

## Homework 5

10. No. When using  $\Delta G^\circ_f$  values in Appendix 4, we have specified a temperature of 25 °C. Further. If gases or solutions are involved, we have specified partial pressures of 1 atm and solute concentrations of 1 molar. At other temperatures and compositions, the reaction may not be spontaneous. A negative  $\Delta G^\circ$  value means the reaction is spontaneous under **standard conditions**.
20. Of the three phases (solid, liquid, gas), solids are the most ordered and gases are the most disordered. Thus, a, b, and f Melting, sublimation, and boiling) involve an increase in entropy of the system since going from a solid to a liquid or a solid to a gas or a liquid to a gas increases disorder. For freezing (process c), a substance goes from the more disordered liquid state to the more ordered solid state, hence entropy decreases. Process d (mixing) involves an increase in disorder (entropy) while separation increases order (decreases the entropy of the system). So of all the processes, a, b, d, and f involve and increase in the entropy of the system.
26. At the boiling point,  $\Delta G = 0$  so  $\Delta H = T \Delta S$ .  
 $T = \Delta H / \Delta S = 58.51 \cdot 10^3 \text{ J/mol} / 92.92 \text{ J/K} \cdot \text{mol} = 629.7 \text{ K}$
34. a.  $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ . Since  $\Delta n$  of gases is negative,  $\Delta S^\circ$  will be negative.  
 $\Delta S^\circ = 1 \text{ mol H}_2\text{O}(\text{l})(70. \text{ J/K} \cdot \text{mol}) - 1 \text{ mol H}_2(\text{g})(131 \text{ J/K} \cdot \text{mol}) + 1/2 \text{ mol O}_2(\text{g})(205 \text{ J/K} \cdot \text{mol})$   
 $\Delta S^\circ = 70. \text{ J/K} = 234 \text{ J/K} = -164 \text{ J/K}$
- b.  $\text{N}_2(\text{g}) + 2 \text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ . Since  $\Delta n$  of gases is negative,  $\Delta S^\circ$  will be negative.  
 $\Delta S^\circ = 2(193) - [1(192) + 3(131)] = -199 \text{ J/K}$
- c.  $\text{HCl}(\text{g}) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ . The gaseous state dominates predictions of  $\Delta S^\circ$ . Here the gaseous state is more disordered than the ions in solution, so  $\Delta S^\circ$  will be negative.  
 $\Delta S^\circ = 1 \text{ mol H}^+(\text{aq}) + 1 \text{ mol Cl}^-(\text{aq})(57 \text{ J/K} \cdot \text{mol}) - 1 \text{ mol HCl}(\text{g})(187 \text{ J/K} \cdot \text{mol}) = -130. \text{ J/K}$
42.  $\Delta G^\circ = -58.03 \text{ kJ} - (298 \text{ K})(-0.1766 \text{ kJ/K}) = -5.40 \text{ kJ}$   
 $\Delta G^\circ = 0 = \Delta H^\circ - T \Delta S^\circ$ ,  $T = \Delta H^\circ / \Delta S^\circ = -58.03 \text{ kJ} / -0.1766 \text{ kJ/K} = 328.6 \text{ K}$   
 $\Delta G^\circ$  is negative below 328.6 K where the favorable  $\Delta H^\circ$  terms dominates.
50. a.  $\Delta G^\circ = 2(-270. \text{ kJ}) - 2(-502 \text{ kJ}) = 464 \text{ kJ}$

b. Since  $\Delta G^\circ$  is positive, this reaction is not spontaneous at standard conditions at 298 K.

$$c. \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ, \Delta H^\circ = \Delta G^\circ + T \Delta S^\circ = 464 \text{ kJ} + 298 \text{ K}(0.179 \text{ kJ/K}) = 517 \text{ kJ}$$

We need to solve for the temperature when  $\Delta G^\circ = 0$ :

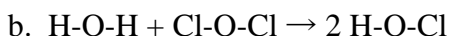
$$\Delta G^\circ = 0 = \Delta H^\circ - T \Delta S^\circ, T = \Delta H^\circ / \Delta S^\circ = 517 \text{ kJ} / 0.179 \text{ kJ/K} = 2890 \text{ K}$$

This reaction will be spontaneous at standard conditions ( $\Delta G^\circ < 0$ ) at  $T > 2890 \text{ K}$ , where the favorable entropy term will dominate.

56. a.  $\Delta H^\circ = 2 \text{ mol}(-92 \text{ kJ/mol}) - [1 \text{ mol}(0) + 1 \text{ mol}(0)] = -184 \text{ kJ}$   
 $\Delta S^\circ = 2 \text{ mol}(187 \text{ J/K}\cdot\text{mol}) - [1 \text{ mol}(131 \text{ J/K}\cdot\text{mol}) + 1 \text{ mol}(223 \text{ J/K}\cdot\text{mol})] = 20. \text{ J/K}$   
 $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = -184 \cdot 10^3 \text{ J} - 298 \text{ K}(20. \text{ J/K}) = -1.90 \cdot 10^5 \text{ J} = -190. \text{ kJ}$   
 $\Delta G^\circ = -RT \ln K, \ln K = -\Delta G^\circ / RT = -(-1.90 \cdot 10^5) / 8.3145 \text{ J/K}\cdot\text{mol}(298 \text{ K}) = 76.683, K = e^{76.683} = 2.01 \cdot 10^{33}$

b. These are standard conditions, so  $\Delta G = \Delta G^\circ = -190. \text{ kJ}$ . Since  $\Delta G$  is negative, the forward reaction is spontaneous, so the reaction shifts right to reach equilibrium.

68. a.  $\Delta G^\circ = -RT \ln K = -(8.3145 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln 0.090, \Delta G^\circ = 6.0 \cdot 10^3 \text{ J/mol} = 6.0 \text{ kJ/mol}$



On each side of the reaction, there are 2 H-O bonds and 2 O-Cl bonds. Both sides have the same number and type of bonds. Thus,  $\Delta H \approx \Delta H^\circ \approx 0$ .

c.  $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ, \Delta S^\circ = \Delta H^\circ - \Delta G^\circ / T = (0 - 6.0 \cdot 10^3 \text{ J}) / 298 \text{ K} = -20. \text{ J/K}$

d. For  $\text{H}_2\text{O}(\text{g})$ ,  $\Delta H^\circ_f = -242 \text{ kJ/mol}$  and  $S^\circ = 189 \text{ J/K}\cdot\text{mol}$

$$\Delta H^\circ = 0 = 2, \Delta H^\circ_f, \text{HOCl} - [1 \text{ mol}(0242 \text{ kJ/mol}) + 1 \text{ mol}(80.3 \text{ J/K}\cdot\text{mol}), \Delta H^\circ_f, \text{HOCl} = -81 \text{ kJ/mol}$$

$$-20. \text{ J/K} = 2S^\circ_{\text{HOCl}} - [1 \text{ mol}(189 \text{ J/K}\cdot\text{mol}) + 1 \text{ mol}(266.1 \text{ J/K}\cdot\text{mol})], S^\circ = 218 \text{ J/K}\cdot\text{mol}$$

e. Assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  are T independent:  $\Delta G^\circ_{500} = 0 - (500. \text{ K})(-20. \text{ J/K}) = 1.0 \cdot 10^4 \text{ J}$

$$\Delta G^\circ = -RT \ln K, K = \exp(-\Delta G^\circ / RT) = \exp(-1.0 \cdot 10^4 / (8.3145)(500.)) = e^{-2.41} = 0.090$$

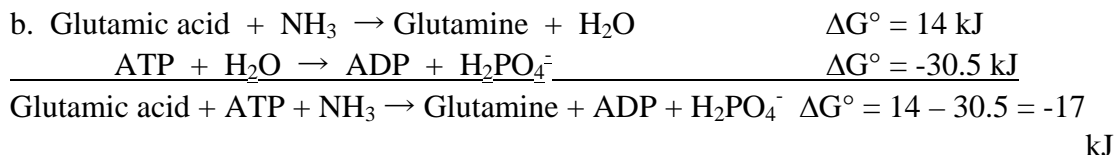
f.  $\Delta G = \Delta G^\circ + RT \ln P^2_{\text{HOCl}} / (P_{\text{H}_2\text{O}} \cdot P_{\text{Cl}_2\text{O}})$ ; From part a,  $\Delta G^\circ = 6.0 \text{ kJ/mol}$ .

We should express all P's in atm. However, because we perform the pressure conversion the same number of times in the numerator and denominator, the factor of 760 torr/atm will all cancel. Thus, we can use the pressures in units of torr.

$$\Delta G = 6.0 \text{ kJ/mol} + (8.3145 \text{ J/K}\cdot\text{mol})(298 \text{ K})/100 \text{ J/kJ} \ln [(0.10)^2/(18)(2.0)] = 6.0 - 20. \\ = -14 \text{ kJ/mol}$$

74. a  $\Delta G^\circ = -RT \ln K$

$$\ln K = -\Delta G^\circ/RT = -14,000 \text{ J}/(8.3145 \text{ J/K}\cdot\text{mol})(298 \text{ K}) = -5.65, K = e^{-5.65} = 3.5 \cdot 10^{-3}$$



$$\ln K = -\Delta G^\circ/RT = -(-17,000 \text{ J})/(8.3145 \text{ J/K}\cdot\text{mol})(298 \text{ K}) = 6.86, K = e^{6.86} = 9.5 \cdot 10^2$$

80. At equilibrium:

$$P_{\text{H}_2} = nRT/V = (1.10 \cdot 10^{13} \cdot 6.022 \cdot 10^{23}) \text{ mol} \times (0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(298 \text{ K})/1\text{L} = \\ 4.47 \cdot 10^{-10} \text{ atm}$$

The pressure of  $\text{H}_2$  decrease from 1 atm to  $4.47 \cdot 10^{-10}$  atm. Essentially, all of the  $\text{H}_2$  and  $\text{Br}_2$  has reacted. Therefore,  $P_{\text{HBr}} = 2.00$  atm since there is a 2:1 ratio between  $\text{HBr}$  and  $\text{H}_2$  in the balanced equation. Since we began with equal moles of  $\text{H}_2$  and  $\text{Br}_2$ , then we will have equal moles of  $\text{H}_2$  and  $\text{Br}_2$  at equilibrium. Therefore,  $P_{\text{H}_2} = P_{\text{Br}_2} = 4.47 \cdot 10^{-10}$  atm.

$$K = P_{\text{HBr}}^2/(P_{\text{H}_2} \cdot P_{\text{Br}_2}) = (2.00)^2/(4.47 \cdot 10^{-10})^2 = 2.00 \cdot 10^{19}$$

$$\Delta G^\circ = -RT \ln K = -8.3145 \text{ J/K}\cdot\text{mol}(298 \text{ K}) \cdot \ln(2.00 \cdot 10^{19}) = -1.10 \cdot 10^5 \text{ J/mol}$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T = -103,800 \text{ J/mol} - (-1.10 \cdot 10^5 \text{ J/mol})/298 \text{ K} = 20 \text{ J/K}\cdot\text{mol}$$