Experiment 5

Le Châtelier's Principle

Pre-lab Assignment

Before coming to lab:

- Read the lab thoroughly.
- Answer the pre-lab questions that appear at the end of this lab exercise. The questions should be answered on a separate (new) page of your lab notebook. Be sure to show all work, round answers, and include units on all answers. Background information can be found in Chapter 15, especially sections 15.6 your textbook (Brown and LeMay).
- Follow the guidelines in the "Lab Notebook Policy and Format for Lab Reports" section of the lab manual to complete in your lab notebook the following sections of the report for this lab exercise: Title, Lab Purpose, Procedure and Data Section. For this lab, there will be no data table since your will not be recording any measurements. You will need space to record your observations however.

Purpose

In this experiment you will observe shifts in four equilibrium systems, and learn to explain the observed changes in terms of molecular/ionic interactions and Le Châtlier's Principle.

Background

Chemical Equilibrium

All chemical reactions eventually reach a state in which the rate of the reaction in the forward direction is equal to the rate of the reaction in the reverse direction. When a reaction reaches this state, it is said to be at **chemical equilibrium**. The concentrations of reactants and products will remain constant. For the generic reaction equation below

$$aA_{(aq)} + bB_{(s)} \rightarrow cC_{(aq)} + dD_{(l)} \qquad \text{Equation (1)}$$

We can express the equilibrium-constant expression for this equation as,

$$K_c = \frac{[C]^c}{[A]^a} \qquad \text{Equation (2)}$$

where the values of [A] and [C] are the concentration of A and C at equilibrium in molarity and *a* and *c* are their respective stoichiometric coefficients. What about B and D in the reaction? Only aqueous species and gases appear in the equilibrium expressions. Pure liquids and solids do not appear in the equilibrium-constant expression; therefore B and D do not appear in the equilibrium constant expression in this example.

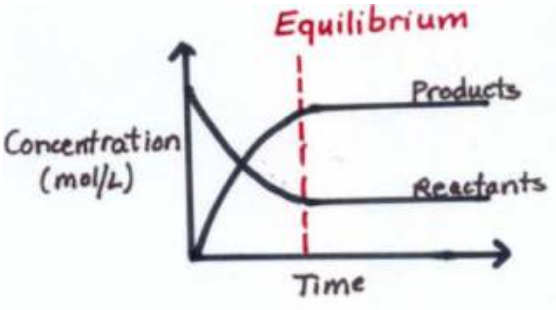

Figure 1
Note that at equilibrium, the concentrations of reactants and are products are not equal; however they are not changing although the reaction is continuing in both the forward and reverse direction.

Le Châtlier's Principle

It has been observed that when a reaction at equilibrium is disturbed by changing either the concentration of one of the chemical components, the total pressure, or the temperature, the reaction will respond by shifting its equilibrium position so as to counteract the effect of the disturbance. This idea was first proposed by Henri-Louis Le Châtelier and has since been referred to as, "Le Châtelier's principle".

When the reaction makes more products as a response to the disturbance, we call it a right-shift. When the reaction makes more reactants in response to the disturbance, we call it a left-shift. These shifts often produce observable results. For example, the color of the solution may change or a precipitate may form or dissolve. To understand how changes in concentration might shift a chemical reaction at equilibrium consider the following generic equation:

$$A + B \rightleftharpoons C + D$$

How might the equilibrium be shifted in the direction of the products? Consider these three possibilities:

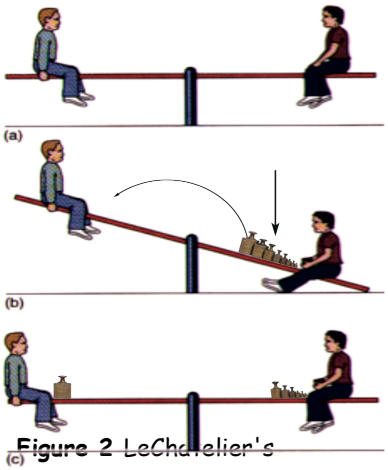

Figure 2 LeChatelier's Principle can be illustrated by this teeter tooter analogy. a) Two equal weight children are balanced (equilibrium). b) Some weight is added to the boy at the right, which causes the teeter tooter to lower at the right end. c) If some of the weight is moved to the left, then the teeter tooter is balance again (equilibrium). This shift to the left results in products returning back to reactant to achieve equilibrium again.

1. **Add More Reactants to the System.** As additional reactants are added (the stress), the reaction system attempts to remove them by shifting to the right (relief of the stress), forming more products. This occurs because the addition of reactants increases the reactants concentration which increases the frequency of collisions between reactant particles- thus increasing the rate of the forward reaction. As the rate of the forward reaction increases, it forms more products. Eventually the rate of the forward and reverse reaction will again be equal in rate and a new equilibrium will be reached.

2. **Remove Products from the System**. This is less intuitive. Removal of a product (the stress) results in a lower concentration of products and therefore fewer collisions between product particles—hence the reverse reaction decreases in rate relative to the forward reaction. This results in the equilibrium shifting towards product formation (right) and —relief of the stress. How can we

remove the products from the reaction system? There are several possibilities. If one of the products were a gas, simply letting the gas escape will remove the product and shift the equilibrium to the right. This is what happens when you leave a soda bottle open. The CO_2 can escape, shifting the equilibrium, below, to the right, and the soda goes flat:

$$CO_{2\ (aq)} \rightleftharpoons CO_{2\ (g)}$$

Another possibility is to chemically react away one of the products. If you remove products from the reaction system, the equilibrium will shift to the right. The reverse is also true; if reactants are removed, the equilibrium will shift to the left.

3. **Changing the temperature.** Heat can also be thought of as a reactant or product in a chemical reaction. Recall that energy can be written into an equation, as follows:

Endothermic reaction: heat + A + B $\rightleftharpoons$ C + D

Exothermic reaction: A + B $\rightleftharpoons$ C + D + heat

Changing the temperature will have the opposite effect on exothermic and endothermic reactions. In the case of an endothermic reaction, heating the system can be thought of as adding additional reactant (heat). The system reacts by shifting to the right, using up the heat. Conversely, cooling the system effectively removes reactant (heat), and the system reacts by shifting to the left.

For exothermic reactions the reverse is true. Adding heat puts a stress on the product side of the equilibrium and the system relieves the stress by shifting to the left. On the other hand, cooling causes a shift to the right.

Procedure

SAFETY: Wear your SAFETY GOGGLES. If you spill any of the solutions on them, wash your hands and clothing immediately with copious amounts of water, Be particularly careful with the silver nitrate solution (Part A) and the concentrated hydrochloric acid (Part B). The silver nitrate ($AgNO_3$) produces permanent black stains on skin and clothing; these stains appear gradually after exposure to sunlight. The concentrated hydrochloric acid (12 M HCl) has irritating vapors and is highly corrosive. If you spill any of this acid on the lab bench, neutralize it with sodium bicarbonate before wiping it up.

WASTE DISPOSAL. Pour the solutions from Part A and Part B into the INORGANIC WASTE containers in the fume hood.

A Note Regarding your data: Throughout the procedure are several "thought" questions which are indicated by lower case letters (a), (b) etc. These are designed to stimulate your thinking about the equilibrium systems as you work with each. **Take time to answer each question as you proceed, being sure to write your answers in your lab notebook.** This will be your data. Letter your responses in your notebook as the questions are lettered below and be sure not to skip any of the questions.

Part A Formation of the $Fe(SCN)^{2+}$ Complex Ion

$$Fe^{3+} + SCN^{-} \rightleftharpoons FeSCN^{2+}$$

Ferric ion	thiocyanate ion	complex
(light yellow)	(colorless)	(deep red)

In this part of the experiment, ferric ion, Fe^{3+}, reacts with thiocyanate ion, SCN^{-} , to form the deep red, complex ion, $FeSCN^{2+}$. The intensity of the red color will tell you if [$FeSCN^{2+}$] changes.

You will make three changes to this equilibrium system:

- Adding solid potassium thiocyanate (KSCN). KSCN is a soluble solid which will dissociate in water to form K^{+} ions and SCN^{-} ions
- Adding silver nitrate ($AgNO_3$) which removes SCN^{-} ions from the equilibrium system by forming an insoluble white precipitate.
- Heating and cooling the system.

Prepare the equilibrium reaction system

1. Add approximately 50 mL of 0.001 M potassium thiocyanate (KSCN) solution to a beaker or flask. Add about 10 drops of 0.10 M ferric nitrate [$Fe(NO_3)_3$] solution, and stir. This should give a red color which is intense enough to see but not so intense that changes in the color cannot be noticed.

2. Pour approximately 1/5 of the solution into each of five large test tubes. Test tube #1 will be your control. You will not be adding anything else to it.

3. **Effect of adding KSCN**

3a. Write the equilibrium chemical reaction you are studying in your notebook.

3b. In a moment, you will be adding KSCN to your reaction system. Adding KSCN should affect the concentration of which species in the equilibrium reaction you are studying?

3c. Should this speed up the forward reaction or reverse reaction?

3d. According to Le Chatelier's Principle, predict which way should the reaction shift (left or right).

Now to test your prediction, to test tube #2 add a **few** crystals of solid potassium thiocyanate (KSCN).

3e. What do you observe happening? Record any color changes or other changes you observe.

3f. Do your observations support your prediction based on Le Chatelier's Principle? Explain

clearly using your color observations as evidence.

4. Effect of adding $AgNO_3$

4a. In a moment, you will be adding $AgNO_3$ to your reaction system. Adding $AgNO_3$ should affect the concentration of which species in the equilibrium reaction you are studying? Would it increase or decrease the coccentration?

4b. According to Le Chatelier's Principle, predict which way should the reaction shift?

Now to test your prediction, to test tube #3 add several drops of 0.1 M silver nitrate solution ($AgNO_3$).

4c. What do you observe happening?

4d. Do your observations support your prediction based on Le Chatelier's Principle? Explain clearly using your color observations as evidence.

5. Effect of Temperature change

To see the effect of temperature changes (heat), place test tube #4 in a 250 mL beaker filled with ice and water. Place test tube #5 in a 150 mL beaker half filled with water, and then heat the water to near boiling with a Bunsen Burner while supporting the beaker on a ring stand.

5a. What do you observe happening to the solution in ice water? To the solution in hot water?

5b. Based on the color change you observe, is the equilibrium for the solution in the ice water shifting left or right?

5c. Based on the color change you observe, is the equilibrium for the solution in the hot water shifting left or right?

5d. Do your observations indicate that the reaction is exothermic or endothermic? That is, based on your observations, is heat a product or a reactant?

5e. Write the net ionic equation for the reaction you are studying including heat in the equation.

6. To see if equilibrium shifts are reversible, move test tube #4 from the ice water to the hot water and test tube #5 from the hot water to the ice water.

6a. What do you observe?

6b. Are equilibrium shifts reversible?

7. Dispose of all solutions in the proper container, not down the sink.

Note to instructors: This procedure has been modified from the Miracosta, Chem 30 lab manual, and UCSB lab manual.

Part B. Complex Ion Equilibrium

Certain metallic ions, most often transition metals, exist in solution as **complex ions** in combination with other ions or molecules, called **ligands.** Common ligands include H_2O, NH_3, Cl^- and OH^-. Many of these complex ions exhibit vibrant colors in solution. For example, the $Co(H_2O)_6^{2+}{}_{(aq)}$ complex ion is pink and the $CoCl_4^{2-}{}_{(aq)}$ complex ion is blue.

In this part of the experiment you will work with the following complex ion formation reaction:

$$\underset{\text{Pink}}{Co(H_2O)_6^{2+}{}_{(aq)}} + 4\ Cl^-{}_{(aq)} \rightleftharpoons \underset{\text{blue}}{CoCl_4^{2-}{}_{(aq)}} + 6\ H_2O_{(l)}$$

The equilibrium constant expression for this reaction is

$$K_f = \frac{[CoCl_4^{2-}]}{[Co(H_2O)_6][Cl^-]}$$

where we denote the equilibrium constant, K, with a subscript f for a complex ion formation reaction.

Prepare the equilibrium reaction system

1. In the hood, add 2 mL (40 drops) of the pink 0.1 M $Co(H_2O)_6^{+2}$ solution to a test tube. Add 12M HCl dropwise until a color change is observed. (Use Caution!! Be sure your goggles are still on and you are working in the hood!)

1a. Write the equilibrium chemical reaction you are studying in your notebook.

1b. The concentration of which species in the equilibrium reaction you are studying would be affected by adding HCl?

1c. According to Le Chatelier's Principle, predict which way should the reaction shift (shift left, right or no effect)?

1d. What do you observe happening?

1e. Do your observations support your prediction based on Le Chatelier's Principle?

Effect of adding water

2. To the same test tube, add deionized water drop-wise until a color change is observed.

2a. How does the equilibrium react when water is added? (shift left, right or no effect)

2b. Is the water just diluting the solution or is it reacting chemically with the solute? How do you know? What is the evidence?

Effect of Temperature change

3. Use a hot plate to heat a 150 mL beaker of water to near boiling.

4. Half fill a new, large test tube with a new portion of the purple $Co(H_2O)_6^{2+}$ solution and add 12 M HCl drop-wise until the color is between pink and blue. Gently heat the test tube by placing it in the boiling water bath.

4a. What color change do you see?

5. Half fill a new, large test tube with a new portion of the purple $Co(H_2O)_6^{2+}$ solution and add 12 M HCl drop-wise until the color is between pink and blue. Cool the test tube by placing it a 250mL beaker filled with ice and water.

5a. What color change do you see?

5b. Is the equilibrium reaction endothermic or exothermic?

5c. Write the net ionic equation for the reaction you are studying including heat in the equation.

Part C. Acid-Base Equiibrium

In the next several parts of the experiment you will make use of **coupled equilibria** to change the equilibrium position of reactions. This is sometime known as the common ion effect.

Let's see how such coupled equilibria work. Suppose we have the two reactions described by the chemical equations below:

$A_{(aq)} \rightleftharpoons B_{(aq)}$ Equation (3)

$B_{(aq)} + C(_{aq)} \rightleftharpoons D_{(aq)}$ Equation (4)

Notice that the species $B_{(aq)}$ is common to both reaction equations. The presence of a common species couples these two reactions.

We can disturb the equilibrium position of the reaction described by Equation (3) by the addition of some C(aq). The addition of C(aq) to this system will cause the equilibrium position of the reaction described by Equation (4) to shift right, in accordance with Le Châtelier's principle. This right shift in the equilibrium position of Equation (4) will result a corresponding decrease in the concentration of $B_{(aq)}$. Because $B_{(aq)}$ is also present in Equation (3), the decrease in the concentration of $B_{(aq)}$ will in turn result in a right shift in the equilibrium position of the reaction described by Equation (3). Thus, the addition of C(aq) to the reaction described by Equation (4) results in a right shift in the equilibrium position of the reaction described by Equation (3) because these two equilibria are coupled. Many of the reactions that we observe in this experiment will also involve the use of coupled equilibria especially involving the reaction of acids and bases to form water. The net ionic equation for this reaction is shown below:

$$\underset{\text{(from an acid)}}{H^+_{(aq)}} + \underset{\text{(from a base)}}{OH^-_{(aq)}} \rightleftharpoons H_2O \quad \text{Equation (5)}$$

Equilibrium of Indicators

The indicator we use most often in lab is phenolphthalein which is a weak acid. As a weak acid, it loses H^+ and turns a different color in the process. It should be noted that all acid-base indicators work on this principle. We can represent this process below where HIn is a shorthand for the formula of an indicator.

$$\underset{\text{colorless}}{HIn_{(aq)}} \rightleftharpoons H^+_{(aq)} + \underset{\text{pink}}{In^-_{(aq)}} \qquad \text{Equation (6)}$$

1. Prepare a phenolphthalein solution by adding one drop of phenolphthalein into 5 mL of water in a test tube and mixing.

Effect of adding NaOH

2a. The concentration of which species in Equation 5 would be affected by adding NaOH? Would it increase or decrease in concentration?

2b. According to Le Chatelier's Principle, predict which way should the reaction in Equation (5) shift?

2c. The shift you predict for Equation 5 will affect the equilibrium of Equation 6. Using your knowledge of the common ion effect, which direction will the equilibrium of Equation 6 shift as NaOH is added?

Now to test you prediction, add 6 M NaOH until there is a color change

2d. What color change did you observe?

2e. Do your observations support your prediction based on Le Chatelier's Principle? Explain clearly using your color observations as evidence.

2f. For phenolphthalein, what is the main species present in basic solution? HIn or In^-?

2g. In contrast, what is the main species present in an acidic solution?

Part D Solubility Equilibrium

$$Mg(OH_2)(s) \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^-_{(aq)} \qquad \text{Equation 7}$$

Prepare the equilibrium reaction system.

1. Label four small test tubes 1-4.

2. To each of **four small** test tubes, place 20 drops of 1.0 M $MgCl_2$ and 10 drops of 0.5 M NaOH.

3. Into test tubes 3 and 4, add one drop of phenolphthalein.

3a. Write the net ionic equation for the equilibrium system you prepared

Effect of adding Na_4EDTA

4a. In a moment you will add Na_4EDTA. Na_4EDTA reacts with Mg^{+2}. Which way should the equilibrium reaction mixture shift?

Now to test your prediction, add one drop of 2.0 M Na_4EDTA solution to test tube 1. Continue to add Na_4EDTA dropwise until you see a change.

4b. What change did you observe?

4c. Do your observations support your prediction based on Le Chatelier's Principle? Explain clearly using your observations as evidence

Effect of HCl

5. Add one drop of 12 M HCl to test tube 2. Continue to add HCl dropwise until you see a change.

5a. What change did you observe? What happens to the precipitate? What happens to the OH^- ions? Which OH^- ions are reacting in this test, the ones in the precipitate, the ones in the solution or both?

5b. Considering first Equation 5, which direction would this equilibrium shift as HCl was added? (left, right or no effect)?

5c. The shift you predict for Equation 5 will affect the equilibrium of Equation 7. Using your knowledge of the common ion effect, which direction will the equilibrium of Equation 7 shift as HCl is added?

5d. Do your observations support your prediction based on Le Chatelier's Principle? Explain clearly using your observed solubility changes as evidence.

Effect of Temperature Changes

To see the effect of temperature changes (heat), place test tube #3 in a 250 mL beaker filled with ice and water. Place test tube #4 in a 150 mL beaker half filled with water, and then heat the water to near boiling while supporting the beaker on a ring stand.

6a. What is the initial color and appearance of the mixtures in Test tubes 3 and 4. If a precipitate is present, note that fact and the color of the precipitate.

6b. What color change do you observe happing to the solution in hot water?

6c. What color change do you observe happing to the solution in ice water?

6d. Based on the color change you observe, is the reaction exothermic or endothermic?

6e. Write the net ionic equation for the reaction you are studying including heat in the equation.

Pre-lab Questions

1. State Le Chatelier's Principle

2. Assume that the following reaction is in chemical equilibrium:

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g) + \text{heat}$$

Use Le Châtelier's Principle to explain the effect each of the following changes will have upon the system—will the equilibrium shift toward the product or reactant side? Why?

a. If more hydrogen is added to the system the equilibrium will shift to the..... (pick one and explain) i. Right ii. Left iii. Remains unchanged

b. If ammonia is removed from the system the equilibrium will shift to the..... (pick one and explain) i. Right ii. Left iii. Remains unchanged

c. If nitrogen is removed from the system the equilibrium will shift to the..... (pick one and explain) i. Right ii. Left iii. Remains unchanged

d. If the temperature is raised the equilibrium will shift to the.....(pick one and explain) i. Right ii. Left iii. Remains unchanged

e. If the pressure of the system is decreased by doubling the total volume the equilibrium will shift to the: (pick one and explain)

i. Right ii. Left iii. Remains unchanged

3. What is the net ionic equation for the reaction of an acid with a base?

4. Does value of the equilibrium constant (K) change if

a. the temperature changes

b. more of a reactant species is add

5. What chemical can be added to remove SCN^- ions from a solution? How about to remove Mg^{2+} ions?

Post-Lab Questions

1.Experience teaches us that most solids are more soluble in warm water than in cold water. Does the solubility of $Mg(OH)_2$ fit this pattern?

2. Considering Part B of the lab, when the test tube was placed in hot water, did the value of K_f get bigger, smaller or remain constant?

3. Dinitrogen tetraoxide (colorless gas) is converted to nitrogen dioxide (dark reddish brown gas) and is **endothermic** in the forward direction:

a. Write a balanced equation for this reaction.

b. If a closed container containing a mixture of these two gases at equilibrium is a light brown in color when it is at room temperature (20.0°C), what change in color would you expect to observe if the container is placed in boiling water (100.0 °C)?

c. If a closed container containing a mixture of these two gases at equilibrium is a light brown in color when it is at room temperature (20.0°C), what change in color would you expect to observe if the container is placed in ice water (0.0 °C)?

4. Hydrogen gas (colorless) reacts with pure iodine vapor (purple) to give hydrogen iodide gas (colorless):

a. Write a balanced equation for this reaction.

b. If the equilibrium mixture of these three gases is light purple in color, what change in color would you expect to observe if more hydrogen gas were added to the system?

c. If the equilibrium mixture of these three gases is light purple in color, what change in color would you expect to observe if some of the hydrogen iodide gas were removed from the system?

5. Consider the following equilibrium

$$\text{heat} + CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

a. If the pressure of $CO_{2(g)}$ is increases, in which direction will the equilibrium shift?

b. If the temperature is increased, in which direction will the equilibrium shift?

c. If the temperature is decreased, in which direction will the equilibrium shift?