Chapter 19

Thermodynamics

Thermodynamics I: Basic Problems

Consider the reaction

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

1. Calculate $\Delta G°$ from $\Delta H°$ and $\Delta S°$ at 25°C

2. Calculate $\Delta G°$ from standard free energies of formation.

3. Calculate the thermodynamic equilibrium constant, K_p.

4. Determine the direction the reaction would proceed and the free energy when starting pressure of each gas is 0.33 atm.

5. What will be the total pressure in the container at equilibrium?

6. Estimate the K_p at 100.0°C assuming $\Delta H°_f$ and $\Delta S°_f$ remain constant at this temperature.

7. The standard free energy, $\Delta G°$, for the acid dissociation of formic acid

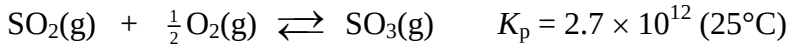
$$HCO_2H + H_2O \rightarrow H_3O^+ + HCO_2^-$$

is 21.4 kJ/mol. Determine the direction that the reaction will proceed and free energy of the reaction, in kJ/mol, when a mixture of formic acid and sodium formate are prepared with an initial concentration of 0.20 M formic acid and 0.10 M sodium formate in neutral pH water.

8. What is the pH of the final solution from problem 7? (Hint: don't get so hung up in thermodynamics calculations that you forget this is an equilibrium problem.)

Thermodynamics II: The Equilibrium Constant as a Function of Temperature

1. The Ostwald process is used to make sulfuric acid from sulfur trioxide, which is itself made from the combustion of sulfur. The first product in the combustion of sulfur is sulfur dioxide which then reacts with excess oxygen to form sulfur trioxide.



$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftarrows SO_3(g) \qquad K_p = 2.7 \times 10^{12}\ (25°C)$$

The sulfur trioxide produced is then passed through a fine mist of water. The sulfur trioxide reacts with the water to produce sulfuric acid.

$$SO_3(g) + H_2O(l) \rightleftarrows H_2SO_4(l) \qquad K = 2.2 \times 10^{14}\ (25°C)$$

Calculate the $\Delta H°$ for the reaction of sulfur trioxide with water.

Calculate the equilibrium constant for the reaction at the boiling point of sulfuric acid (340°C).