Chapter 19 – Reaction Rates and Equilibrium

Section 19.1 Rates of Reaction

1.1: Explain the collision theory of reactions (q. 38). 19.1

Chemical reactions require collisions with sufficient energy to break and form bonds.

1.2: How is the activation energy of a reaction like a wall or barrier (q. 39)? 19.1

Reactant particles must have a certain minimum amount of energy to react to form product, just as it takes a certain minimum amount of energy to climb over a wall or barrier.

1.3: Where is the formula of a catalyst written in a chemical equation (q. 40)? Why? 19.1

Above the reaction arrow, because a catalyst is neither a reactant or product. It emerges from the reaction unscathed.

Ex.: $2\ H_2(g) + O_2(g) \xrightarrow{Pt} 2\ H_2O(l)$

1.4: How is the rate of a reaction influenced by a catalyst? How do catalysts make this possible (q. 41)? 19.1

A catalyst increases the rate of reactions by providing an alternative reaction mechanism with a lower activation energy.

1.5: When the gas to a stove is turned on, the gas does not burn unless lit by a flame. Once lit, however, the gas burns until turned off. Explain these observations in terms of the effect of temperature on reaction rate (q. 43). 19.1

Gas molecules and oxygen molecules mix readily but do not have enough energy to react at room temperature. The flame raises the temperature along with the energy of collisions, thus the reaction rate is increased. The heat released by the reaction maintains the high temperature, and the reaction continues spontaneously.

Section Review 19.1

1. What is meant by the *rate* of a chemical reaction?

The rate of a reaction describes the number of atoms, ions, or molecules that react per given unit of time to form products.

2. How does each factor affect the rate of a chemical reaction?

a. temperature – an increase usually speeds up the rate of a reaction.

b. concentration – an increase in reactant concentration speeds up a reaction.

c. particle size – smaller particles speed up a reaction.

d. an inhibitor – slows down the rate of a reaction.

3. Does every collision between reacting particles lead to products? Explain.

No; the reacting particles must have (1) sufficient energy to break and form bonds, and (2) have the correct orientation.

4. Suppose a thin sheet of zinc containing 0.2 mol of the metal is completely covered in air to zinc oxide (ZnO) in one month. How would you express the rate of conversion of the zinc?

Rate = 0.2 mol Zn/ month

5. Refrigerated food stays fresh for long periods. The same food stored at room temperature quickly spoils. Why?

Chemical reactions involved in food spoilage occur faster at higher temperatures because there is more kinetic energy in the particles.

Section 19.2 Reversible Reactions and Equilibrium

2.1: In your own words, define a *reversible reaction* (q. 44). 19.2

In a reversible reaction, reactants are continuously forming products and products are continuously forming reactants.

2.1: A reversible reaction has reached a state of *dynamic equilibrium*. What does this information tell you (q. 45)? 19.2

The rate of formation of products from reactants and the rate of formation of reactants from products are equal.

2.3: How do the rates of the forward and reverse reactions compare at a state of dynamic chemical equilibrium (q. 46)? 19.2

The rates are equal.

2.4: What is Le Chatelier's principle? Use it to explain why carbonated drinks go flat when their containers are left open (q. 47). 19.2

A system in dynamic equilibrium changes to relieve the stress applied to it. Carbonated drinks in closed containers have achieved a state of dynamic equilibrium between the carbon dioxide in the liquid and gas states. When the containers are opened, carbon dioxide gas escapes, thus gas from the liquid phase goes into the gas state in an attempt to re-establish equilibrium.

Practice Problems

6. How is the equilibrium position of this reaction affected by the following changes?

$C(s) + H_2O(g) + \text{heat} \rightleftharpoons CO(g) + H_2(g)$

a. lowering the temperature – reactants favored

b. increasing the pressure – reactants favored

c. removing H_2 – products favored

d. adding H_2 – reactants favored

7. What effect does each change have on the equilibrium position of this reaction?

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g) + 92\ kJ$

a. addition of heat – favors reactants

b. addition of pressure – favors products

c. addition of catalyst – no effect

d. removal of heat – favors products

8. Analysis of an equilibrium mixture of nitrogen, hydrogen, and ammonia contained in a 1-L flask at 300℃ gives the following results: hydrogen, 0.15 mol; nitrogen, 0.25 mol; ammonia, 0.10 mol. Calculate K_{eq} for the reaction.

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

$$K_{eq} = \frac{[0.10]^2}{[0.25]^1[0.15]^3} = 11.85, or\ 12\ with\ sig.fig.$$

9. Assume you have the mixture described in Problem 8 with the same volume, temperature, and equilibrium concentrations.

a. Calculate K_{eq} for the reaction $2\ NH_3(g) \rightleftharpoons 3\ H_2(g) + N_2(g)$

$$K_{eq} = \frac{[0.25]^1[0.15]^3}{[0.10]^2} = 0.084375, or\ 0.084$$

b. Based on your answers to Problem 8 and Problem 9a, how is the K_{eq} for a forward reaction related to the K_{eq} for a reverse reaction?

One is the inverse of the other.

10. Suppose the following system reaches equilibrium at a high temperature.

$N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$

An analysis of the equilibrium mixture in a 1-L flask gives the following results: nitrogen, 0.50 mol; oxygen, 0.50 mol; nitrogen monoxide, 0.020 mol. Calculate K_{eq} for the reaction.

$$K_{eq} = \frac{[0.020]^2}{[0.50][0.50]} = 0.0016\ or\ 1.6\ x\ 10^{-3}$$

11. At 750℃ the following reaction reaches equilibrium in a 1-L container.

$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

An analysis of the equilibrium mixture provides the following results: hydrogen, 0.053 mol; carbon dioxide, 0.053 mol; water vapor, 0.047 mol; carbon monoxide, 0.047 mol. Calculate K_{eq} for the reaction.

$$K_{eq} = \frac{[0.047][0.047]}{[0.053][0.053]} = 0.79$$

12. The decomposition of hydrogen iodide at 450℃ in a 1-L container produces an equilibrium mixture that contains 0.50 mol of hydrogen. The equilibrium constant is 0.020 for the reaction. How many moles of iodine and hydrogen iodide are present in the equilibrium mixture?

$2\,HI(g) \rightleftharpoons H_2(g) + I_2(g)$ $[HI]^2 = \frac{[H_2][I_2]}{K_{eq}}; [HI]^2 = \frac{[0.50][0.50]}{0.020} = 12.5; \sqrt{12.5} = 3.5$

Concentration of iodine is 0.50 mol; concentration of hydrogen iodide is 3.5

13. Write the expression for the equilibrium constant for each:

a. $2\,HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$ $K_{eq} = \frac{[H_2][Br_2]}{[HBr]^2}$

b. $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$ $K_{eq} = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$

c. $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$ $K_{eq} = \frac{[CO][H_2O]}{[CO_2][H_2]}$

d. $4\,NH_3(g) + 5\,O_2(g) \rightleftharpoons 6\,H_2O(g) + 4\,NO(g)$ $K_{eq} = \frac{[H_2O]^6[NO]^4}{[NH_3]^4[O_2]^5}$

Section Review 19.2

14. How can changes in the equilibrium position be predicted from changes in concentration, temperature, and pressure?

By applying Le Chatelier's Principle: if a stress is applied to a system in dynamic equilibrium, the system changes to relieve the stress.

15. How can a balanced chemical equation and experimental data be used to write an equilibrium-constant expression and to calculate its value?

An equilibrium constant is a ratio. In the numerator, product concentrations are multiplied. In the denominator, reactant concentrations are multiplied. Each concentration is raised to a power equal to the coefficient for that species in the balanced equation. To calculate a numerical value for the equilibrium constant, you need to substitute concentration data from an experiment into the expression.

16. What is the significance of double arrows in an equation?

The double arrows show that the reaction is reversible.

17. How do the amounts of reactants and products change once a reaction has achieved chemical equilibrium?

At equilibrium, the concentrations of reactants and products do not change.

18. Can a pressure change shift the equilibrium position in every reversible reaction? Explain your answer.

No; only in reversible reactions in which the mole ratios of gaseous reactants and products are unequal.

19. Imagine you have determined the following equilibrium constants for several reactions. In which of these reactions are the products favored over the reactants? Why?

a. $K_{eq} = 1 \times 10^2$ b. $K_{eq} = 0.003$ c. $K_{eq} = 3.5$ d. $K_{eq} = 6 \times 10^{-4}$

Products are favored in reactions a and c, because $K_{eq} > 1$.

Section 19.3 Determining Whether a Reaction Will Occur

Section Review 19.3

20 Explain what is meant by the following:

a. entropy – a measure of a system's disorder

b. free energy – energy available to do work

c. spontaneous reaction – a reaction that occurs naturally

d. nonspontaneous reaction – a reaction that must be forced

21. What two factors determine whether a reaction is spontaneous?

a. the change in heat content, or enthalpy

b. the change in a systems entropy

22. Where does lost free energy typically end up? Does free energy lost as heat ever serve a useful function? Explain.

As heat; waste heat from chemical reactions in the body maintains body temperature at 37℃. Similarly, waste heat from industrial processes and electrical generation can be used to heat water, buildings, and so on.

23. What can change a reaction from nonspontaneous to spontaneous?

Depending on the reaction, a change in temperature or pressure.

24. Suppose the products in a spontaneous process are more ordered than the reactants. Is the entropy change favorable or unfavorable? Explain.

Unfavorable, spontaneous processes are naturally higher in disorder.

Section 19.4 Calculating Entropy and Free Energy

Practice Problem

25. The standard entropies for some substances at 25℃ are

$KBrO_3(s)$ S^0 = 149.2 J/K · mol
$KBr(s)$ S^0 = 96.4 J/ K · mol
$O_2(g)$ S^0 = 205.0 J/ K · mol

Calculate the ΔS^0 for the reaction

$KBrO_3(s) \rightarrow KBr(s) + 3/2\ O_2(g)$

254.7 J/ K ▪ mol