Chapter 20
Chemical Equilibrium

Chapter 20–Assignment A: Chemical Equilibrium. What is it?

Virtually everything you encounter, including your own bodily processes and senses, the color and smell of a flower, and the formation of mountains, is the result of one or more equilibrium reactions. Equilibrium exists, you will recall from Chapters 15 and 16, when reversible reactions occur at equal rates. In this chapter, we look at chemical equilibria more closely.

Look for the following big ideas:

1) **Chemical equilibria** are dynamic. The opposing rates are equal, but they are not zero, even though you see no visible changes. Equilibria exist only in closed systems. In a closed system, no matter is lost.

2) All chemical reactions start with **molecular collisions**, but not all molecular collisions give a chemical reaction.

3) An energy-reaction graph shows potential energies of reactants, activated complex, and products in a reaction, and the activation energy as the reaction proceeds in either direction.

4) Reaction rates are higher at higher temperatures because a larger fraction of the sample has enough kinetic energy to participate in reaction-producing collisions. The energy of collision must be enough to overcome the mutual repulsion of each reactant's valence electrons.

5) A catalyst increases reaction rate by providing an alternative reaction path with a lower activation energy.

6) Collision rates are higher at higher concentrations, so reaction rates are higher at higher reactant concentrations.

Learning Procedures

**Study**  Sections 20.1–20.5. Focus on Goals 1–7 as you study.
Chapter 20–Assignment B: Le Chatelier's Principle; More Chemical Equilibria

In Assignment A you learned that temperature, catalysts, and reactant concentration each affect reaction rate. It seems logical, then, to expect that if a system is at equilibrium, and we change one of these variables, the forward and the reverse reactions rates will no longer be equal. What happens then? That is what you learn in this assignment.

Look for these big ideas:

1) According to Le Chatelier's Principle, if you do anything to alter the rates of reaction in an equilibrium, the equilibrium responds in a way that counteracts partially the initial change until a new equilibrium is reached.

2) A second way to interpret Le Chatelier's Principle might be: “Whatever a chemist does to an equilibrium system, the system itself tries to undo.”

3) An equilibrium system can be described by an equilibrium constant, K. The constant K is a concentration ratio; the form of the ratio depends on how the equilibrium equation is written.

4) All equilibrium constants have the general algebraic form

$$K = \frac{[\text{products}]}{[\text{reactants}]}$$

5) If K is very large, the equilibrium is favored in the forward direction; if K is very small, the equilibrium is favored in the reverse direction. If K is between 0.01 and 100, all reactants and products exist in appreciable concentrations at equilibrium.

Learning Procedures

Study Sections 20.6–20.8. Focus on Goals 8–12 as you study.

Strategy Le Chatelier's Principle is very important in understanding equilibrium systems. Learn it well. Also, practice writing equilibrium constant expressions until you master them.
**Chapter 20–Assignment C: Equilibrium Calculations (Optional)**

This optional assignment explores the quantitative relationships between the size of the equilibrium constant for a reaction and the variable concentrations of reactants and products in that reaction. Look for the following big ideas:

1) All equilibrium calculations begin with the chemical equation for the reaction under study. Equilibria in water solutions are described using net ionic equations.

2) Given concentrations of substances in a reversible reaction, you can compute the value of the equilibrium constant for that reaction.

3) Given the initial concentrations of the substances that react to form an equilibrium and the numeric value of the equilibrium constant, you can determine the composition of the equilibrium mixture.

**Learning Procedures**

**Study** Section 20.9. Focus on Goals 13–19 as you study.

**Strategy** Assignments A and B laid down the concepts of equilibrium; this assignment focuses on calculations. Practice these calculations.


**Workbook** If your instructor recommends the *Active Learning Workbook*, do Questions, Exercises, and Problems 30–39.

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**Chapter 20–Assignment D: Summary and Review**

Sometimes a picture is worth a thousand words. Look at the energy-reaction graph below.
There's a lot of information here. The high activation energy \((a - c)\) means the reaction rate is slow in the forward direction. The products are of higher energy than the reactants, so \(\Delta E\) \((b - c)\) is greater than zero, and this reaction is endothermic.

Anything you can do to ensure that more reactants have the needed activation energy, \(E_a\), gives a faster reaction. If you raise temperature, all particles are moving faster, so more have the \(E_a\) needed for reaction. If you increase concentrations, a greater number of collisions occur. If you add a catalyst, a new reaction pathway with a lower \(E_a\) is available, so more particles react.

The major problem students have when writing equilibrium constant expressions is putting in too many terms. Pure solids and water do not appear in equilibrium expressions in water solution. The only concentrations listed in an equilibrium constant expression are those that are variable.

Let's use \(K_{sp}\) to illustrate the common problems students have with equilibrium. There are four trouble spots: (1) writing the chemical equation for the slightly soluble salt incorrectly; (2) including the concentration of the pure solid in the \(K_{sp}\) expression; (3) forgetting stoichiometry when setting up the solubility terms; and (4) forgetting parentheses with the solubility terms.

Bypass these trouble spots by remembering: (a) the \(K_{sp}\) expression demands that the solid appear on the left side of the chemical equation; (b) concentrations of pure solids are not included in equilibrium expressions; (c) if one mole of a salt dissolves to give two moles of a particular ion, the concentration of that ion is \(2s\), not \(s\); (d) \((2s)^2 = 4s^2\), not \(2s^2\).

Weak acid equilibrium problems have one trouble spot, conversion between pH and \([H^+]\). This is usually an arithmetic problem, not a chemistry problem. If you are unsure how to manage these conversions on your calculator, find the calculator's instruction book or consult Appendix I.A.

Learning Procedures

**Review**

your lecture and textbook notes.

the Chapter in Review and the Key Terms and Concepts, and read the Study Hints and Pitfalls to Avoid.

**Answer**

Concept-Linking Exercises 1–5. Check your answers with those at the end of the chapter.

Questions, Exercises, and Problems 40–42. Include Questions 43–46 if assigned by your instructor. Check your answers with those at the end of the chapter.

**Workbook**

If your instructor recommends the *Active Learning Workbook*, do Questions, Exercises, and Problems 40. Include Questions 41–45 if assigned by your instructor.

**Take**

the chapter summary test that follows. Check your answers with those at the end of this assignment.
Chapter 20 Sample Test

1) Which is the incorrect statement about equilibrium systems?
   a) Forward and reverse reaction rates are the same at equilibrium.
   b) The amounts of products and reactants are the same when the system reaches equilibrium.
   c) No substance can enter or leave an equilibrium system.
   d) Both chemical and physical equilibria exist.

2) Which is the correct statement about collision theory?
   a) Most collisions are effective collisions.
   b) Particles with low kinetic energy are most likely to have effective collisions.
   c) Particles with high kinetic energy always have effective collisions.
   d) Most collisions do not lead to a chemical reaction.

3) Consider the energy-reaction graph shown below.

Which statement concerning the reaction depicted by this graph is correct?
   a) The products are of higher energy than the reactants.
   b) The ΔE for the forward reaction is greater than zero.
   c) The products are of lower energy than the reactants.
   d) The activation energy is the energy at point c minus the energy at point b.

4) All of the following increase reaction rate except
   a) lowering the temperature  b) adding a catalyst
   c) raising concentrations  d) lowering the activation energy

Questions 5–7 refer to $2 \text{CO(g)} + 2 \text{NO(g)} \rightleftharpoons 2 \text{CO}_2(g) + \text{N}_2(g) + 747 \text{kJ}$

5) Adding some NO(g) causes the equilibrium to
   a) shift to the left  b) shift to the right  c) remain unchanged

6) Increasing the container volume causes the equilibrium to
   a) shift to the left  b) shift to the right  c) remain unchanged

7) Lowering the temperature causes the equilibrium to
   a) shift to the left  b) shift to the right  c) remain unchanged
8) The reaction \( \text{A(g)} + \text{B(g)} \rightleftharpoons \text{AB(g)} \) has an equilibrium constant of \( 2.1 \times 10^7 \). This reaction is favored
a) very strongly in the reverse direction
b) slightly in the reverse direction
c) very strongly in the forward direction
d) slightly in the forward direction

Questions 9–11: Write the equilibrium constant expressions for the following reactions.

9) \( 2 \text{CO(g)} + \text{O}_2(g) \rightleftharpoons 2 \text{CO}_2(g) \)

10) \( \text{PbBr}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2 \text{Br}^-(aq) \)

11) \( \text{NH}_3(aq) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \)

Chapter 20–Assignment C Sample Test (Optional)

12) Calculate the solubility of silver sulfate, in moles per liter. \( K_{sp} = 1.2 \times 10^{-5} \).

13) What is the pH of a 1.2 M HCHO_2 solution? \( K_a = 2.0 \times 10^{-4} \).
14) A solution contains 6.10 g HCHO\(_2\) (\(K_a = 2.0 \times 10^{-4}\)) and 43.1 g NaCHO\(_2\). At what pH is this solution buffered?

15) At 325°C, the system \(N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)\) reaches equilibrium with \([N_2] = 0.057 \text{ M}, [H_2] = 0.17 \text{ M}, [NH_3] = 0.042 \text{ M}\). Find K for the system at this temperature.

**Answers to Chapter 20 Sample Test**

1) b  
2) d  
3) c  
4) a  
5) b  
6) a  
7) b  
8) c  

9) \(K = \frac{[CO_2]^2}{[CO]^2[O_2]}\)

10) \(K = [Pb^{2+}] [Br^-]^2\)
11) \[ K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \]

12) \[ \text{Ag}_2\text{SO}_4(s) \rightleftharpoons 2 \text{Ag}^+(aq) + \text{SO}_4^{2-}(aq) \quad K_{sp} = [\text{Ag}^+]^2 [\text{SO}_4^{2-}] = 1.2 \times 10^{-5} \]

Let \( s \) = solubility of \( \text{Ag}_2\text{SO}_4(s) \) in moles per liter; therefore, \( [\text{Ag}^+] = 2s \) and \( [\text{SO}_4^{2-}] = s \)

\[ K_{sp} = (2s)^2 s = 1.2 \times 10^{-5} = 4s^3 \quad s = 0.014 \text{ M} \]

13) \( \text{GIVEN: } K_a = 2.0 \times 10^{-4} \); \( 1.2 \text{ M HCHO}_2 \) \( \text{WANTED: pH} \)

\[ EQUATION: [\text{H}^+] = \sqrt{K_a [\text{HCHO}_2]} = \sqrt{(2.0 \times 10^{-4})(1.2)} = 0.015 \text{ M} \]

\[ EQUATION: \text{pH} = -\log [\text{H}^+] = -\log (0.015) = 1.82 \]

14) \( 6.10 \text{ g HCHO}_2 \div \frac{1 \text{ mol HCHO}_2}{46.03 \text{ g HCHO}_2} = 0.133 \text{ mol HCHO}_2 \)

\( 43.1 \text{ g NaCHO}_2 \div \frac{1 \text{ mol NaCHO}_2}{68.01 \text{ g NaCHO}_2} = 0.634 \text{ mol NaCHO}_2 = 0.634 \text{ mol CHO}_2^- \)

Let \( V \) = solution volume in L; therefore \( [\text{HCHO}_2] = 0.133/V \) and \( [\text{CHO}_2^-] = 0.634/V \)

\[ EQUATION: [\text{H}^+] = K_a \frac{[\text{HCHO}_2]}{[\text{CHO}_2^-]} = 2.0 \times 10^{-4} \frac{0.133/V}{0.634/V} = 4.2 \times 10^{-5} \]

\[ EQUATION: \text{pH} = -\log [\text{H}^+] = -\log (4.2 \times 10^{-5}) = 4.38 \]

15) \[ K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.042)^2}{(0.057)(0.17)^3} = 6.3 \]