H_\text{fus}^\circ = T \Delta S_\text{fus}^\circ$

$\Delta S_\text{fus}^\circ = \frac{35400 \text{ J}}{3683 \text{ K}} = 9.61 \text{ J/(K mol)}$

Sn (white) $\rightarrow$ Sn (gray)

$\Delta H^\circ = -2.1$ kJ/mol; $\Delta S^\circ = -7.4$ J/(K mol) at $-30^\circ$C

a. $\Delta G_{298 \text{ K}}^\circ = -2100 \text{ J} - (298 \text{ K})(-7.4 \text{ J/K}) = -302 \text{ J/mol}$

b. For 2.50 mol of white time being converted to gray tin at 243 K, $\Delta G_{243 \text{ K}}^\circ = 2.50 \text{ mol}(-302 \text{ J/mol}) = -745 \text{ J}$

c. The value of $\Delta G_{243 \text{ K}}^\circ$ is negative, so white tin should spontaneously change to gray tin at $-30^\circ$C and 1 atm. However, the magnitude of $\Delta G_{243 \text{ K}}^\circ$ is quite small and the conversion might not occur under arbitrary conditions.

d. White tin and gray tin should be in equilibrium at a temperature around $(2100 \text{ J}/7.4 \text{ J/K} =) 284 \text{ K}$ or $11^\circ$C.
p. 514, #33
a. Li (s) + ½ Cl₂ (g) → LiCl (s)

\[ \Delta G_r^\circ = -408610 \text{ J} - (298.15 \text{ K})(-81.27 \text{ J/K}) = -384379 \text{ J} = -384.38 \text{ kJ} \]

b. Na (s) → Na (g)

\[ \Delta G_r^\circ = 107320 \text{ J} - (298.15 \text{ K})(102.39 \text{ J/K}) = 76792 \text{ J} = 76.79 \text{ kJ} \]

c. C (graphite) + 2 H₂ (g) +½ O₂ (g) → CH₃OH (l)

\[ \Delta G_r^\circ = -238660 \text{ J} - (298.15 \text{ K})(- 242.6 \text{ J/K}) = -166330 \text{ J} = -166.33 \text{ kJ} \]

p. 515, #39
a. If \( \Delta H_r^\circ \) is negative and \( \Delta S_r^\circ \) is also negative,
\( \Delta G_r^\circ \) is negative at low temperature.

b. If \( \Delta H_r^\circ \) is negative and \( \Delta S_r^\circ \) is positive,
\( \Delta G_r^\circ \) is negative at low temperature.

c. If \( \Delta H_r^\circ \) is positive and \( \Delta S_r^\circ \) is negative,
\( \Delta G_r^\circ \) is positive at low temperature.

d. If \( \Delta H_r^\circ \) is positive and \( \Delta S_r^\circ \) is also positive,
\( \Delta G_r^\circ \) is positive at low temperature.

“Low temperature” is a temperature at which \( \Delta H_r^\circ \) dominates \( T \Delta S_r^\circ \).
a. $4 \text{Fe (s)} + 3 \text{O}_2 (g) \rightarrow 2 \text{Fe}_2\text{O}_3 (s)$
$\Delta H_r^{\circ} = -1648.4 \text{ kJ/mol and } \Delta S_r^{\circ} = -549.41 \text{ J/(K mol)}$
Spontaneous at temperatures below 3000 K

b. $\text{SO}_2 (g) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{SO}_3 (g)$
$\Delta H_r^{\circ} = -98.89 \text{ kJ/mol and } \Delta S_r^{\circ} = -93.98 \text{ J/(K mol)}$
Spontaneous at temperatures below 1050 K

c. $\text{NH}_4\text{NO}_3 (s) \rightarrow \text{N}_2\text{O (g)} + 2 \text{H}_2\text{O (g)}$
$\Delta H_r^{\circ} = -36.03 \text{ kJ/mol and } \Delta S_r^{\circ} = 259.38 \text{ J/(K mol)}$
Spontaneous at all temperatures

p. 515, #43
$\text{WO}_3 (s) + 3 \text{H}_2 (g) \rightarrow \text{W (s)} + 3 \text{H}_2\text{O (g)}$
$\Delta H_r^{\circ} = +117.41 \text{ kJ/mol and } \Delta S_r^{\circ} = 131.19 \text{ J/(K mol)}$
Spontaneous at temperatures above 895 K

p. 516, #51
$\text{H}_2\text{PO}_4^{\text{aq}} + \text{H}_2\text{O (l)} \rightarrow \text{HPO}_4^{2- (aq)} + \text{H}_3\text{O}^+ (aq)$
$\Delta G_r^{\circ} = +41.13 \text{ kJ/mol}$
$\ln K = -41130 J/((8.314 J/K)(298.15 K)) = -16.59$
$K = 6.2 \times 10^{-8}$

p. 516, #60
$2 \text{CH}_3\text{OH (g)} \rightarrow \text{CH}_3\text{OCH}_3 (g) + \text{H}_2\text{O (g)}$
$\Delta H_r^{\circ} = -24.55 \text{ kJ/mol and } \Delta S_r^{\circ} = -24.41 \text{ J/(K mol)}$
Spontaneous at temperatures below 1005 K or 732°C

In accord with LeChatelier’s Principle, one would expect an exothermic reaction to be favored at low temperature. Because there are two mols of gas on each side of the equation, adjustments to pressure should not affect the position of equilibrium.