Lab 4: Chemical Equilibrium and Le Chatelier's Principle

Objective: To observe the effects of concentration and temperature on the position of reversible reactions, and to use these observations as an introduction to Le Chatelier's Principle.

Materials: 0.1 M potassium chromate (K_2CrO_4); 3 M sulfuric acid (H_2SO_4); 1 M sodium hydroxide (NaOH); 1 M acetic acid (CH_3COOH); solid sodium acetate (CH_3COONa); methyl orange indicator; 0.10 M cobalt(II) chloride ($CoCl_2$); conc. hydrochloric acid (HCl); saturated ammonium chloride solution and solid ammonium chloride (NH_4Cl); distilled water.

Equipment: Test tubes; 10 mL graduate cylinder; 250 mL beaker; medicine droppers; glass stirring rod; micro-spatula; test tube holder.

Safety: Many of the solutions used in this exercise are toxic or caustic. Specific safety hazards are discussed under the procedure sections dealing with these chemicals. **Safety goggles should be worn at all times in the lab.**

Waste Disposal: Waste disposal protocols for the chemicals used in this lab will be discussed under the procedure sections dealing with these chemicals.

INTRODUCTION

In the previous lab we explored the factors that control *how fast* a reaction occurs. In this lab exercise we will explore the concept of **equilibrium**, or *how far* a reaction proceeds toward the formation product, and what factors can be manipulated to control the position of equilibrium for a reaction. Just as the knowledge of kinetics has important applications, knowledge of equilibrium can be used to force a reaction to the right to form more of a desired product or to the left to suppress the formation of undesirable products. An important industrial example to illustrate this idea is the Haber process used to manufacture ammonia.

Ammonia (NH_3) is an important chemical; it is used agriculturally as a major fertilizer and is used as an industrial reagent in the synthesis of many nitrogen-containing compounds. The synthesis reaction for the formation of ammonia is given in Equation 4.1.

$$N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g) \qquad \text{(Equation 4.1)}$$

This reaction is **reversible**; once some nitrogen and hydrogen have reacted to form ammonia, some of the ammonia will decompose to generate the original reactants, as shown in Equation 4.2:

$$2\ NH_3(g) \rightarrow N_{2(}(g) + 3\ H_2(g) \qquad \text{(Equation 4.2)}$$

Equation 4.1 is called the **forward reaction**, and Equation 4.2 is called the **reverse reaction.** The reversible nature of a reaction is often indicated by using a double arrow ($\leftrightarrows$) in the reaction equation:

$$N_{2(}(g) + 3\ H_2(g) \leftrightarrows 2\ NH_3(g) \qquad \text{(Equation 4.3)}$$

Because reversible reactions can proceed in either the forward or the reverse direction, these systems are in a dynamic state of interchange between products and reactants. When the rate of the forward reaction (Equation 4.1) equals the rate of the reverse reaction (Equation 4.2), then the system reaches a steady state known as **equilibrium**. For a system at equilibrium, the concentrations of products and reactants reach a constant level—they are not necessarily equal, but they no longer change over time.

The **equilibrium position** of a reversible reaction can be described in terms of the relative amounts of products and reactants at equilibrium. For an equilibrium system that has a significantly greater amount of products compared to reactants, the equilibrium position is said to lie **to the right**, or in favor of products. For systems with significantly more reactants than products, the equilibrium position lies **to the left**, or in favor of reactants.

Look again at the definition of equilibrium. Equilibrium is defined as the state of a reaction at which the rates of the forward and reverse reactions are equal. However, if the system is somehow altered, or "stressed," in a way that increases the rate of the forward reaction, then the reaction shifts to the right until a new equilibrium position is obtained. Likewise, if the rate of the reverse reaction increases, then the reaction shifts to the left.

By examining the effect of a stress on either the forward or reverse reaction, we can predict how a chemical system at equilibrium will respond to various stresses. This idea is summarized by **Le Chatelier's Principle**, which states that if a stress is applied to a system at equilibrium, the reaction will shift in a direction to minimize the impact of the stress until a new equilibrium position is attained.

Consider the reversible reaction presented by Equation 4.2. At equilibrium, the concentrations of reactants (N_2, H_2) and products (NH_3) have reached some constant level, and the rates of the forward and reverse reaction rates are equal. What happens if more N_2 is added to the reaction mixture? An increase in $[N_2]$ will increase the rate of the forward reaction, and the reaction will "shift right." As the reaction shifts right, the concentration of reactants will decrease and the concentration of products will increase. As these concentrations change, the rates of the forward and reverse reactions will change accordingly; the rate of the forward reaction will decrease, and the rate of the reverse reaction will increase. When these rates are once again equal, the system establishes a new equilibrium position.

In a similar fashion, if we add products (NH_3), the rate of the reverse reaction increases and the reaction "shifts left." Conversely, removing NH_3 will decrease the rate of the reverse reaction relative to the forward reaction, and the system will "shift right." This is the method used in the Haber process; continuously removing NH_3 as it forms forces the reaction to "shift right," yielding more product.

Another factor that affects the rate of reactions is temperature. Based on kinetic theory, increasing temperature increases the rate of a reaction. But what about reversible systems? As it turns out, increasing temperature increases the rate of both the forward *and* the reverse reactions, but not to the same extent. We can predict the effect of temperature by considering heat as a product or a reactant. For **exothermic** reactions, heat is a product of the reaction. Increasing temperature (i.e., adding heat) is equivalent to adding products to the system, with a corresponding shift to the left. For **endothermic** reactions, heat must be added to the system and can therefore be treated as a reactant. Increasing the temperature of an endothermic reaction would be equivalent to adding a reactant, and the system would shift to the right.

In this lab activity we will apply Le Chatelier's Principle as we examine the effect of various stresses on four different reversible chemical systems. We will determine whether the reaction shifts right or left by observing physical changes in the reaction mixture (i.e., change in color, formation of solid or gas, evolution of heat, etc.).

Pre-Lab Questions

1. Briefly discuss the safety hazards associated with the list of reagents used in this laboratory and the precautions taken to minimize or avoid injury.

a) 3 M H_2SO_4 solution:

b) 0.1 M K_2CrO_4 solution:

c) Concentrated HCl:

d) 1 M NaOH:

2. Briefly define the following terms:

a) Equilibrium:

b) Reversible reaction:

c) Le Chatelier's Principle:

3. Consider the following equilibrium:

$$N_2O_4\text{(gas, colorless)} + \text{heat} \leftrightarrows 2\ NO_2\text{(gas, red-brown)}$$

Predict the direction of shift for this equilibrium for each of the following conditions, and indicate what changes you would observe to indicate this shift.

a) Add $N_2O_4(g)$:

b) Decrease temperature:

PROCEDURE

I. Chromate/Dichromate Equilibrium

In acidic aqueous solutions, an equilibrium is established between chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), as shown in Equation 4.4:

$$2\ CrO_4^{2-}\text{ (aq, yellow)} + 2\ H_3O^+\text{ (aq)} \leftrightarrows Cr_2O_7^{2-}\text{(aq, orange)} + 3\ H_2O\text{(l)} \qquad \text{(Equation 4.4)}$$

The relative position of equilibrium can be determined by observing the color of the solution. Anything that causes a shift to the right will result in the solution turning orange, while a shift to the left would result in formation of a yellow solution. You will observe the effect of adding acid and base to this reaction mixture.

Caution: Potassium chromate is a suspected carcinogen; avoid contact with the potassium chromate solutions. Sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) solutions are caustic and corrosive and can cause burns. Handle all solutions carefully and avoid contact with skin. Wear gloves, and wash hands/skin thoroughly with soap and water should contact occur. Inform your TA should any spills occur. Wear safety goggles at all times.

1. Obtain two test tubes, label one as "Control" and another one as "Reaction". Use a micropipette to transfer 3 mL of 0.10 M K_2CrO_4 solution into the "Control" test tube. Transfer another 3 mL of 0.10 M K_2CrO_4 solution into the "Reaction" test tube. Record the color of the solution on your data sheet.

2. Add 3 M H_2SO_4 solution into the "Reaction" test tube, one drop at a time, while stirring with a clean glass rod. Continue adding H_2SO_4 until you observe a color change in the solution. Do not remove the stirring rod from the test tube at this point. Compare the solution with the solution in the "Control" test tube and record your observations on the data sheet.

3. Add 1 M NaOH solution to the "Reaction" test tube, one drop at a time, while stirring with the glass rod. Continue adding NaOH until you observe a color change in the reaction mixture. Record your observations on your data sheet.

Waste Disposal: Pour the chromate/dichromate reaction mixture into the designated waste beaker in the fume hood. Rinse the graduated cylinder and test tube with several 3–5 ml portions of tap water and add these washes to the waste beaker. Finally, rinse the graduated cylinder and test tube with 5 mL of deionized water and pour these rinses into the beaker.

II. Dissociation of Acetic Acid in Water

Acetic acid is a weak acid; a reversible equilibrium is established between the undissociated acid on the left and the ionized acid on the right, as indicated in Equation 4.5:

$$CH_3COOH\text{(aq)} + H_2O\text{(l)} \leftrightarrows CH_3COO^-\text{(aq)} + H_3O^+\text{(aq)} \qquad \text{(Equation 4.5)}$$

In this case the reactants and products are colorless so there is no obvious change in the color of the solution. By adding a pH indicator, methyl orange, we can identify the chemical changes that occur as the reaction shifts left or right. Methyl orange turns red in the presence of high concentrations of hydronium ion (H_3O^+) and is yellow when the hydronium ion concentration is low. You will observe the changes in this system when water-soluble sodium acetate trihydrate ($CH_3COONa{\cdot}3H_2O$) and NaOH are added to the solution.

4. Obtain two test tubes, label one as "Control" and another one as "Reaction". Use a micropipette to transfer 3 mL of 1 M acetic acid (CH_3COOH) into the "Control" test tube. Add 3 drops of methyl orange indicator to the test tube. Stir with a clean, dry glass stirring rod. Repeat the same for the "Reaction" test tube and record the initial color of this equilibrium mixture on your data sheet.

5. Using a micro-spatula, add about 10 crystals (a quarter of the size of a pea) of sodium acetate trihydrate ($CH_3COONa{\cdot}3H_2O$) to the test tube. Stir the solution until the crystals dissolve. Continue to add crystals, while stirring, until you observe a color change in the solution. Record your observations on the data sheet.

6. Prepare a second "Reaction" test tube by transferring 3 mL of 1 M CH_3COOH into a new, clean test tube. Add three drops of methyl orange indicator solution and stir. Record the initial color of this solution on your data sheet.

7. Add 1 M NaOH, dropwise, to the second "Reaction" test tube while stirring with the glass rod. Continue adding the NaOH until you observe a color change in the equilibrium mixture. Compare the solution with the solution in the "Control" test tube and record your observations on the data sheet.

Waste Disposal: Pour the reaction mixtures for this equilibrium system down the drain and flush with plenty of water. Rinse your graduated cylinder and test tubes as indicated previously.

III. $[CoCl_4]^{2-}$ / $[Co(H_2O)_6]^{2+}$ Equilibrium

This system involves the equilibrium between two complex ions formed by the cobalt(II) ion, as illustrated in Equation 4.6:

$$[CoCl_4]^{2-}(aq, blue) + 6\ H_2O(l) \leftrightarrows [Co(H_2O)_6]^{2+}(aq, pink) + 4\ Cl^-(aq) \qquad \text{(Equation 4.6)}$$

You will determine the responses of this system by observing the color change as hydrochloric acid (HCl) and water are added to the solution.

Caution: Concentrated hydrochloric acid (HCl) is toxic and corrosive and can cause severe burns. Wear gloves and goggles to prevent contact with skin and eyes. If contact occurs, wash affected areas thoroughly with water. Notify your TA if any spills occur.

8. Prepare a hot water bath to be used later in this lab. Pour 100 mL of hot tap water into a 250 mL beaker and place it on a hot plate. Set the hot plate dial on medium and heat the beaker gently until needed in Part IV.

9. Obtain two test tubes, label one as "Control" and another one as "Reaction". Using a micropipette transfer 3 mL of 0.1 M $CoCl_2$ solution into the clean, dry "Control" test tube. Transfer another 3 mL of 0.1 M $CoCl_2$ solution into the clean, dry "Reaction" test tube and record the color of this initial solution on your data sheet.

10. Add 2 mL of concentrated HCl into the "Reaction" test tube while stirring the solution with a glass stirring rod. Continue adding dropwise until you observe a change in the equilibrium mixture. Compare the solution with the solution in the "Control" test tube and record your observations on the data sheet.

11. Add distilled water dropwise to the "Reaction" solution from step 10 while stirring. Continue adding water until a change is observed in the equilibrium mixture. Record your observations on the data sheet. Continue adding water, while stirring, until no further changes are observed in the solution. Record these observations on the data sheet.

Waste Disposal: Discard the equilibrium mixtures in the designated waste beaker in the fume hood. Wash the graduated cylinder and test tube with tap water and distilled water and dispose of these wash solutions in the waste container.

IV. Dissolution of NH_4Cl Equilibrium

The dissolution equilibrium of ammonium chloride (NH_4Cl) is given in Equation 4.7:

$$NH_4Cl(s) \leftrightarrows NH_4^+(aq) + Cl^-(aq) \qquad \text{(Equation 4.7)}$$

Starting with a saturated solution of NH_4Cl at equilibrium, you will observe the effect of adding HCl on the equilibrium position and of heating and cooling the solution.

12. Obtain two test tubes, label one as "Control" and one as "Reaction". Use a micropipette to transfer 3 mL of saturated NH_4Cl solution in the clean, dry "Control" test tube. Transfer another 3 mL of saturated NH_4Cl solution in the clean, dry "Reaction" test tube.

13. Use a clean pipet to add concentrated HCl, dropwise, into the "Reaction" test tube while stirring the solution. Continue adding HCl until you observe a change in the equilibrium mixture. Compare the solution with the solution in the "Control" test tube and record your observations on the data sheet.

14. Using a test tube holder, place the "Reaction" test tube (including the stirring rod) into the hot water bath prepared previously. Stir the solution while carefully holding the test tube in the hot water bath for 3 minutes. Record your observations on the data sheet. Turn off the hot plate and leave the test tube in the 250 mL beaker until you are ready to dispose of the reaction mixtures.

15. Measure 5 mL of distilled water into a clean 10 mL graduated cylinder and pour into a clean, dry test tube, feel the temperature of the test tube and set aside.

16. Obtain a clean, dry test tube and carefully add enough crystals of solid NH_4Cl to cover the bottom of the test tube, about ½ inch of NH_4Cl crystals. Add 5 mL of distilled water into a clean 10 mL graduated cylinder and pour into the test tube containing the NH_4Cl crystals. Stir the mixture with a clean glass rod. Feel the test tube to determine if the dissolution of NH_4Cl produced a temperature change in the solution compared to the pure water in sept 15. Record your observations on the data sheet

Waste Disposal: Discard of your equilibrium mixtures in the designated waste beaker in the fume hood. Wash/rinse your graduated cylinder and test tubes with distilled water and add these rinses to the waste container.

Collect the used micropipette tips, wash with soap and water, rinse thoroughly with water and deionized water and store in the designated bin in the fume hood.

Data Sheet

I. Chromate/Dichromate Equilibrium

(1) What is the color of the solution in step 1?

(2) What change do you observe when you add H_2SO_4 solution (step 2)?

(3) What change do you observe when you add NaOH solution (step 3)?

(4) What experimental evidence do you have that the equilibrium is affected by the addition of H_2SO_4 solution? Explain.

(5) Explain how your observation and explanation in (4) are consistent with Le Chatelier's Principle.

(6) What experimental evidence do you have that the equilibrium is affected by the addition of NaOH solution in step 3? Explain.

(7) Explain how your observation and explanation in (6) are consistent with Le Chatelier's Principle.

II. Dissociation of Acetic Acid in Water

(1) What is the color of the original equilibrium mixture in step 4?

(2) What change do you observe when you add solid $CH_3COONa{\cdot}3H_2O$ in step 5?

(3) What change is observed after adding NaOH solution to the equilibrium mixture in step 7?

(4) What experimental evidence did you observe to indicate that the equilibrium is affected by addition of solid $CH_3COONa{\cdot}3H_2O$? Explain.

(5) Are your observations and explanation in (4) consistent with Le Chatelier's Principle? Explain.

(6) What experimental evidence did you observe to indicate that the equilibrium is affected by addition of NaOH solution? Explain.

(7) Are your observations and explanation in (6) consistent with Le Chatelier's Principle? Explain.

III. $[CoCl_4]^{2-}$ / $[Co(H_2O)_6]^{2+}$ Equilibrium

(1) What is the color of the original equilibrium mixture in step 9?

(2) What changes do you observe after adding concentrated HCl in step 10?

(3) What changes do you observe after adding distilled water in step 11?

(4) What experimental evidence did you observe to indicate that the equilibrium is affected by addition of concentrated HCl? Explain.

(5) Are your observations and explanation in (4) consistent with Le Chatelier's Principle? Explain.

(6) What experimental evidence did you observe to indicate that the equilibrium is affected by addition of distilled water? Explain.

(7) Are your observations and explanation in (6) consistent with Le Chatelier's Principle? Explain.

IV. Dissolution of NH_4Cl Equilibrium

(1) What changes do you observe after adding concentrated HCl in step 13?

(2) What changes do you observe after heating the equilibrium mixture in step 15?

(3) What changes do you observe when solid NH_4Cl dissolved in distilled water (step 16)?

(4) Is the dissolution of NH_4Cl endothermic or exothermic? Explain.

(5) What experimental evidence did you observe to indicate that the equilibrium is affected by addition of concentrated HCl? Explain.

(6) Are your observations and explanation in (5) consistent with Le Chatelier's Principle? Explain.

(7) What experimental evidence did you observe to indicate that the equilibrium is affected by temperature? Explain.

(8) Are your observations and explanation in (7) consistent with Le Chatelier's Principle? Explain.

Post-Lab Questions

1. Write reactions to illustrate how the equilibrium mixture in Part I is affected by the addition of NaOH. Explain in terms of Le Chatelier's Principle.

2. Write reactions to illustrate how the equilibrium mixture in Part II is affected by the addition of NaOH. Explain in terms of Le Chatelier's Principle.

3. Write a reaction to illustrate how the equilibrium in Part IV is affected by heat. Explain in terms of Le Chatelier's Principle.

4. A student extended the study of the cobalt ion equilibrium in Part III. When silver nitrate was added to a test tube containing a blue equilibrium mixture of $[CoCl_4]^{2-}$, a white precipitate formed, and the solution turned pink. The student correctly concluded that the white precipitate was silver chloride (AgCl). Explain this result using Le Chatelier's Principle and include appropriate chemical reactions to support your explanation.