Section 17.3 Reaction Rate Laws

Objectives

- **Express** the relationship between reaction rate and concentration.
- **Determine** reaction orders using the method of initial rates.

Vocabulary

rate law
specific rate constant
reaction order
method of initial rates

In Section 17.1, you learned how to calculate the average rate of a chem reaction given the initial and final times and concentrations. The word *a age* is important because most chemical reactions slow down as the react are consumed. To understand why most reaction rates slow over time, r that the collision theory states that chemical reactions can occur only v the reacting particles collide and that reaction rate depends upon rea concentration. As reactants are consumed, fewer particles collide and reaction slows. Chemists use the concept of rate laws to quantify the re of the collision theory in terms of a mathematical relationship betwee rate of a chemical reaction and the reactant concentration.

Reaction Rate Laws

The equation that expresses the mathematical relationship between the of a chemical reaction and the concentration of reactants is called a **rate** For example, the reaction A $\longrightarrow$ B, which is a one-step reaction, has onl activated complex between reactants and products. The rate law for this tion is expressed as

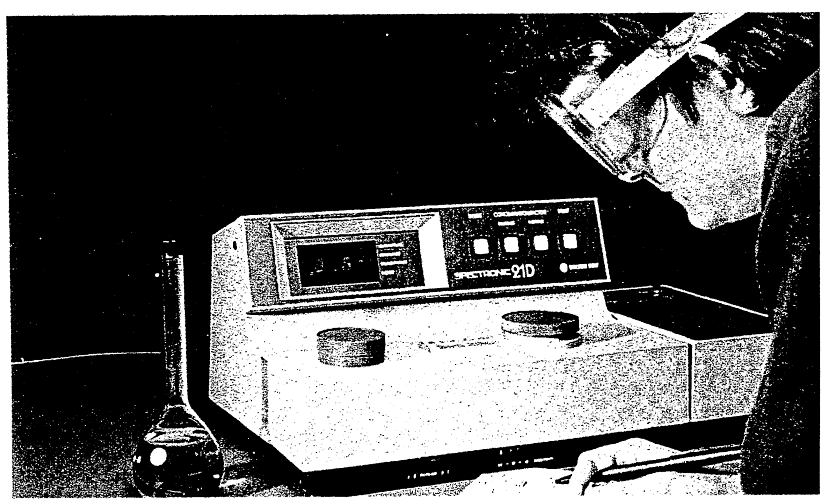
$$\text{Rate} = k[\text{A}]$$

where k is the **specific rate constant**, or a numerical value that relates tion rate and concentration of reactants at a given temperature. Units f rate constant include L/(mol·s), $L^2/(mol^2 \cdot s)$, and s^{-1}. Depending on the tion conditions, especially temperature, k is unique for every reaction.

The rate law means that the reaction rate is directly proportional to the concentration of A. Thus, doubling the concentration of A will double the tion rate. Increasing the concentration of A by a factor of 5 will increa reaction rate by a factor of 5. The specific rate constant, k, does not chang concentration; however, k does change with temperature. A large valu means that A reacts rapidly to form B. What does a small value of k mea

Figure 17-14

Specific rate constants are determined experimentally. Scientists have a number of methods at their disposal that can be used to establish k for a given reaction.



ⓐ A spectrophotometer measures the absorption of specific wavelengtl light by a reactant or product as a reaction progresses to determine the ic rate constant for the reaction.

Reaction order In the expression Rate = $k[A]$, it is understood that the notation [A] means the same as $[A]^1$. In other words, for reactant A, the understood exponent 1 is called the reaction order. The **reaction order** for a reactant defines how the rate is affected by the concentration of that reactant. For example, the rate law for the decomposition of H_2O_2 is expressed by the following equation.

$$\text{Rate} = k[H_2O_2]$$

Because the reaction rate is directly proportional to the concentration of H_2O_2 raised to the first power, $[H_2O_2]^1$, the decomposition of H_2O_2 is said to be first order in H_2O_2. Because the reaction is first order in H_2O_2, the reaction rate changes in the same proportion that the concentration of H_2O_2 changes. So if the H_2O_2 concentration decreases to one-half its original value, the reaction rate is halved as well.

Recall from Section 17.1 that reaction rates are determined from experimental data. Because reaction order is based on reaction rates, it follows that reaction order also is determined experimentally. Finally, because the rate constant describes the reaction rate, k, too, must be determined experimentally. **Figure 17-14** illustrates two of several experimental methods that are commonly used to measure reaction rates.

Math Handbook

Review direct and inverse relationships in the **Math Handbook** on page 905 of this text.

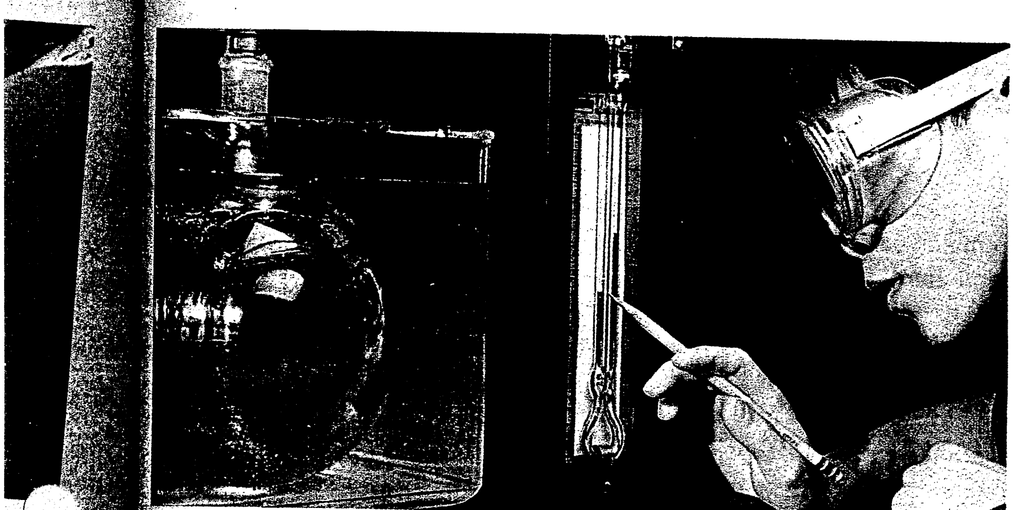
Other reaction orders The overall reaction order of a chemical reaction is the sum of the orders for the individual reactants in the rate law. Many chemical reactions, particularly those having more than one reactant, are not first order. Consider the general form for a chemical reaction with two reactants. In this chemical equation, a and b are coefficients.

$$aA + bB \longrightarrow \text{products}$$

The general rate law for such a reaction is

$$\text{Rate} = k[A]^m[B]^n$$

where m and n are the reaction orders for A and B, respectively. Only if the reaction between A and B occurs in a single step (and with a single activated complex) does $m = a$ and $n = b$. That's unlikely, however, because single-step reactions are uncommon.



b A manometer measures pressure changes that result from the production of gas as a reaction progresses. The reaction rate is directly proportional to the rate at which the pressure increases.

Physics

CONNECTION

The time it takes for bonds to form and break during a chemical reaction is measured in femtoseconds. A femtosecond is one thousandth of a trillionth of a second. Until recently, scientists could only calculate and imagine the actual atomic activity of chemical bonding. In 1999, Dr. Ahmed Zewail of the California Institute of Technology won a Nobel Prize for his achievements in the field of femtochemistry. Zewail has developed an ultrafast laser device that can monitor and record chemical reactions in real time. Zewail's laser "flashes" every ten femtoseconds, allowing chemists to record changes in the wavelengths (colors) that vibrating molecules emitted during the course of a reaction. The changes correspond to bond formation and breakage and are mapped to the various intermediates and products that are formed during a reaction and that were previously impossible to witness.

For example, the reaction between nitrogen monoxide (NO) and hydrogen (H_2) is described by the following equation.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

This reaction, which occurs in more than one step, has the following rate law.

$$\text{Rate} = k[NO]^2[H_2]$$

This rate law was determined experimentally. The data tell that the rate depends on the concentration of the reactants as follows. If [NO] doubles, the rate quadruples; if [H_2] doubles, the rate doubles. The reaction is described as second order in NO, first order in H_2, and third order overall because the sum of the orders for the individual reactants (the sum of the exponents) is (2 + 1), or 3.

Determining Reaction Order

One common experimental method of evaluating reaction order is called the method of initial rates. The **method of initial rates** determines reaction order by comparing the initial rates of a reaction carried out with varying reactant concentrations. To understand how this method works, let's use the general reaction $aA + bB \rightarrow$ products. Suppose that this reaction is carried out with varying concentrations of A and B and yields the initial reaction rates shown in **Table 17-3**.

Table 17-3

Experimental Initial Rates for $aA + bB \rightarrow$ products

Trial	Initial [A] (M)	Initial [B] (M)	Initial Rate (mol/(L·s))
1	0.100	0.100	2.00×10^{-3}
2	0.200	0.100	4.00×10^{-3}
3	0.200	0.200	16.0×10^{-3}

Recall that the general rate law for this type of reaction is

$$\text{Rate} = k[A]^m[B]^n$$

To determine m, the concentrations and reaction rates in Trials 1 and 2 are compared. As you can see from the data, while the concentration of B remains constant, the concentration of A in Trial 2 is twice that of Trial 1. Note that the initial rate in Trial 2 is twice that of Trial 1. Because doubling [A] doubles the rate, the reaction must be first order in A. That is, because $2^m = 2$, m must equal 1. The same method is used to determine n, only this time Trials 2 and 3 are compared. Doubling the concentration of B causes the rate to increase by four times. Because $2^n = 4$, n must equal 2. This information suggests that the reaction is second order in B, giving the following overall rate law.

$$\text{Rate} = k[A]^1[B]^2$$

The overall reaction order is third order (sum of exponents 2 + 1 = 3).

PRACTICE PROBLEMS

16. Write the rate law for the reaction $a\text{A} \rightarrow b\text{B}$ if the reaction is third order in A. [B] is not part of the rate law.

17. Given the following experimental data, use the method of initial rates to determine the rate law for the reaction $a\text{A} + b\text{B} \rightarrow$ products. Hint: Any number to the zero power equals one. For example, $(0.22)^0 = 1$ and $(55.6)^0 = 1$.

Practice Problem 17 Experimental Data

Trial	Initial [A] (M)	Initial [B] (M)	Initial Rate (mol/(L·s))
1	0.100	0.100	2.00×10^{-3}
2	0.200	0.100	2.00×10^{-3}
3	0.200	0.200	4.00×10^{-3}

18. Given the following experimental data, use the method of initial rates to determine the rate law for the reaction $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$.

Practice Problem 18 Experimental Data

Trial	Initial [CH_3CHO] (M)	Initial rate (mol/(L·s))
1	2.00×10^{-3}	2.70×10^{-11}
2	4.00×10^{-3}	10.8×10^{-11}
3	8.00×10^{-3}	43.2×10^{-11}

Practice! For more practice determining reaction orders, go to **Supplemental Practice Problems in Appendix A.**

In summary, the rate law for a reaction relates reaction rate, the rate constant k, and the concentration of the reactants. Although the equation for a reaction conveys a great deal of information, it is important to remember that the actual rate law and order of a complex reaction can be determined only by experiment.

Section 17.3 Assessment

19. What does the rate law for a chemical reaction tell you about the reaction?

20. Use the rate law equations to show the difference between a first-order reaction having a single reactant and a second-order reaction having a single reactant.

21. What relationship is expressed by the specific rate constant for a chemical reaction?

22. Thinking Critically When giving the rate of a chemical reaction, explain why it is significant to know that the reaction rate is an average reaction rate.

23. Designing an Experiment Explain how you would design an experiment to determine the rate law for the general reaction $a\text{A} + b\text{B} \rightarrow$ products using the method of initial rates.

61. How does the activation energy of the rate-determining step in a complex reaction compare with the activation energies of the other elementary steps? (17.4)

Mastering Problems

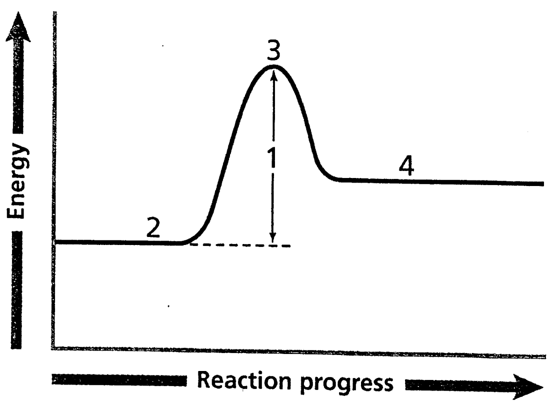
A Model for Reaction Rates (17.1)

62. In the gas-phase reaction $I_2 + Cl_2 \longrightarrow 2ICl$, the $[I_2]$ changes from 0.400*M* at time = 0 to 0.300*M* at time = 4.00 min. Calculate the average reaction rate in moles I_2 consumed per liter per minute.

63. If a chemical reaction occurs at a rate of 2.25×10^{-2} moles per liter per second at 322 K, what is the rate expressed in moles per liter per minute?

64. On the accompanying energy level diagram, match the appropriate number with the quantity it represents.

a. reactants **c.** products
b. activated complex **d.** activation energy



65. Given the following data for the decomposition of hydrogen peroxide, calculate the average reaction rate in moles H_2O_2 consumed per liter per minute for each time interval.

Decomposition of H_2O_2

Time (min)	$[H_2O_2]$ (*M*)
0	2.50
2	2.12
5	1.82
10	1.48
20	1.00

66. At a given temperature and for a specific time interval, the average rate of the following reaction is 1.88×10^{-4} moles N_2 consumed per liter per second.

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Express the reaction rate in moles H_2 consumed per liter per second and in moles NH_3 produced per liter per second.

Factors Affecting Reaction Rates (17.2)

67. Estimate the rate of the reaction described in problem 63 at 332 K. Express the rate in moles per liter per second.

68. Estimate the rate of the reaction described in problem 63 at 352 K and with $[I_2]$ doubled (assume the reaction is first order in I_2).

Reaction Rate Laws (17.3)

69. Nitrogen monoxide gas and chlorine gas react according to the equation $2NO + Cl_2 \longrightarrow 2NOCl$. Use the following data to determine the rate law for the reaction by the method of initial rates. Also, calculate the value of the specific rate constant.

$2NO + Cl_2$ Reaction Data

Initial [NO] (*M*)	Initial $[Cl_2]$ (*M*)	Initial rate (mol/(L·min))
0.50	0.50	1.90×10^{-2}
1.00	0.50	7.60×10^{-2}
1.00	1.00	15.20×10^{-2}

70. Use the following data to determine the rate law and specific rate constant for the reaction $2ClO_2(aq) + 2OH^-(aq) \longrightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(l)$.

$2ClO_2(aq) + 2OH^-(aq)$ Reaction Data

Initial $[ClO_2]$ (*M*)	Initial $[OH^-]$ (*M*)	Initial rate (mol/(L·min))
0.0500	0.200	6.90
0.100	0.200	27.6
0.100	0.100	13.8

Instantaneous Reaction Rates and Reaction Mechanisms (17.4)

71. The gas-phase reaction $2HBr + NO_2 \longrightarrow H_2O + NO + Br_2$ is thought to occur by the following mechanism.

$HBr + NO_2 \longrightarrow HOBr + NO \quad \Delta H = 4.2$ kJ (slow)

$HBr + HOBr \longrightarrow H_2O + Br_2 \quad \Delta H = -86.2$ kJ (fast)

Draw the energy diagram that depicts this reaction mechanism. On the diagram, show the energy of the reactants, energy of the products, and relative activation energies of the two elementary steps.