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

1 To observe the effect on equilibrium of adding or removing products and reactants.

2 To predict the direction in which the equilibrium shifts upon a change in concentration of one of the components.

3 To determine whether a reaction is endothermic or exothermic based on equilibrium shifts.

4 To gain practice calculating an equilibrium constant.

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:

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

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

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

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:

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

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)

Reagents[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 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, three equilibrium systems will be examined. All 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.

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

Another equilibrium involves two complex ions of cobalt:

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

[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.

In Part C of the experiment, students will use a spectrophotometer to calculate the equilibrium constant of bromothymol blue at three different hydronium ion (H_3O^+) concentrations.** According to Le Châtelier's principle, the amount of reactant and product present will adjust when a stress is applied, such that the same equilibrium constant is obtained. Bromothymol blue ($HC_{27}H_{27}Br_2O_5S$) is an indicator which is yellow in acidic solution and blue in basic solution. The equilibrium reaction with hydronium ion (H_3O^+) is shown below. For simplicity, the acid form will be represented as HBB and the base form will be represented by BB^-.

$$\begin{array}{ccc} \mathrm{HBB(aq)} + \mathrm{H_2O(l)} & \rightleftharpoons & \mathrm{BB^-} + \mathrm{H_3O^+(aq)} \\ \text{yellow} & \rightleftharpoons & \text{blue} \\ \mathrm{A_{max}} \sim 470\mathrm{nm} & & \mathrm{A_{max}} \sim 635\mathrm{nm} \end{array} \tag{6}$$

Students will be provided with solutions at three different hydronium concentrations as buffers. A buffer solution is a solution that contains a consistent amount of hydronium ion (H_3O^+) and is resistant to pH changes. The hydronium ion concentration of the solution remains the same when other acids or bases are mixed with it. The relative amounts of the yellow-colored acidic form and the blue-colored basic form can be determined using a spectrophotometer. The yellow-colored acidic form absorbs maximum light (A_{max}) at a violet wavelength near 470 nm. The blue-colored basic form absorbs light at an orange wavelength near 635 nm.

* 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 CH 101 textbook has more information on the chemistry of transition metals.

** Klotz, E.; Doyle, R.; Gross, E.; Mattson, B. *J. Chem. Educ.* **2011**, *88*, 637-639.

EQUIPMENT

1 ceramic spot plate

2 glass stir rods

1 hot plate

1 250 mL beaker for waste collection

1 MicroLab spectrophotometer

4 MicroLab spectrophotometer vials

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 0.10 M $AgNO_3$

~0.1 mL 1.0 M $NaNO_3$

~0.1 mL 0.10 M $Co(NO_3)_2$

? mL 12 M HCl

~1 mL bromothymol blue indicator solution

~5 mL phosphate buffer of pH 6.3

~5 mL phosphate buffer of pH 6.8

~5 mL phosphate buffer of pH 7.3

deionized water

SAFETY

Concentrated hydrochloric acid (12 M HCl) is very corrosive, and its vapor is a respiratory irritant. Work with it under the fume hood at your lab bench, 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 station for at least 15 minutes; hold your eyes open or have someone assist you. If you spill the concentrated acid on your skin or clothing, flush the area immediately with water for at least 15 minutes. Have your lab partner notify your lab teaching assistant and the lab director 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.

Students will have access to and are encouraged to use gloves during the lab period owing to the use of 12M HCl.

WASTE DISPOSAL

Solutions from Part A and B of the 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. All of the solutions prepared in Part C of the experiment may be rinsed down the drain.

PRIOR TO CLASS

Please complete WebAssign prelab assignment. Check your WebAssign Account for due dates. Students who do not complete the WebAssign prelab are required to bring and hand in the prelab worksheet.

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) solution, 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 Data Table A.

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

5 Add 1 drop of 0.10 M $AgNO_3$ to Well 4. Record your observations in Data Table A.

6 Add 1 drops of 1.0 M $NaNO_3$ to Well 5. Record your observations in Data 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.

Data Table A: Observations for the Equilibrium: $Fe^{3+} + SCN^{-} \rightleftharpoons FeSCN^{2+}$

Question 1: When $Fe(NO_3)_3$ was added to the system,

a Which ion in the equilibrium system caused the "stress"?

b Which way did the equilibrium shift?

c What happened to the concentration of SCN^{-}?

d What happened to the concentration of $FeSCN^{2+}$?

Question 2: When NaSCN was added to the system,

a Which ion in the equilibrium system caused the "stress"?

b Which way did the equilibrium shift?

c What happened to the concentration of Fe^{3+}?

d What happened to the concentration of $FeSCN^{2+}$?

Question 3: When $AgNO_3$ was added to the system, it caused the precipitation of solid AgSCN.

a Which ion in the equilibrium had its concentration changed by addition of $AgNO_3$?

b Did the concentration of that ion *in solution* increase or decrease?

c When $AgNO_3$ was added, which way did the equilibrium shift?

Question 4: When you added $NaNO_3$, did anything happen? Can you explain this result?

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 at your bench, 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 Data Table B as “Well 1A”. Now add deionized water dropwise to the same well until another color change occurs. Record this observation in Data Table B as “Well 1B”.

3 Under the HOOD at your bench, 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 Data Table B as “Well 2A”. The result will be similar to that in Step 2, but note it anyway. Next, add 3 drops of 0.10 M $AgNO_3$ dropwise, with mixing, to the same well. Record your observations in Data Table B as “Well 2B”.

4 Please view the video titled “Effect of Temperature on Cobalt Complex Equilibrium”[5] on YouTube. Students are asked to view the video due to the large amount of hydrochloric acid required to set up the experiment, which is not environmentally friendly. Record any color changes that you observe in Data Table B.

5 Rinse the contents of the well plate 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 all your equipment and return it to the set-up area where you found it.

Data Table B: Observations for the Equilibrium: $CoCl_4^{2-} + 6\ H_2O \rightleftharpoons Co(H_2O)_6^{2+} + 4\ Cl^-$

Question 5: Adding HCl has the effect of adding Cl^- ions to the system. When Cl^- was added to the system,

a Which way did the equilibrium shift?

b What happened to the concentration of $CoCl_4^{2-}$?

c What happened to the concentration of $Co(H_2O)_6^{2+}$?

[5] https://youtu.be/2O6MHhUbjtA

Question 6: When water was added to the system,

a Which way did the equilibrium shift?

b What happened to the concentration of $CoCl_4{}^{2-}$?

c What happened to the concentration of $Co(H_2O)_6{}^{2+}$?

Question 7: When you added $AgNO_3$, it caused the precipitation of solid AgCl.

a Which ion in the equilibrium had its concentration changed by addition of $AgNO_3$?

b Did the concentration of that ion *in solution* increase or decrease?

c When $AgNO_3$ was added, which way did the equilibrium shift?

Question 8: State a general rule concerning a system at equilibrium when more of one of the components is added.

Question 9: State a general rule concerning a system at equilibrium when one of the components is removed.

Question 10: For the $CoCl_4{}^{2-} + 6\ H_2O \rightleftharpoons Co(H_2O)_6{}^{2+} + 4\ Cl^-$ Equilibrium

a Which way did the equilibrium shift upon heating?

b Which way did the equilibrium shift upon cooling?

c A general rule concerning temperature changes to equilibrium systems is that the input of energy (raising the temperature) shifts the equilibrium to the higher energy side of the equilibrium. Based on your observations, which side of the equilibrium is the higher energy side?

d Is the reaction, $CoCl_4{}^{2-} + 6\ H_2O \rightleftharpoons Co(H_2O)_6{}^{2+} + 4\ Cl^-$ endothermic or exothermic?

Part C: Bromothymol Blue Equilibrium

1 Make sure that the MicroLAB528 interface is connected to the computer and that the power is on.

2 Select the MicroLab icon in the program list to start the software. A box will appear to choose an experiment. Highlight **"Beer's Law Concentration"** and click **"OK"**. Select "OK" again to accept settings.

3 The spectrophotometer is calibrated from a blank solution. Place a vial containing a blank solution (water) in the spectrophotometer and cover the opening with the black tube provided, to avoid incident light sources. Select "**Perform full LED calibration**" then click "**Read Blank**." It takes approximately 30 seconds to calibrate and the progress will be shown on the screen. During this time, do not remove the cover on the vial. Once the scan is complete, switch the display using the top menu to **"Absorbance"**.

4 Fill a fresh vial approximately 1/2 full with pH 6.30 buffer solution. Add six drops of bromothymol blue indicator solution. Be careful not to add more than six drops, as the spectrophotometer does not function accurately with absorbance values above 1.2000. Cap the vial and mix the solution by gently shaking the vial. Note the color of the solution in the vial in Data Table C.

Data Table C: Observations and Measurements for Bromothymol Blue Equilibrium

5 Place the vial in the spectrophotometer and cover the opening with the black tube provided. Select "Add" and enter 6.30 as the sample ID. Note the absorbance values for the peaks at approximately 635 nm and 470 nm in Data Table C. You must select each peak by clicking on it to display the absorbance reading.

6 Repeat steps 4 and 5 for the pH 6.80 and 7.30 buffer solutions.

Question 11a: In the series from pH 6.30 to 6.80 to 7.30, the pH is increasing and the $[H_3O^+]$ is decreasing. As the $[H_3O^+]$ decreases, what happens to the concentration of BB^- represented by the absorbance at $\sim$635 nm?

Question 11b: Explain how this observation agrees with Le Châtelier's principle.

Question 12a: As the $[H_3O^+]$ decreases, what happens to the concentration of HBB represented by the absorbance at $\sim$470 nm?

Question 12b: Explain how this observation agrees with Le Châtelier's principle.

Question 13: What is the equilibrium expression for the reaction under study? See Equation 6.

7 The contents of the vials can be discarded in the sink with water. Be sure to rinse the vials with deionized water. Return the vials to the placement. Turn off the MicroLab unit and close the software.

8 Enter your results in the InLab 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 teaching assistant. When all results are correct, note them and log out of WebAssign. The InLab assignment must be completed by the end of the lab period. If additional time is required, please consult with your teaching assistant.