**Introduction to Equilibrium and Aqueous Acids**

**Equilibrium reactions are those that are dynamic: the reaction can shift to form more reactants or more products depending on the physical or chemical conditions present. They were discovered and described empirically, but have a thermodynamic basis in the Gibbs Energy of the reaction. A reaction at equilibrium has both reactants and products present, and the rate of formation of products is equal to the rate of formation of reactants. A common application of equilibrium is the chemistry of aqueous acids. Acid strength is measured by the pH scale.**

**Learning Objectives**: Upon completion of this exercise, you should be able to:

1. Write the equilibrium constant expression from the law of mass action
2. Predict the response of a reaction at equilibrium to an external “stress”
3. Determine whether a given species is an acid or base
4. Calculate the pH of a solution of a weak acid in water
5. Write the chemical equation for the autoprotolyis of water
6. Calculate the solubility of a sparingly soluble salt

**Terms You Should Know:** equilibrium, reversibility, law of mass action, equilibrium constant (Keq), the relationship between ∆G and Keq, Le Chatelier’s principle, Brønsted-Lowry Acid, Lewis Acid, pH, autoprotolyis, Kw, Ksp

**Background Reading**: see last page

**After Completing this Exercise, Textbook Problems You Should be Able to Answer**:

**Background Reading**: Atkins, Jones, & Laverman, Chapter 11, Sections 11.1, 11.2, 11.3, 11.9-10; Chapter 12, Sections 12.1, 12.2, 12.5, 12.7, 12.11, 12.18; Chapter 13, Sections 13.8, 13.10.

**After Completing this Exercise, Textbook Problems You Should be Able to Answer**:

11.1, 11.2, 11.3, 11.4, 11.15, 11.16, 11.69, 11.70, 11.71, 12.1, 12.2, 12.13, 12.21, 12.31, 12.55(a,b), 13.57, 13.61, 13.70

**Reading and problems (to be submitted on Sakai)**

This reading assignment serves as a general introduction to aqueous equilibrium. This serves as a preview for more advanced equilibrium calculations.

The law of mass action allows you do write the equilibrium expression for a chemical reaction from the balanced chemical reaction. Consider the following chemical reactions. Write the equilibrium expression for each using the law of mass action.

1) 2 H2S (g) + 3 O2 (g) = 2 SO2 (g) + 2 H2O (g)

2) lactic acid (aq) + H2O (l) = lactate- (aq) + H3O+ (aq)

(lactic acid is CH3CH(OH)CO2H; only the carboxylic acid dissociates in water, not the alcohol)

There is a succinct mathematical relationship between Keq and ∆rG. This allows you to predict the direction of spontaneity of a chemical reaction given a standard Gibbs Energy of a reaction and the actual partial pressures or concentrations present.

3) The standard Gibbs free energy of reaction for N2O4 (g) = 2 NO2 (g) is ∆rG° = 4.73 kJ/mol at 298 K. What is the value of ∆rG when the partial pressures of N2O4 and NO2 are 0.80 and 2.10 bar respectively? What is the spontaneous direction of the reaction?

Le Chatelier’s principle states (anthropomorphically) that when stress is applied to a system in dynamic equilibrium, the system responds in such a way as to reduce the effect of that stress. Consider the following chemical reactions at equilibrium, and describe what would happen to the reaction if the given “stress” was applied.

4) H2O (g) + C (s) = H2 (g) + CO (g); compress the reaction in a piston

5) 2 HCl (g) + I2 (g) = 2 HI (g) + Cl2 (g); compress the reaction in a piston

6) 3 H2 (g) + 2 N2 (g) = 2 NH3 (g); remove NH3 by condensing the liquid

The most common acids that you will encounter in your life are Brønsted-Lowry acids: proton donors. However, transition metal cations can also be relatively strong acids due to their strong Lewis acid behavior. For example, a solution of iron(III) in water is more acidic than a similar solution of acetic acid. Acidity is measured using pH.

The chemical reaction that describes the acidity of iron(III) in water relies on its ability to form an octahedral complex with water as a ligand (remember the crystal field unit?). One of the coordinated water molecules loses a proton to reduce the charge density on the iron complex according to the following reaction:

Fe(OH2)63+ (aq) + H2O (l) = Fe(OH)(OH2)53+ (aq) + H3O+ (aq)

7) write the chemical reaction for acetic acid (CH3CO2H) acting as an acid in water.

8) Calculate the pH of a 0.50 M solution of acetic acid (Ka = 1.8·10-5). You can neglect the autoionization of water.

9) Calculate the pH of a 0.50 M solution of iron(III) chloride (Ka = 1.5·10-3). You can neglect the autoionization of water.

There are times when you can NOT neglect the autoionization of water. To demonstrate why this is true, calculate the pH of the following solutions *neglecting* the Kw expression (in other words, using the simple calculation method).

10) 2.14·10-3 M HCl (for problems 10-12, you can assume complete dissociation of HCl)

11) 2.14·10-6M HCl

12) 2.14·10-9 M HCl

Finially, lets consider the solubility product, or Ksp. You can write the equilibrium for dissolution of a sparingly soluble solid using the law of mass action. Given tabulated Ksp values, you can then determine the solubility. Alternatively, given concentrations of ions, you can determine whether or not a precipitate forms.

13) what is the concentration of iodide in equilibirum with an excess of AgI?

14) If 50.0 mL of a solution containing 1.00·10-4 M Pb2+ is mixed with 50.0 mL of a solution containing 1.00·10-5 M SO42-, do you expect PbSO4 to precipitate?

Summary problems on equilibrium and acidity

15) write the equilibrium constant expression for the following reaction of acetic acid:

CH3CO2H (aq) + H2O (l) = CH3CO2- (aq) + H3O+ (aq)

16) If the pH of a 0.10 M solution of acetic is 5.74 at 298 K, what is the ∆rG° for this reaction?