

CHEM 3410: Physical Chemistry I — Fall 2009

**Homework 6 — Model Solutions**

1. (a) We know the composition of the system at equilibrium in mole percent or mole fraction. The number of moles of each side of the equation are equal, meaning that  $K_x = K_p$ :

$$K_p = K_x = \frac{X_{CO_2} X_{H_2}}{X_{CO} X_{H_2O}} = \frac{(0.271)(0.271)}{(0.229)(0.229)}$$

$$\boxed{K_p = 1.40}$$

$$\Delta G_{rxn}^\circ = -RT \ln K_p = -(8.314 \text{ J/molK})(1000 \text{ K}) \ln 1.40$$

$$\boxed{\Delta G_{rxn}^\circ = -2797 \text{ J/mol} \approx -2.8 \text{ kJ/mol}}$$

- (b) Using tabulated data we can find the enthalpy change for the reaction at 298 K:

$$\Delta H_{rxn}^\circ = \Delta H_f^\circ(CO_{2(g)}) + \Delta H_f^\circ(H_{2(g)}) - \Delta H_f^\circ(CO_{(g)}) - \Delta H_f^\circ(H_2O_{(g)})$$

$$\Delta H_{rxn}^\circ = -393.5 \text{ kJ/mol} + 0 - (-110.5 \text{ kJ/mol}) - (-241.8 \text{ kJ/mol}) = -41.2 \text{ kJ/mol}$$

We can now find  $K_p$  at 298 assuming that the enthalpy of the reaction calculated above is fairly constant of the temperature range 298–1000 K.

$$\ln K_p(298 \text{ K}) = \ln K_p(1000 \text{ K}) + \frac{\Delta H_{rxn}}{R} \left( \frac{1}{1000} - \frac{1}{298} \right)$$

$$\ln K_p(298 \text{ K}) = \ln 1.4 + \frac{-41.2 \times 10^3 \text{ J}}{8.314 \text{ J/molK}} \left( \frac{1}{1000} - \frac{1}{298} \right)$$

$$\ln K_p(298 \text{ K}) = 12.01$$

$$\Delta G_{rxn}(298 \text{ K}) = -RT \ln K_p(298 \text{ K}) = -(8.314 \text{ J/molK})(298 \text{ K})(12.01)$$

$$\boxed{\Delta G_{rxn}(298 \text{ K}) = -29.8 \text{ kJ/mol}}$$

2. At equilibrium,  $\Delta G_{rxn} = 0$ , so:

$$\Delta G_{rxn}^\circ = -RT \ln K_p = -(8.314 \text{ J/molK})(700) \ln 0.379$$

$$\boxed{\Delta G_{rxn}^\circ = 5646 \text{ J/mol}}$$

To find the composition of the system at equilibrium we can write the equilibrium constant as (assuming a reference pressure of 1 atm):

$$K_p = 0.379 = \frac{P_{NO} P_{O_2}^{\frac{1}{2}}}{P_{NO_2}} = \frac{P_{NO} (0.378)^{\frac{1}{2}}}{P_{NO_2}}$$

$$\frac{P_{NO}}{P_{NO_2}} = 0.616$$

We have two unknowns in this equation, so we need another equation in order to solve for both  $P_{NO}$  and  $P_{NO_2}$ . The total pressure and the pressure of oxygen are known, therefore:

$$P_{total} = P_{O_2} + P_{NO} + P_{NO_2}$$

$$2 = 0.378 + P_{NO} + P_{NO_2}$$

Solving the two equations simultaneously we arrive at:

$$P_{NO_2} = 1.003 \text{ atm and } P_{NO} = 0.619 \text{ atm}$$

3. The reaction involves the decomposition of a solid into another solid and two gaseous substances. The expression for the equilibrium constant for this system is:

$$K_p = P_{H_2O}P_{CO_2}$$

For simplicity, I assumed that  $1 \text{ bar} \approx 1 \text{ atm}$ .

- (a) If we start with no products, at equilibrium the partial pressure of water and carbon dioxide must be equal because they are produced in a 1:1 ratio.

$$P_{H_2O} + P_{CO_2} = 2P_{H_2O} = 0.115 \text{ bar}$$

$$P_{H_2O} = P_{CO_2} = 0.0575 \text{ bar}$$

The equilibrium constant can now be found:

$$K_p = P_{H_2O}P_{CO_2} = (0.056)(0.056) = 0.00311 = 3.11 \times 10^{-3}$$

- (b) Let  $x$  be the amount of  $CO_2$  formed at equilibrium. We can write the pressures of the two gases at equilibrium as:

$$P_{CO_2} = x$$

$$P_{H_2O} = 0.225 + x$$

Substituting these into the expression for the equilibrium constant:

$$K_p = 3.31 \times 10^{-3} = (x)(0.225 + x)$$

$K_p$  doesn't seem small enough to assume that  $x$  is really small, so we need to solve this using the quadratic formula. To refresh your memory, the roots of an equation in the form of  $ax^2 + bx + c$  are:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

We can write our equation in the correct form to apply the quadratic formula:

$$x^2 + 0.225x - 3.31 \times 10^{-3} = 0$$

$$x = P_{CO_2} = 0.0139 \text{ atm}$$