Experiment 23

EQUILIBRIUM STUDIES

Learning Objectives

By the end of this experiment the student should have learned:

1. Le Chatelier's Principle
2. The nature of a complex.
3. Concepts of acid-base indicators.
4. How to write expressions for the equilibrium constant.

Text Topics

Le Chatelier's Principle, equilibrium constant expressions (Malone, Chapter 15).

Exercises

For additional problem solving experience with equilibrium concepts, see Exercise 28.

Discussion

Many chemical reactions are reversible. In other words, if two chemical species, in solution, are mixed and form new species, there is some tendency for the new species to react reforming the original chemical species. The rate of formation of the new species will, for a time be faster than the reverse reaction. However, when the visible reaction ceases, the rate of formation of the new species becomes equal to the rate of the reverse reaction to the original components and a state of equilibrium is said to be reached. Equilibrium equations are written with two arrows pointed in opposite directions between reactants and products, indicating that both processes are taking place simultaneously.

For example, the equilibrium for saturated silver chloride (undissolved AgCl remains in the bottom of the test tube) is represented by the expression:

$$AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$$

Solid silver chloride is breaking into silver and chloride ions at the same rate that silver ions and chloride ions are coming together to reform solid silver chloride.

Acetic acid slightly dissociates according to:

$$HC_2H_3O_{2(aq)} \rightleftharpoons H^{+}_{(aq)} + C_2H_3O_2{}^{-}_{(aq)}$$

and equilibrium is achieved when the rate of the forward reaction equals the rate of the reverse reaction. For systems for which a state of equilibrium exists, it can be shown that the product of the concentrations of the products divided by the product of the concentrations of the reactants is equal to a constant. For example, for a system with two reactants, A and B, and two products, C and D,

$$A + B \rightleftharpoons C + D \qquad K_{eq} = \frac{[C]\,[D]}{[A]\,[B]}$$

The mathematical relationship for K_{eq} demonstrates Le Chatelier's Principle that a stress placed on a system will cause the system to shift in a direction to reachieve equilibrium. If an aqueous acetic acid solution (for which $K_a = \dfrac{[H^+]\,[C_2H_3O_2{}^-]}{[HC_2H_3O_2]}$

is disturbed by the addition of HCl, the system will shift to the left as the hydrogen ion concentration has increased. Looking at the equilibrium expression, addition of H^+ makes the numerator large relative to the denominator. Consequently, some H^+ must react with $C_2H_3O_2{}^-$ to decrease the numerator and increase the denominator until the hydrogen ion concentration multiplied by acetate concentration divided by the acetic acid concentration once again equals K_a. Addition of NaOH to the system would decrease the hydrogen ion concentration and the system would shift to the right to reestablish equilibrium.

Solubility Products:

The equilibrium constant for compounds that have very low solubilities in water is called a solubility product. For example, only 2×10^{-4} g of silver chloride dissolves in 100 mL water to give silver and chloride ions.

$$AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$$

For the system the equilibrium constant

$$K_{eq} = \frac{[Ag^+]\,[Cl^-]}{[AgCl]}$$

However, since the concentration of solid AgCl is a constant, the equation can be written $K_{eq}\,[AgCl] = [Ag^+]\,[Cl^-]$. The solubility product (K_{sp}) is defined as the product $K_{eq}\,[AgCl] = K_{sp}$ or $K_{sp} = [Ag^+]\,[Cl^-]$.

Calcium hydroxide also has a low solubility in water (0.1 g/100 mL). The K_{sp} for the

$$Ca(OH)_{2(s)} \rightleftharpoons Ca^{+2}_{(aq)} + 2\ OH^{-}_{(aq)}$$

For the system which will be studied in today's experiment, $K_{sp} = [Ca^{+2}]\,[OH^{-}]^2$. This means that the concentration of one ion is dependent on the concentration of the other ion.

Complex Ions:

Copper(II) ions react with ammonia to form a complex ion according to the equation:

$$Cu^{+2}_{(aq)} + 4\ NH_{3(aq)} \rightleftharpoons Cu(NH_3)_4{}^{+2}_{(aq)}$$

Reduction of the concentration of either reactant should cause the complex to dissociate into reactants in order to reestablish equilibrium.

Indicators are very useful additives for acid-base titrations for the visualization of the endpoint. Indicators are themselves often acids of the general formula HIn. In a solution an indicator is in equilibrium with its conjugate base according to:

$$HIn \rightleftharpoons H^{+} + In^{-}$$

The position of equilibrium varies with the acidity of the solution (or the pH) and is different at any pH value for each indicator. For compounds that are used as indicators, the color of HIn and In^- are different. As the system shifts from a preponderance of HIn to a preponderance of In^- over a narrow pH range (usually about 1.5 units), it is possible to detect pH changes by observing color changes of an appropriate indicator. For example, when titrating a strong acid with a strong base an indicator which changes color around a pH of 7 is used to detect the neutralization point. In this section, you will study the shift in the position of equilibrium for the indicator thymol blue as acid or base is added to the system.

Procedure

A.
1. To 5 mL of a saturated solution of calcium hydroxide, add 5 mL of 6 M sodium hydroxide. Report and explain your observations.
2. To the above mixture, add 5 mL of 1.0 M calcium chloride. Report and explain your observations.
3. Now add 8 mL of 6 M HCl to the above mixture. Stopper the tube and mix the contents. Report and explain your observations.

B.
1. Mix 3 mL of a 0.1 M $CuSO_4$ and 3 mL of 6 M NH_3 together in a test tube. Report and explain your observations.
2. To the above mixture add 3 mL of 6 M HCl to the system. Report and explain your observations.

C.
1. Add 10 drops of thymol blue indicator to 10 mL of deionized water in a 20 × 150 mm test tube. Mix and record the color of the system.
2. Add 0.010 M NaOH to the mixture drop by drop while mixing and record your observations. Then add 0.012 M HCl drop by drop and record your observations.
3. Thymol blue exhibits the rather unusual property of undergoing a second color change at a very low pH. Add 1.0 M HCl drop by drop, with mixing, to the thymol blue solution. Report your observations.

Prelaboratory Exercises—Experiment 23

EQUILIBRIUM STUDIES

For additional problem solving experience with equilibrium concepts, see Exercise 28.

1. Write equilibrium constant expressions for the following reactions:

   a. $PCl_5 = PCl_3 + Cl_2$

   b. $2\ NO = N_2 + O_2$

2. Write the expression for the solubility product for the dissolving of $CaSO_4$ in water:

   $CaSO_{4(s)} = Ca^{+2}{}_{(aq)} + SO_4{}^{-2}{}_{(aq)}$

   What would you expect to observe in a saturated $CaSO_4$ solution if:

   a. $Ca(NO_3)_2$ is added?

   b. H_2SO_4 is added?

   c. NaCl is added?

3. For the reaction of ammonia with water:

$$NH_{3(aq)} + H_2O_{(l)} \rightleftarrows NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

in which direction (right or left) would the system shift to achieve equilibrium if:

a. NaOH is added to the solution? ______________________

b. HCl is added to the solution? ______________________

c. NH_3 evaporates out of the solution? ______________________

Solutions to Prelaboratory Exercises

1. a. $K_{eq} = \dfrac{[PCl_3][Cl_2]}{PCl_5}$ b. $K_{eq} = \dfrac{[N_2][O_2]}{[NO]^2}$

2. $K_{sp} = [Ca^{+2}][SO_4^{-2}]$

   a. The addition of calcium ion to the solution should cause the system to shift to the left resulting in the precipitation of calcium sulfate.

   b. The addition of sulfate ion to the solution should cause the system to shift to the left resulting in the precipitation of calcium sulfate.

   c. Neither sodium ions or chloride ions are involved in the dissolving of calcium sulfate and the addition of sodium chloride should not cause an observable result.

3. a. The addition of hydroxide to the solution should cause the system to shift to the *left*.

   b. The addition of hydrogen ion to the solution will cause a depletion in the amount of hydroxide ion. This will cause the system to shift to the *right*.

   c. The loss of ammonia from the solution will cause the system to shift to the *left*.

Results and Questions—Experiment 23

EQUILIBRIUM STUDIES

Date ________ Name ______________________________ Lab Sec. ________ Desk No. ______

A. Write the expression for the solubility product for the dissolving of calcium hydroxide in water:

$Ca(OH)_{2(s)} = Ca^{+2}{}_{(aq)} + 2\ OH^{-}{}_{(aq)}$

$K_{sp} =$

1. Observations when 6 M NaOH was added to saturated calcium hydroxide:

   Explanation:

2. Observations when 1.0 M $CaCl_2$ was added to solution from A-1:

   Explanation:

3. Observations when 6 M HCl was added to the mixture from A-2:

   Explanation:

B. Write the equilibrium expression for the reaction of Cu^{+2} and ammonia:

$Cu^{+2} + 4\ NH_3 = Cu(NH_3)_4{}^{+2}$ K = ______________

1. Observations when 0.1 M copper(II) sulfate mixed with 6 M ammonia:

   Explanation:

2. Observations when 6 M HCl was added to the mixture from B-1:

   Explanation:

C. Write the equilibrium expression for the dissociation of thymol blue:

$HIn_{(aq)} = H^{+}{}_{(aq)} + In^{-}{}_{(aq)}$ K =

1. Color of thymol blue in deionized water: ____________

2. Observations on addition of 0.010 M NaOH and 0.012 M HCl:

Number of drops of NaOH	*Color*	*Number of drops of HCl*	*Color*
1	________	1	________
2	________	2	________
3	________	3	________
4	________	4	________
5	________	5	________
6	________	6	________
7	________	7	________
8	________	8	________
9	________	9	________
10	________	10	________

3. What was the predominant species in acid solution, HIn or In^{-}? ____________

4. What was the predominant species present in base solution, HIn or In^{-}? ____________

5. Did you observe an intermediate color for the indicator between the two extremes? If so, how do you explain it?

6. Observations when 1.0 M HCl was added to the system: