EXPERIMENT 24

Chemical Equilibrium

Performance Goals

24–1 Given the equation for a chemical equilibrium, predict and explain, on the basis of LeChatelier's Principle, the direction of a shift in the position of an equilibrium caused by a change in the concentration of one species.

CHEMICAL OVERVIEW

Some chemical reactions *proceed to completion,* that is, until one of the reacting species is for all practical purposes completely consumed. One example of such a reaction is the precipitation of Cl^- ions from solution:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s) \tag{24.1}$$

When the Cl^- concentration is essentially zero, the reaction is complete.

Other reactions are *reversible.* This means that when the reactants are introduced into the reaction vessel, the reaction will start, but as soon as the reaction products begin to accumulate, they will react with each other to produce some of the starting species. At any time, *two* reactions are occurring, one going in the *forward* direction and one in *reverse.* For example, consider the ionization of acetic acid in water:

$$CH_3COOH(aq) + H_2O(\ell) \rightleftarrows CH_3COO^-(aq) + H_3O^+(aq) \tag{24.2}$$

While some neutral acetic acid molecules are reacting with water, some of the hydronium ions (H_3O^+) and acetate ions (CH_3COO^-) formed by the ionization are recombining to yield the undissociated acid. The two arrows indicate the simultaneous occurrence of two reactions. *When the rate of the forward reaction exactly equals the rate of the reverse reaction, the system is said to be at equilibrium,* and no more detectable change occurs. This condition does not mean that all reactions have ceased, but only that the opposing reactions proceed at the same rate.

Consider the generalized reaction

$$A + B \rightleftarrows C + D \tag{24.3}$$

When the concentration of any one of the species in this equilibrium is changed, the equilibrium is ''disturbed,'' and a ''shift'' will occur, either in the forward or reverse direction. **LeChatelier's Principle** predicts the direction of such a shift by stating: *When some stress is applied to a system originally at equilibrium, the system (reaction) will shift in such a direction as to counteract the stress, until a new equilibrium is reached.*

Let us consider how we can apply the preceding principle to the reaction shown in Equation 24.3. Suppose we add more of compound A. What will happen? The outside stress is an increase in the concentration of A. The reaction will shift in a direction that will counteract this increase. That is, the reaction will shift to reduce the concentration of A. Compound A is consumed, and its concentration reduced, if the reaction shifts in the forward direction (as you read the equation from left to right). Based on the same reasoning, we can predict that if more C is added, the reverse shift will occur (consuming some of C). The displacement of an equilibrium by the addition of more of one of the species involved in the equilibrium is known as the **common ion effect.**

Evidence of a shift in equilibrium can easily be observed in the laboratory if one or more of the substances are colored or if a change in phase, such as precipitation or dissolution, accompanies the shift.

In this experiment, you will observe qualitatively the effect of changing the concentration of one or more substances in a chemical equilibrium, and then correlate your observations with LeChatelier's Principle. A chemical description of each equilibrium you will study is given in the Procedure section.

SAFETY PRECAUTIONS AND DISPOSAL METHODS

Solutions of sodium hydroxide react with your skin (or eyes), giving a slippery feeling. If this should occur, wash with plenty of water until no more slippery feeling is detected. Handle acid solutions with care, avoiding contact with skin. Stopper all reagent bottles as soon as you are through using them. Wear goggles when performing this experiment.

Solutions containing heavy metal ions (Co^{2+} and Fe^{3+}) should be disposed of in bottles provided. The rest of the solutions can be poured down the drain.

PROCEDURE

1. Cobalt(II) Ion Complexes

Cobalt(II) ions, Co^{2+}, exist in water as aquo-complexes, $Co(H_2O)_6{}^{2+}$, that have a pink color. Other complexes exhibit different colors; the $CoCl_4{}^{2-}$ complex, for example, is blue. Depending on the relative concentration of chloride ions, the equilibrium shown in the following equation may be altered to yield a solution that is more blue or more pink:

$$\underset{Pink}{Co(H_2O)_6^{2+}(aq)} + 4\,Cl^-(aq) \rightleftarrows \underset{Blue}{CoCl_4^{2-}(aq)} + 6\,H_2O(\ell) \qquad (24.4)$$

A. Pour about 10–15 drops of cobalt(II) chloride, $CoCl_2$, solution into each of three small test tubes. To the first one add 10 drops of concentrated hydrochloric acid, HCl. Note the change, if any.

B. To the second test tube, add a small amount of solid ammonium chloride, NH_4Cl, and shake to make a saturated solution. You should have undissolved solid on the bottom of the test tube.

C. Compare the color of the solution with that in the third test tube, which contains only the cobalt(II) chloride solution. Place test tubes 2 and 3 into a beaker containing boiling water and note the change, if any. Cool the tubes under running cold water. Tabulate and explain your observations. [*Hint:* The dissolution of NH_4Cl is endothermic.]

2. Ionization of Acetic Acid

Consider the equilibrium

$$CH_3COOH(aq) + H_2O(\ell) \rightleftarrows CH_3COO^-(aq) + H_3O^+(aq) \qquad (24.5)$$

Since no species in this reaction is colored, an auxiliary reagent is needed to help detect any shift in the equilibrium. You will use an indicator, methyl orange, for this purpose. In strongly acidic solutions (high H_3O^+ concentrations), methyl orange is red. A decrease in H_3O^+ concentration will cause a color change from red to yellow, with an intermediate color of orange.

A. Pour 10–15 drops of 0.1 M acetic acid, Ch_3COOH, into a test tube and add 1 or 2 drops of methyl orange. Place a few crystals of sodium acetate, CH_3COONa, in the solution and shake gently to dissolve them. Explain your observations.

B. Do not do experimentally, but reason out what change you would see if instead of sodium acetate, you added a few drops of 1 M NaOH. Explain.

3. Ionization of Aqueous Ammonia

When ammonia gas is dissolved in water the following equilibrium is established:

$$NH_3(aq) + H_2O(\ell) \rightleftarrows NH_4{}^+(aq) + OH^-(aq) \qquad (24.6)$$

This solution is sometimes also called ammonium hydroxide because of the presence of ammonium and hydroxide ions, but more properly it should be called aqueous ammonia. As with the equilibrium in Part 2, no species is colored. Therefore, we will use an indicator to signal the shifts in equilibrium. Phenolphthalein is colorless in slightly basic solutions, but it turns pink as the OH^- ion concentration increases.

A. Pour 10–15 drops 0.1 M ammonia, NH_3, into a test tube and add 1 or 2 drops of phenolphthalein. Note the color of the solution. Add solid ammonium chloride, NH_4Cl, to the solution and shake gently to dissolve the crystals. Record and explain your observations.

B. Repeat the procedure in Step A, but instead of solid ammonium chloride, add 10 drops of 1 M zinc chloride, $ZnCl_2$. Record and explain your observations. [*Hint:* $Zn(OH)_2$ is quite insoluble.]

4. The Thiocyano-Iron(III) Complex Ion

The thiocyano-iron(III) complex ion can be formed from iron(III) ions (Fe^{3+}) and thiocyanate ions (SCN^-) according to the equation

$$\underset{\textit{Tan}}{Fe^{3+}(aq) + SCN^-(aq)} \rightleftarrows \underset{\textit{Blood}\ \text{Red}}{Fe(SCN)^{2+}(aq)} \qquad (24.7)$$

Pour 10–15 drops of 0.1 M iron(III) nitrate, $FeCl_3$, and 10–15 drops of 0.1 M potassium thiocyanate, KSCN, into a 50-mL beaker. Dilute with 25 to 30 mL of deionized water to reduce the intensity of the deep red color. Pour 2- or 3-mL portions of this solution into each of three test tubes and proceed as follows:

A. Add about 10 drops of 1.0 M iron(III) nitrate solution to the contents of the first test tube.

B. To the second test tube, add 10 drops of 0.1 M potassium thiocyanate solution.

C. To the third test tube, add 4–5 drops of 10 percent sodium hydroxide.

Record and explain any changes you observed in Parts (A) through (C). (*Hint:* Iron(III) hydroxide is very insoluble.)

5. Saturated Sodium Chloride Equilibrium

When a saturated solution of sodium chloride is in contact with undissolved solute, the following equilibrium exists:

$$NaCl(s) \rightleftarrows Na^{+}(aq) + Cl^{-}(aq) \qquad (24.8)$$

The solution contains the maximum number of ions the solubility of NaCl allows. Pour 10–15 drops of saturated solution into a small test tube and add a few drops of concentrated hydrochloric acid, HCl. Note the result and give an explanation for it.

Name *Date* *Section*

Experiment 24

Advance Study Assignment

1. State how and explain why the equilibrium $2X + Y \rightleftarrows Z$ will shift if

a. X is removed.

b. extra Y is added.

c. some Z is added.

2. Define, state, or describe:

a. The common ion effect

b. LeChatelier's Principle

c. Are there any reactions occurring when a system is at equilibrium?

3. Consider the equilibrium $2\ CrO_4^{2-}(aq) + 2H^+(aq) \rightleftarrows Cr_2O_7^{2-}(aq) + H_2O(\ell)$. Predict the direction the equilibrium will shift upon the

a. addition of NaOH.

b. addition of hydrochloric acid.

4. Give reasons for your predictions in Question 3.

Name ______________________ Date ____________ Section ____________

Experiment 24

Work Page

Part 1—Cobalt(II) Ion Complex Equilibrium

$$Co(H_2O)_6^{2+}(aq) + 4\ Cl^-(aq) \rightleftarrows CoCl_4^{2-}(aq) + 6\ H_2O(\ell)$$

1A. *HCl addition:* Color change, if any: ______________________

Direction of shift (foward, reverse, none): ______________________

Explanation:

1B. *NH_4Cl addition:* Colors of solutions in test tubes 2 and 3 at different temperatures:

	Test Tube 2	*Test Tube 3*
Room temperature		
Boiling water temperature		
After cooling		

Explanation:

Part 2—Ionization Equilibrium of Acetic Acid

$$CH_3COOH(aq) + H_2O(\ell) \rightleftarrows CH_3COO^-(aq) + H_3O^+(aq)$$

2A. *CH_3COONa addition:* Color change, if any: ____________________________

Direction of shift (forward, reverse, none): ____________________________

Explanation:

2B. *NaOH addition:* Predicted direction of shift (forward, reverse, none): __________________

Explanation:

Part 3—Ionization Equilibrium of Aqueous Ammonia

$$NH_3(aq) + H_2O(\ell) \rightleftarrows NH_4^+(aq) + OH^-(aq)$$

3A. *NH_4Cl addition:* Color change, if any: ____________________________

Direction of shift (forward, reverse, none): ____________________________

Explanation:

Name ______________________ Date ____________ Section ____________

Experiment 24

Work Page

3B. *$ZnCl_2$ addition:* Color change, if any: ______________________

Direction of shift (forward, reverse, none): ______________________

Explanation:

Part 4—Thiocyano-Iron(III) Complex Ion Equilibrium

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftarrows Fe(SCN)^{2+}(aq)$$

4A. *$Fe(NO_3)_3$ addition:* Color change, if any: ______________________

Direction of shift (forward, reverse, none): ______________________

Explanation:

4B. *KSCN addition:* Color change, if any: ______________________

Direction of shift (forward, reverse, none): ______________________

Explanation:

4C. *NaOH addition:* Color change, if any: ______________________________

Direction of shift (forward, reverse, none): ______________________________

Explanation:

Part 5—Saturated Sodium Chloride Equilibrium

$$NaCl(s) \rightleftarrows Na^+(aq) + Cl^-(aq)$$

HCl addition: Change, if any: ______________________________

Direction of shift (forward, reverse, none): ______________________________

Explanation:

Name ______ *Date* ______ *Section* ______

Experiment 24

Report Sheet

Part 1—Cobalt(II) Ion Complex Equilibrium

$$Co(H_2O)_6^{2+}(aq) + 4\ Cl^-(aq) \rightleftarrows CoCl_4^{2-}(aq) + 6\ H_2O(\ell)$$

1A. *HCl addition:* Color change, if any: ______

Direction of shift (forward, reverse, none): ______

Explanation:

1B. *NH_4Cl addition:* Colors of solutions in test tubes 2 and 3 at different temperatures:

	Test Tube 2	*Test Tube 3*
Room temperature		
Boiling water temperature		
After cooling		

Explanation:

Weiner_5209_ch24, 12/29/8, 17:51, page: 324

Part 2—Ionization Equilibrium of Acetic Acid

$$CH_3COOH(aq) + H_2O(\ell) \rightleftarrows CH_3COO^-(aq) + H_3O^+(aq)$$

2A. *CH_3COONa addition:* Color change, if any: ______________________________

Direction of shift (forward, reverse, none): ______________________________

Explanation:

2B. *NaOH addition:* Predicted direction of shift (forward, reverse, none): ____________________

Explanation:

Part 3—Ionization Equilibrium of Aqueous Ammonia

$$NH_3(aq) + H_2O(\ell) \rightleftarrows NH_4{}^+(aq) + OH^-(aq)$$

3A. *NH_4Cl addition:* Color change, if any: ______________________________

Direction of shift (forward, reverse, none): ______________________________

Explanation:

Name ______________________ Date ____________ Section ____________

Experiment 24

Report Sheet

3B. *$ZnCl_2$ addition:* Color change, if any: ______________________

Direction of shift (forward, reverse, none): ______________________

Explanation:

Part 4—Thiocyano-Iron(III) Complex Ion Equilibrium

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftarrows Fe(SCN)^{2+}(aq)$$

4A. *$Fe(NO_3)_3$ addition:* Color change, if any: ______________________

Direction of shift (forward, reverse, none): ______________________

Explanation:

4B. *KSCN addition:* Color change, if any: ______________________

Direction of shift (forward, reverse, none): ______________________

Explanation:

4C. *NaOH addition:* Color change, if any: ______________________________

Direction of shift (forward, reverse, none): ______________________________

Explanation:

Part 5—Saturated Sodium Chloride Equilibrium

$$NaCl(s) \rightleftarrows Na^{+}(aq) + Cl^{-}(aq)$$

HCl addition: Change, if any: ______________________________

Direction of shift (forward, reverse, none): ______________________________

Explanation: