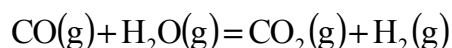


## Chemistry 217 Problem Set 7

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



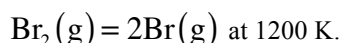
- 6.2. Hydrogen is being considered as a replacement for petroleum based fuels. In order to produce extra hydrogen from "synthesis gas" ( $CO + H_2$ ) the water gas shift reaction is used:



Calculate  $K_p$  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  $\Delta G_f^\circ$  for atomic Br (g) is  $31,794 \text{ J}\cdot\text{mole}^{-1}$ .

- (a) Calculate the change in free energy  $\Delta G^\circ$  and the equilibrium constant for the reaction:



- (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:  $S^\circ(\text{graphite}) = 20.1 \text{ J}\cdot\text{K}^{-1}$ ;  $S^\circ(H_2) = 163 \text{ J}\cdot\text{K}^{-1}$  and  $S^\circ(CH_4) = 234 \text{ J}\cdot\text{K}^{-1}$ , all at  $600^\circ C$ . And given that  $\Delta H^\circ(600^\circ C) = -88,050 \text{ J}$  for the following reaction:



- (a) Calculate  $K_p$  for the reaction at  $600^\circ C$ .  
(b) Assume  $\Delta H^\circ$  is independent of temperature and calculate  $K_p$  at  $800^\circ C$ .  
(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  $C(\text{diamond}) = C(\text{graphite})$ ,  $\Delta G^\circ(298 \text{ K}) = -2866 \text{ J}\cdot\text{mol}^{-1}$ ,  $\Delta H^\circ(298 \text{ K}) = -1883 \text{ J}\cdot\text{mol}^{-1}$ , and  $\Delta S^\circ(298 \text{ K}) = +3.30 \text{ J}\cdot\text{K}^{-1}$ . At 1 bar, the density of graphite is  $2.25 \text{ g}\cdot\text{cm}^{-3}$  and the density of diamond is  $3.51 \text{ g}\cdot\text{cm}^{-3}$ .
- (a) At 298K what is the applied pressure at which the diamond and graphite forms of carbon are in equilibrium? You may assume that  $\Delta V$  is independent of pressure.  
(b) Can one find a temperature at which these two forms are in equilibrium at  $p = 1 \text{ bar}$ ? You may assume that  $\Delta C_p = 0$ .