Chemistry 217
Problem Set 7

6.1. A 2-liter reaction vessel containing 0.466 moles of N_2 and 0.682 moles of PCl_5 is heated to 250°C. The total pressure at equilibrium is 29.33 bar. Assuming that all gases are ideal, calculate Kp for the only reaction that occurs, *viz.*:

$$PCl_5(g) = PCl_3(g) + Cl_2(g)$$

6.2. Hydrogen is being considered as a replacement for petroleum based fuels. In order to produce extra hydrogen from "synthesis gas" ($CO + H_2$) the water gas shift reaction is used:

$$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$$

Calculate Kp at 500 and 1000 K and the equilibrium extent of reaction starting with an equimolar mixture of CO and H_2O. Use the appropriate chemical thermodynamic data.

6.3. At high temperatures, Br_2 vapor dissociates into atomic Br. At 1200 K, the free energy of formation ΔG_f^o for atomic Br (g) is 31,794 $J.mole^{-1}$.

(a) Calculate the change in free energy ΔG^o and the equilibrium constant for the reaction:

$$Br_2(g) = 2Br(g) \text{ at 1200 K.}$$

(b) Calculate the fraction of Br_2 dissociated when 1 mole of Br_2 is brought to 1200 K and 1 bar total pressure.

(c) What is the fraction dissociated at 10^{-2} bar (and 1200 K)?

6.4. Given the following entropies: S°(graphite) = 20.1 $J.K^{-1}$; S°(H_2) = 163 $J.K^{-1}$ and S°(CH_4) = 234 $J.K^{-1}$, all at 600°C. And given that ΔH^o(600°C) = -88,050 J for the following reaction:

$$C(graphite) + 2H_2(g) = CH_4(g)$$

(a) Calculate Kp for the reaction at 600°C.

(b) Assume ΔH^o is independent of temperature and calculate Kp at 800°C.

(c) In order to improve the yield of methane at equilibrium, would you increase or decrease the pressure?

6.5. For the change in state C(diamond) = C(graphite), ΔG^o(298 K) = −2866 $J.mol^{-1}$, ΔH^o(298 K) = −1883 $J.mol^{-1}$, and ΔS^o(298 K) = +3.30 $J.K^{-1}$. At 1 bar, the density of graphite is 2.25 g/cm^3 and the density of diamond is 3.51 g/cm^3.

(a) At 298K what is the applied pressure at which the diamond and graphite forms of carbon are in equilibrium? You may assume that ΔV is independent of pressure.

(b) Can one find a temperature at which these two forms are in equilibrium at p = 1 bar? You may assume that $\Delta C_P = 0$.