EXPERIMENT 17

Chemical Equilibrium and Le Châtelier's Principle

Objective

In this experiment, you will study the equilibrium conditions of six different reactions. You will first establish the equilibrium by mixing the solutions provided for each reaction and then add reagents in order to perturb the established equilibrium. Each time that you cause a change in the equilibrium, you will observe the changes (look for evidence of reaction), write a net ionic equation illustrating the changes and then comment on how the reaction rate is affected, either the forward or reverse reaction rate. The goal is to learn how equilibria respond to changes in concentrations and changes in temperature.

Introduction

Many chemical reactions are considered to be reversible, meaning that the reactants are not completely converted into the products due to a competing reverse reaction. Consider the reaction:

$$A + B \rightleftharpoons C + D \qquad \textbf{(EQ 17.1)}$$

The forward reaction is $A + B \rightarrow C + D$ and the reverse reaction is $C + D \rightarrow A + B$. Both of these reactions occur simultaneously as indicated by the double-headed arrow in the original reaction. The forward reaction occurs at some characteristic rate dependent upon the concentrations of the reactants and the temperature. The reverse reaction also occurs at some particular rate that is also dependent upon concentrations and temperature. When the rate of the forward reaction is equal to the rate of the reverse reaction, the system is said to be at equilibrium. At equilibrium, the products react at the same rate they are produced; thus the concentrations of the substances do not change.

Equilibrium Effects from Changes in Concentration

Le Châtelier's Principle states that, for a system at equilibrium, if the conditions are changed, the system responds in such a manner to counteract the change. For example, in the reaction above, the rate of forward reaction is increased when component A is added to the system. This results in a decrease in the concentration of component B and an increase in the concentrations of C and D. This shows that the equilibrium has been shifted to the right.

Looking at the effect of changing the concentrations of any of the reactants or products we see that:

- An increase in the concentration of A or B will increase the rate of the forward reaction and shift the equilibrium to the right.
- An increase in the concentration of C or D will increase the rate of the reverse reaction and shift the equilibrium to the left.
- A decrease in the concentration of A or B will decrease the rate of the forward reaction and shift the equilibrium to the left.
- A decrease in the concentration of C or D will decrease the rate of the reverse reaction and shift the equilibrium to the right.

Equilibrium Effects from Changes in Temperature

Temperature changes can also affect the position of equilibrium. For the endothermic reaction shown here:

$$A + \text{heat} \rightleftharpoons B \qquad \textbf{(EQ 17.2)}$$

a temperature increase would increase the rate of both reactions. However, the forward reaction requires heat to proceed and an increase in temperature would provide this heat thereby increasing the rate significantly. The reverse reaction generates heat and more available heat in the form of increased temperature does not significantly affect the rate. Thus, in this case, a temperature increase will shift the equilibrium to the right.

Stated another way: an endothermic reaction shifts to the right if the temperature of reaction is increased. An exothermic reaction shifts to the left if the temperature of reaction is increased.

When studying chemical equilibria, one must observe a system, determine measurable indications of equilibrium shifts, and write chemical equations describing the shifts that are occurring. Following is a sample experiment.

Sample Write-Up

The following equilibrium can be established:

$[Ni(NH_3)_6]^{2+}{}_{(aq)}$	+	$4\ CN^-{}_{(aq)}$	$\rightleftharpoons$	$[Ni(CN)_4]^{2-}{}_{(aq)}$	+	$6\ NH_{3\,(aq)}$	**(EQ 17.3)**
hexaamminenickel(II) ion		cyanide ion		tetracyanonickelate(II) ion		ammonia	
blue-violet		colorless		yellow		colorless	

Reagents available to establish this equilibrium: 0.1 *M* $NiCl_2$, 6 *M* NH_3, 1 *M* NaCN, 12 *M* HCl

1. What is the equilibrium expression for Equation 17.3?

Answer: Equilibrium expression: $K_c = \dfrac{[Ni(CN)_4{}^{2-}][NH_3]^6}{[Ni(NH_3)_6{}^{2+}][CN^-]^4}$

2. What reaction will produce hexaamminenickel(II) complex ion, $[Ni(NH_3)_6]^{2+}$?

Answer: Mixing nickel(II) chloride, $NiCl_2$, with ammonia, NH_3, will generate the complex:

a. Write the net ionic reaction taking place:

Answer: $$NiCl_{2\,(aq)} + 6\,NH_{3\,(aq)} \rightarrow [Ni(NH_3)_6]^{2+}{}_{(aq)} + 2\,Cl^-{}_{(aq)} \qquad \textbf{(EQ 17.4)}$$

$$Ni^{2+}{}_{(aq)} + 2\,Cl^-{}_{(aq)} + 6\,NH_{3\,(aq)} \rightarrow [Ni(NH_3)_6]^{2+}{}_{(aq)} + 2\,Cl^-{}_{(aq)} \qquad \textbf{(EQ 17.5)}$$

$$Ni^{2+}{}_{(aq)} + 6\,NH_{3\,(aq)} \rightarrow [Ni(NH_3)_6]^{2+}{}_{(aq)} \qquad \textbf{(EQ 17.6)}$$

3. Addition of what reagent will shift the equilibrium to the right?

Answer: Add 1 M sodium cyanide, NaCN.

4. What do you observe?

Answer: Color changes from blue violet to yellow.

5. What is the net ionic equation?

Answer: $$[Ni(NH_3)_6]^{2+}{}_{(aq)} + 4\,CN^-{}_{(aq)} \rightleftharpoons [Ni(CN)_4]^{2-}{}_{(aq)} + 6\,NH_{3\,(aq)} \qquad \textbf{(EQ 17.7)}$$

6. What is the reason for the shift?

Answer: The rate of the forward reaction has increased.

7. If the sodium cyanide, NaCN, is used up, how else could the reaction be shifted to the right?

Answer: Add 12 M hydrochloric acid, HCl.

8. What do you observe?

Answer: Color changes from blue violet to yellow.

9. What is the net ionic equation?

Answer: $$NH_{3\,(aq)} + H^+{}_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} \qquad \textbf{(EQ 17.8)}$$

10. What is the reason for the shift?

Answer: The rate of the reverse reaction has decreased.

11. Addition of what reagent will shift the equilibrium to the left?

Answer: Add 6 M aqueous ammonia, NH_3.

12. What do you observe?

Answer: Color changes from yellow to blue violet.

13. What is the net ionic equation?

Answer: $$[Ni(CN)_4]^{2-}{}_{(aq)} + 6\,NH_{3\,(aq)} \rightleftharpoons [Ni(NH_3)_6]^{2+}{}_{(aq)} + 4\,CN^-{}_{(aq)} \qquad \textbf{(EQ 17.9)}$$

14. What is the reason for the shift?

Answer: The rate of the reverse reaction has increased.

Equilibrium Experiment Demonstration

Your instructor will demonstrate how to manipulate the following equilibrium. Complete the questions that follow.

Equilibrium established:

$[Co(H_2O)_6]^{2+}{}_{(aq)}$	+	$4\ Cl^-{}_{(aq)}$	$\rightleftharpoons$	$[CoCl_4]^{2-}{}_{(aq)}$	+	$6\ H_2O_{(l)}$	**(EQ 17.10)**
hexaaquacobalt(II) ion		chloride ion		tetrachlorocobaltate(II) ion		water	
pink		colorless		blue		colorless	

Reagents: 0.1 *M* $CoCl_2$, 2 *M* HCl, 0.1 *M* $AgNO_3$

1. Equilibrium expression:
2. Hexaaquacobalt(II) ion, $[Co(H_2O)_6]^{2+}$, is produced by:
3. The net ionic equation is:
4. The equilibrium will be shifted to the RIGHT by (Choose a reagent to add in order to shift equilibrium):
5. Observation that suggests the equilibrium is shifted to the right: (Color change, gas formation, temperature change, precipitate formation)
6. The net ionic equation is:
7. The reason for the shift: (Forward or reverse reaction speeds up or slows down)
8. The equilibrium will be shifted to the LEFT by: (Choose a reagent to add in order to shift equilibrium)
9. Observation that suggests the equilibrium is shifted to the left: (Color change, gas formation, temperature change, precipitate formation)
10. The net ionic equation is:
11. The reason for the shift::(Forward or reverse reaction speeds up or slows down)
12. Increasing the temperature will shift the equilibrium in which direction?
13. Observation that suggests the equilibrium is shifting: (Color change, gas formation, temperature change, precipitate formation)
14. The reasons for the shift: (Forward or reverse reaction speeds up or slows down)
15. Is the reaction exothermic or endothermic?
16. The net ionic equation is:

Procedure

There are six reactions to study in this part of the experiment. For each reaction, select solutions from the **list of reagents** to establish the equilibrium, that is, to produce ALL the species shown in the equilibrium equation.

Once you have established the equilibrium, manipulate the concentrations in order to shift the equilibrium first to the right and then to the left. Record your observations, verifying that the shift has occurred and write the ionic equations to illustrate what is happening on a molecular level. Indicate the change in reaction rate (for the forward or reverse reaction) after each change that you induce in the equilibrium.

Use small test tubes and minimal amounts of solutions; usually a few drops will suffice. Do not add more reagent than the minimum amount needed to change the equilibrium. If the concentration of a reagent becomes too great, you may not be able to shift the equilibrium back again, or, unexpected side reactions may occur. If you keep your solutions dilute, you should be able to shift the equilibrium back and forth with relative ease.

1. **Reagents:** 0.1 *M* $K_2Cr_2O_7$, 1 *M* HCl, 1 *M* NaOH

$$\underset{\text{orange}}{Cr_2O_7{}^{2-}{}_{(aq)}} + H_2O_{(l)} \rightleftharpoons \underset{\text{yellow}}{2\ CrO_4{}^{2-}{}_{(aq)}} + 2\ H^+{}_{(aq)} \qquad K_c = ? \qquad \textbf{(EQ 17.11)}$$

   a. Dichromate ion produced by
   b. Equilibrium shifted to the right by
   c. Observation
   d. Net Ionic Equation
   e. Reason for shift
   f. Equilibrium shifted to the left by
   g. Observation
   h. Net Ionic Equation
   i. Reason for shift

2. **Reagents:** 0.1 *M* $BaCl_2$, 0.1 *M* $(NH_4)_2C_2O_4$, 1 *M* HCl, 1 *M* NH_3

$$\underset{\text{white}}{BaC_2O_{4\,(s)}} + H^+{}_{(aq)} \rightleftharpoons Ba^{2+}{}_{(aq)} + HC_2O_4{}^-{}_{(aq)} \qquad K_c = ? \qquad \textbf{(EQ 17.12)}$$

   a. Barium oxalate produced by
   b. Net Ionic Equation
   c. Equilibrium shifted to the right by
   d. Observation
   e. Net Ionic Equation
   f. Reason for shift
   g. Equilibrium shifted to the left by
   h. Observation
   i. Net Ionic Equation
   j. Reason for shift

3. Reagents: 0.1 M $AgNO_3$, 6 M NaCl, 6 M NH_3

$$AgCl_{(s)} + 2\,NH_{3\,(aq)} \rightleftharpoons [Ag(NH_3)_2]^+_{(aq)} + Cl^-_{(aq)} \qquad K_c = ? \qquad \textbf{(EQ 17.13)}$$

white — diamminesilver(I) ion

a. Silver chloride produced by
b. Net Ionic Equation
c. Equilibrium shifted to the right by
d. Observation
e. Net Ionic Equation
f. Reason for shift
g. Equilibrium shifted to the left by
h. Observation
i. Net Ionic Equation
j. Reason for shift

4. Reagents: 0.01 M $FeCl_3$, 0.01 M NH_4SCN, 0.01 M $HgCl_2$

$$[Fe(SCN)_6]^{3-}_{(aq)} \rightleftharpoons Fe^{3+}_{(aq)} + 6\,SCN^-_{(aq)} \qquad K_c = ? \qquad \textbf{(EQ 17.14)}$$

hexathiocyanatoferrate(III) ion

red — yellow

Hint: A few drops of $Hg^{2+}_{(aq)}$ removes SCN^- ions from solution:

$$Hg^{2+}_{(aq)} + 4\,SCN^-_{(aq)} \rightleftharpoons [Hg(SCN)_4]^{2-}_{(aq)} \qquad \textbf{(EQ 17.15)}$$

tetrathiocyanatomercurate(II) ion

a. Hexathiocyanatoferrate(III) ion, $[Fe(SCN)_6]^{3-}$ produced by
b. Net Ionic Equation
c. Equilibrium shifted to the right by
d. Observation
e. Net Ionic Equation
f. Reason for the shift
g. Equilibrium shifted to the left by
h. Observation
i. Net Ionic Equation
j. Reason for the shift

5. **Reagents:** 0.1 *M* $Cu(NO_3)_2$, 1 *M* HCl, 1 *M* NH_3

For reaction 5, there are two equilibria to consider:

$K_c = ?$

$$2\,H_2O_{(l)} + \underset{\text{pale blue}}{Cu^{2+}_{(aq)}} + 2\,NH_{3\,(aq)} \rightleftharpoons \underset{\text{blue ppt}}{Cu(OH)_{2\,(s)}} + 2\,NH_4{}^{+}{}_{(aq)} \quad \textbf{(EQ 17.16)}$$

$K_c = ?$

$$\underset{\text{blue ppt}}{Cu(OH)_{2\,(s)}} + 4\,NH_{3\,(aq)} \rightleftharpoons \underset{\substack{\text{tetraamminecopper(II) ion}\\ \text{deep blue}}}{[Cu(NH_3)_4]^{2+}{}_{(aq)}} + 2\,OH^{-}{}_{(aq)} \quad \textbf{(EQ 17.17)}$$

⚠ Be careful with the amount of reagent added. It is easy to make $[Cu(NH_3)_4]^{2+}$ instead of $Cu(OH)_2$!

a. $Cu(OH)_{2\,(s)}$ produced by
b. Net Ionic Equation
c. Equilibrium shifted to the left by
d. Observation
e. Net Ionic Equation
f. Reason for shift
g. Equilibrium shifted to the right by
h. Observation
i. Net Ionic Equation
j. Reason for the shift

6. **Reagents:** $NH_4Cl_{(s)}$, DI water, saturated $NH_4Cl_{(aq)}$, 12 M $HCl_{(aq)}$

$$NH_4Cl_{(s)} \rightleftharpoons NH_4^+{}_{(aq)} + Cl^-{}_{(aq)} \qquad K_c = ? \qquad \textbf{(EQ 17.18)}$$

Hint: Be sure that the saturated ammonium chloride is saturated (i.e has solid ppt at the bottom of the reagent container). If not add ammonium chloride to your beaker until saturated.

a. Add about 0.5 g of ammonium chloride to a small test tube, which is about one-third full with DI water. After adding the solid stir and feel the bottom of the test tube to note any temperature change. Record your observations in your lab book.

   Is the solution of ammonium chloride exothermic or endothermic?

   Write the net ionic equation, putting heat as a reactant or product.

b. To a second test tube add about 3.0 mL of saturated ammonium chloride.

c. To this test tube, add 12 M hydrochloric acid (**CAUTION**!) drop wise until you see a definite change. Record your observations of this change in your lab book.

   Is the reaction shifted to right or the left?

   Reason for shift.

   Write the net ionic equation.

d. Put the resulting test tube into a hot water bath while stirring the mixture. Record your observations.

   Is the reaction shifted to the right or the left?

   Reason for shift.

   Write the net ionic equation.

e. Put the test tube in ice water. Record your observations.

   Is the reaction shifted to the right or the left?

   Reason for the shift.

   Write the net ionic equation.