Equilibrium and Le Châtelier's Principle

PURPOSE

To observe systems at equilibrium, and to determine what happens when stresses are applied to such systems.

GOALS

- To observe the effect on equilibrium of adding or removing products and reactants.
- To predict the direction in which the equilibrium shifts upon a change in concentration of one of the components.
- To determine the thermicity of a reaction based on equilibrium shifts.

INTRODUCTION

Many chemical systems are considered to be reversible. For example, drop the temperature of water to 0°C and it freezes; raise the temperature above 0°C and it melts. Many chemical reactions are also reversible. If one mixes ammonia and oxygen, the products form according to Equation 1:

$$4\ \mathrm{NH_3}(g) + 3\ \mathrm{O_2}(g) \rightarrow 2\ \mathrm{N_2}(g) + 6\ \mathrm{H_2O}(g) \tag{1}$$

Conversely, a mixture of nitrogen and water, under the right conditions, can give ammonia and oxygen:

$$2\ \mathrm{N_2}(g) + 6\ \mathrm{H_2O}(g) \rightarrow 4\ \mathrm{NH_3}(g) + 3\ \mathrm{O_2}(g) \tag{2}$$

Perhaps unsurprisingly, in either case one actually obtains a mixture of all four gases. A reaction in which the reactants are not completely consumed to form products because the reverse reaction also occurs (products form reactants) is a **reversible reaction**[1]. Such reactions are indicated by the use of double arrows as shown in Equation 3:

$$4\ \mathrm{NH_3}(g) + 3\ \mathrm{O_2}(g) \rightleftharpoons 2\ \mathrm{N_2}(g) + 6\ \mathrm{H_2O}(g) \tag{3}$$

In dealing with equilibrium reactions, several definitions are useful and are given below.

Products[2] are the chemical species to the right of the equilibrium arrow, as the reaction equation is written.

[1] http://en.wikipedia.org/wiki/Reversible_reaction
[2] http://en.wikipedia.org/wiki/Product_(chemistry)

Reactants[3] are the chemical species to the left of the equilibrium arrow, as the reaction equation is written.

The **forward reaction** is the process as written from left to right in the reaction equation.

The **reverse reaction** is the process as written from right to left in the reaction equation.

In mixtures of the sort shown in Equation 3, products are constantly being transformed to reactants and vice versa. When the rate of the forward reaction is equal to the rate of the reverse reaction, the amounts of the chemical species remain constant, and the system is in a state of **equilibrium**[4]. Anything that changes a variable associated with the equilibrium induces a **stress** on the system. If a stress is applied, the system will shift to accommodate and offset this stress, and a new equilibrium condition will be established.

This principle was first articulated by a French chemist, Henri-Louis Le Châtelier, in 1884, and it still bears his name. His concise expression of the principle is:

If a stress is applied to a system at equilibrium, the system will respond by shifting in the direction that reduces the stress.

As an example of a stress, consider the addition of more ammonia to the equilibrium in Equation 3. To reduce this stress, some of the added ammonia reacts with oxygen to produce more products (nitrogen and water). A new equilibrium condition is established.

Consequently, the amount of oxygen decreases, the amounts of nitrogen and water vapor increase, and the equilibrium **shifts to the right** or **favors the products**.

If nitrogen were added to the equilibrium in Equation 3, the result would be exactly the opposite and there would be a **shift to the left** to **favor the reactants**. Another way of inducing a stress on such a system is to remove a reactant or product; the system responds by replacing some of the substance that was removed.

In this experiment, two equilibrium systems will be examined. Both are easy to study because they involve color changes. The first is the reaction between the iron(III) ion (Fe^{3+}) and the thiocyanate anion (SCN^{1-}). These ions form the red complex cation* ferrithiocyanate ($FeSCN^{2+}$) according to Equation 4.

$$\begin{array}{ccc} Fe^{3+} + SCN^{-} & \rightleftharpoons & FeSCN^{2+} \\ \text{colorless} & \rightleftharpoons & \text{red} \end{array} \tag{4}$$

The other equilibrium involves two complex ions of cobalt:

$$\begin{array}{ccc} CoCl_4^{2-} + 6\ H_2O & \rightleftharpoons & Co(H_2O)_6^{2+} + 4\ Cl^{-} \\ \text{blue} & \rightleftharpoons & \text{pink} \end{array} \tag{5}$$

[3] http://en.wikipedia.org/wiki/Reactant
[4] http://en.wikipedia.org/wiki/Chemical_equilibrium

The $CoCl_4^{2-}$ ion is an intense blue, the color of the patterns on Delft china. The $Co(H_2O)_6^{2+}$ ion is pale pink.

You will be stressing these equilibria by adding products and reactants, and observing the color changes that result.

* Complex ions are formed when metals (usually transition metals) or their ions form covalent bonds with molecules or ions that have electron pairs to donate. The electron donors, species such as H_2O, NH_3, and halide anions, are called ligands. The electrons are shared between vacant d orbitals (or hybrid orbitals formed from them) on the metal and nonbonding pairs on the ligand. There are usually vacant d orbitals in complex ions. Visible light promotes electrons into these orbitals. Thus, complex ions absorb visible light, and have intense and beautiful colors.
Chapter 14 of your textbook has more information on the chemistry of transition metals.

EQUIPMENT

2 30 mL beakers

1 100 mL beaker

1 ceramic spot plate

2 glass stir rods

1 hot plate

1 250 mL beaker for waste collection

1 deionized water squirt bottle

REAGENTS

~3 mL 0.010 M $Fe(NO_3)_3$

~1 mL 0.10 M $Fe(NO_3)_3$

~1 mL 0.05 M NaSCN

~0.1 mL 1.0 M $AgNO_3$

~0.1 mL 1.0 M $NaNO_3$

~15 mL 0.10 M $Co(NO_3)_2$ (plus some in a dropper bottle)

? mL 12 M HCl

ice

SAFETY

Concentrated hydrochloric acid (12 M HCl) is very corrosive, and its vapor is a respiratory irritant. Work with it under the fume hood and avoid inhaling the vapor. Liquid hydrochloric acid can attack the skin and cause permanent damage to the eyes. If it splashes into your eyes, flush them in the eyewash; hold your eyes open or have someone assist you. If you spill concentrate on skin or clothing, flush the area immediately with water. Have your lab partner notify your instructor about the spill.

Silver solution will form dark spots on skin if spilled. The spots will not appear for about 24 hours, as the ions are slowly reduced to the metal. They are not hazardous, and will fade in a few days.

WASTE DISPOSAL

All of the solutions prepared in this experiment should be discarded in the waste container on the bench. You may wish to have a beaker in your work area to collect waste while you are doing the experiment. Make sure it is labeled. Use a squeeze bottle of deionized water to rinse the solutions into the beaker; use a minimum amount of water to avoid creating large volumes of waste solution. The plates and test tubes can then be washed in the normal manner.

LAB PROCEDURE

Please print the worksheet for this lab. You will need this sheet to record your data.

Part A: $Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+}$ Equilibrium

1 In five wells on a ceramic spot plate, place 2 drops of 0.05 M NaSCN (sodium thiocyanate), 2 drops of 0.01 M $Fe(NO_3)_3$ solution, and 3 drops of deionized water. **Make sure you have taken the correct concentrations of each solution**. Mix each with a stirring rod; all of the solutions should appear **red**.

2 Add 2 drops of deionized water to Well 1. This well will serve as your color comparison for the following experiments.

3 Add 2 drops of 0.10 M $Fe(NO_3)_3$ to Well 2. Record your observations in Table A.

4 Add 2 drops of 0.05 M NaSCN to Well 3. Record your observations in Table A.

5 Add 1 drop of 1.0 M $AgNO_3$ to Well 4. Record your observations in Table A.

6 Add 1 drop of 1.0 M $NaNO_3$ to Well 5. Record your observations in Table A.

7 After answering the questions below, rinse the contents of wells 1–5 into your waste beaker with a minimum amount of deionized water.

Part B: $CoCl_4{}^{2-} + 6\ H_2O \rightleftharpoons Co(H_2O)_6{}^{2+} + 4\ Cl^-$ Equilibrium

1 In each of two wells of a ceramic spot plate, place 1 drop of 0.10 M $Co(NO_3)_2$.

2 Under the HOOD, add 12 M HCl (**CAUTION**) dropwise to Well 1, with gentle mixing (use a stirring rod) until a distinct color change occurs. Record your observations in Table B as "Well 1A". Now add deionized water dropwise to the same well until another color change occurs. Record this observation in Table B as "Well 1B".

3 Under the HOOD, add 12 M HCl (**CAUTION**) dropwise to Well 2, with gentle mixing (use a stirring rod) until a distinct color change occurs, as you did before. Record your observations in Table B as "Well 2A". The result will be similar to that in step 2, but note it anyway. Next, add 3 drops of 1.0 M $AgNO_3$ dropwise, with mixing, to the same well. Record your observations in Table B as "Well 2B".

4 Place about 15 mL of the pink cobalt solution in a 30 mL beaker. Under the hood, add 12 M HCl until the solution is purple in color. Put half of the solution in a second 30 mL beaker. Warm one of the beakers on a hot plate, and cool the second beaker in an ice bath. Record any color changes that you observe in Table B.

5 After answering the questions below, rinse the contents of the well plate and the two beakers into your waste beaker with a minimum amount of deionized water. Empty your waste beaker into the waste container provided on the side shelf, rinsing with a minimum amount of deionized water. Clean and dry all your equipment and return it to the set-up area where you found it.

6 Before leaving, go to a computer in the laboratory and enter your results in the In-Lab assignment. If all results are scored as correct, log out. If not all results are correct, try to find the error or consult with your lab instructor. When all results are correct, note them and log out of WebAssign. The In-Lab assignment must be completed by the end of the lab period. If additional time is required, please consult with your lab instructor.