

## 1.1 RATES OF REACTIONS

The rate of a chemical reaction is expressed as a change in concentration of some species with time. Therefore, the dimensions of the *rate* must be those of concentration divided by time (moles/liter sec, moles/liter min, etc.). A reaction that can be written as



has a rate that can be expressed either in terms of the disappearance of A or the appearance of B. Because the concentration of A is *decreasing* as A is consumed, the rate is expressed as  $-d[A]/dt$ . Because the concentration of B is *increasing* with time, the rate is expressed as  $+d[B]/dt$ . The mathematical equation relating concentrations and time is called the *rate equation* or the *rate law*. The relationships between the concentrations of A and B with time are represented graphically in Figure 1.1 for a first-order reaction in which  $[A]_0$  is 1.00 M and  $k = 0.050 \text{ min}^{-1}$ .

If we consider a reaction that can be shown as



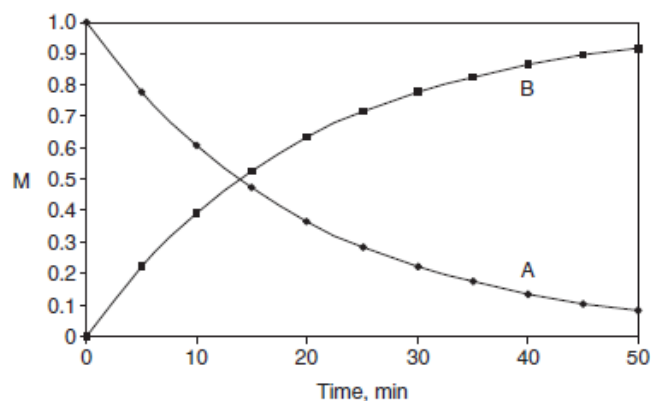


FIGURE 1.1 Change in concentration of A and B for the reaction  $A \rightarrow B$ .

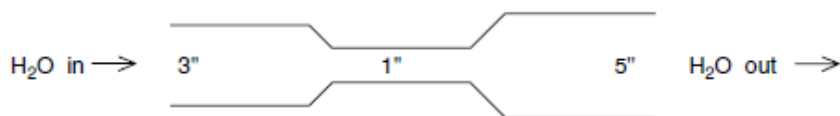
the rate law will usually be represented in terms of a constant times some function of the concentrations of A and B, and it can usually be written in the form

$$\text{Rate} = k[A]^x[B]^y \quad (1.4)$$

where  $x$  and  $y$  are the exponents on the concentrations of A and B, respectively. In this rate law,  $k$  is called the rate constant and the exponents  $x$  and  $y$  are called the *order* of the reaction with respect to A and B, respectively. As will be described later, the exponents  $x$  and  $y$  may or may not be the same as the balancing coefficients  $a$  and  $b$  in Eq. (1.3). The overall order of the reaction is the sum of the exponents  $x$  and  $y$ . Thus, we speak of a second-order reaction, a third-order reaction, etc., when the sum of the exponents in the rate law is 2, 3, etc., respectively. These exponents can usually be established by studying the reaction using different initial concentrations of A and B. When this is done, it is possible to determine if doubling the concentration of A doubles the rate of the reaction. If it does, then the reaction must be first-order in A, and the value of  $x$  is 1. However, if doubling the concentration of A quadruples the rate, it is clear that  $[A]$  must have an exponent of 2, and the reaction is second-order in A. One very important point to remember is that there is no *necessary* correlation between the balancing coefficients in the chemical equation and the exponents in the rate law. They *may* be the same, but one can not *assume* that they will be without studying the rate of the reaction.

If a reaction takes place in a series of steps, a study of the rate of the reaction gives information about the slowest step of the reaction. We can

see an analogy to this in the following illustration that involves the flow of water,

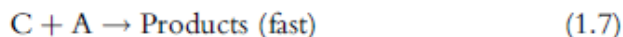


If we study the rate of flow of water through this system of short pipes, information will be obtained about the flow of water through a 1" pipe since the 3" and 5" pipes do not normally offer as much resistance to flow as does the 1" pipe. Therefore, in the language of chemical kinetics, the 1" pipe represents the *rate-determining step*.

Suppose we have a chemical reaction that can be written as



and let us also suppose that the reaction takes place in steps that can be written as



The amount of C (known as an *intermediate*) that is present at any time limits the rate of the overall reaction. Note that the sum of Eqs. (1.6) and (1.7) gives the overall reaction that was shown in Eq. (1.5). Note also that the formation of C depends on the reaction of one molecule of A and one of B. That process will likely have a rate that depends on  $[A]^1$  and  $[B]^1$ . Therefore, even though the balanced overall equation involves *two* molecules of A, the *slow step* involves only one molecule of A. As a result, formation of products follows a rate law that is of the form  $\text{Rate} = k[A][B]$ , and the reaction is second-order (first-order in A and first-order in B). It should be apparent that we can write the rate law directly from the balanced equation only if the reaction takes place in a *single step*. If the reaction takes place in a series of steps, a rate study will give information about steps up to and including the slowest step, and the rate law will be determined by that step.

### 1.2.1 First-Order

Suppose a reaction can be written as



and that the reaction follows a rate law of the form

$$\text{Rate} = k[A]^1 = -\frac{d[A]}{dt} \quad (1.9)$$

This equation can be rearranged to give

$$-\frac{d[A]}{[A]} = k dt \quad (1.10)$$

Equation (1.10) can be integrated but it should be integrated between the limits of time = 0 and time equal to  $t$  while the concentration varies from the initial concentration  $[A]_o$  at time zero to  $[A]$  at the later time. This can be shown as

$$-\int_{[A]_o}^{[A]} \frac{d[A]}{[A]} = k \int_0^t dt \quad (1.11)$$

When the integration is performed, we obtain

$$\ln \frac{[A]_o}{[A]} = kt \quad \text{or} \quad \log \frac{[A]_o}{[A]} = \frac{k}{2.303} t \quad (1.12)$$

If the equation involving natural logarithms is considered, it can be written in the form

$$\ln [A]_o - \ln [A] = kt \quad (1.13)$$

or

$$\begin{aligned} \ln [A] &= \ln [A]_o - kt \\ y &= b + mx \end{aligned} \quad (1.14)$$

It must be remembered that  $[A]_o$ , the initial concentration of A, has some fixed value so it is a constant. Therefore, Eq. (1.14) can be put in the

form of a linear equation where  $y = \ln[A]$ ,  $m = -k$ , and  $b = \ln [A]_0$ . A graph of  $\ln[A]$  versus  $t$  will be linear with a slope of  $-k$ . In order to test this rate law, it is necessary to have data for the reaction which consists of the concentration of A determined as a function of time. This suggests that in order to determine the concentration of some species, in this case A, simple, reliable, and rapid analytical methods are usually sought. Additionally, one must measure time, which is not usually a problem unless the reaction is a very rapid one.

It may be possible for the concentration of a reactant or product to be determined directly within the reaction mixture, but in other cases a sample must be removed for the analysis to be completed. The time necessary to remove a sample from the reaction mixture is usually negligibly short compared to the reaction time being measured. What is usually done for a reaction carried out in solution is to set up the reaction in a vessel that is held in a constant temperature bath so that fluctuations in temperature will not cause changes in the rate of the reaction. Then the reaction is started, and the concentration of the reactant (A in this case) is determined at selected times so that a graph of  $\ln[A]$  versus time can be made or the data analyzed numerically. If a linear relationship provides the best fit to the data, it is concluded that the reaction obeys a first-order rate law. Graphical representation of this rate law is shown in Figure 1.2 for an initial concentration of A of 1.00 M and  $k = 0.020 \text{ min}^{-1}$ . In this case, the slope of the line is  $-k$ , so the kinetic data can be used to determine  $k$  graphically or by means of linear regression using numerical methods to determine the slope of the line.

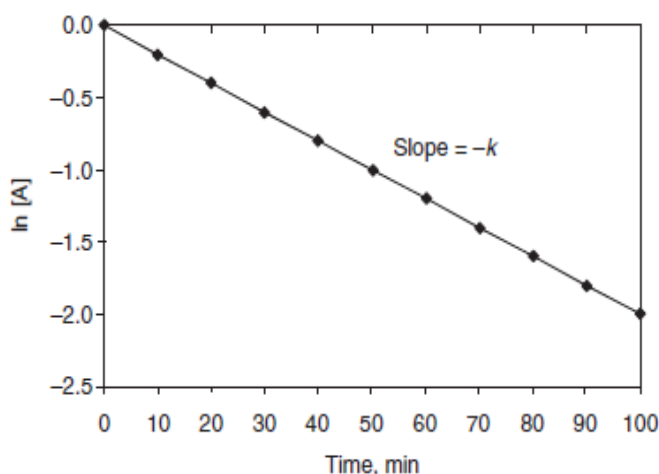


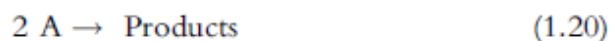
FIGURE 1.2 First-order plot for  $A \rightarrow B$  with  $[A]_0 = 1.00 \text{ M}$  and  $k = 0.020 \text{ min}^{-1}$ .

### 1.2.2 Second-Order

A reaction that is second-order in one reactant or component obeys the rate law

$$\text{Rate} = k[\text{A}]^2 = -\frac{d[\text{A}]}{dt} \quad (1.19)$$

Such a rate law *might* result from a reaction that can be written as



However, as we have seen, the rate law cannot always be written from the balanced equation for the reaction. If we rearrange Eq. (1.19), we have

$$\frac{-d[\text{A}]}{[\text{A}]^2} = k dt \quad (1.21)$$

If the equation is integrated between limits on concentration of  $[A]_0$  at  $t = 0$  and  $[A]$  at time  $t$ , we have

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = k \int_0^t dt \quad (1.22)$$

Performing the integration gives the integrated rate law

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt \quad (1.23)$$

Since the initial concentration of A is a constant, the equation can be put in the form of a linear equation,

$$\begin{aligned} \frac{1}{[A]} &= kt + \frac{1}{[A]_0} \\ y &= mx + b \end{aligned} \quad (1.24)$$

As shown in Figure 1.4, a plot of  $1/[A]$  versus time should be a straight line with a slope of  $k$  and an intercept of  $1/[A]_0$  if the reaction follows the second-order rate law. The units on each side of Eq. (1.24) must be  $1/\text{concentration}$ . If concentration is expressed in mole/liter, then  $1/\text{concentration}$  will have units of liter/mole. From this we find that the units on  $k$  must be liter/mole time or  $\text{M}^{-1} \text{time}^{-1}$  so that  $kt$  will have units  $\text{M}^{-1}$ .

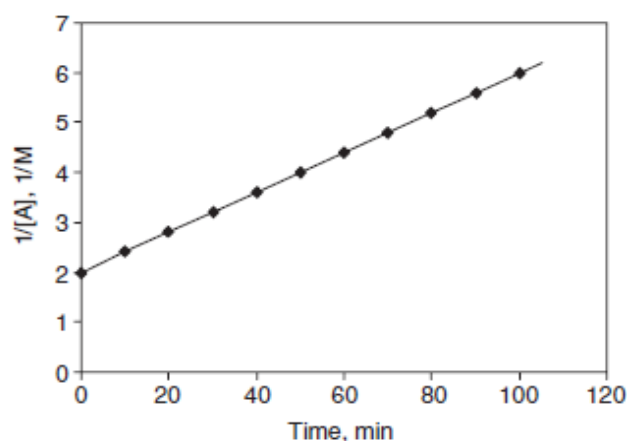


FIGURE 1.4 A second-order rate plot for  $A \rightarrow B$  with  $[A]_0 = 0.50 \text{ M}$  and  $k = 0.040$  liter/mol min.

The half-life for a reaction that follows a second-order rate law can be easily calculated. After a reaction time equal to one half-life, the concentration of A will have decreased to one-half its original value. That is,  $[A] = [A]_o/2$ , so this value can be substituted for  $[A]$  in Eq. (1.23) to give

$$\frac{1}{\frac{[A]_o}{2}} - \frac{1}{[A]_o} = kt_{1/2} \quad (1.25)$$

Removing the complex fraction gives

$$\frac{2}{[A]_o} - \frac{1}{[A]_o} = kt_{1/2} = \frac{1}{[A]_o} \quad (1.26)$$

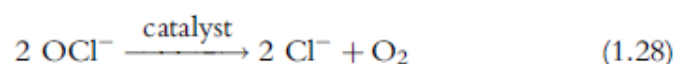
Therefore, solving for  $t_{1/2}$  gives

$$t_{1/2} = \frac{1}{k[A]_o} \quad (1.27)$$

Here we see a major difference between a reaction that follows a second-order rate law and one that follows a first-order rate law. For a first-order reaction, the half-life is independent of the initial concentration of the reactant, but in the case of a second-order reaction, the half-life is inversely proportional to the initial concentration of the reactant.

### 1.2.3 Zero-Order

For certain reactions that involve one reactant, the rate is independent of the concentration of the reactant over a wide range of concentrations. For example, the decomposition of hypochlorite on a cobalt oxide catalyst behaves this way. The reaction is



The cobalt oxide catalyst forms when a solution containing  $\text{Co}^{2+}$  is added to the solution containing  $\text{OCl}^-$ . It is likely that some of the cobalt is also oxidized to  $\text{Co}^{3+}$ , so we will write the catalyst as  $\text{Co}_2\text{O}_3$ , even though it is probably a mixture of  $\text{CoO}$  and  $\text{Co}_2\text{O}_3$ .

The reaction takes place on the active portions of the surface of the solid particles of the catalyst. This happens because  $\text{OCl}^-$  is adsorbed to the solid, and the surface becomes essentially covered or at least the active sites do. Thus, the *total* concentration of  $\text{OCl}^-$  in the solution does not matter as long as there is enough to cover the active sites on the surface of the



catalyst. What *does* matter in this case is the surface area of the catalyst. As a result, the decomposition of  $\text{OCl}^-$  on a specific, fixed amount of catalyst occurs at a constant rate over a wide range of  $\text{OCl}^-$  concentrations. This is not true as the reaction approaches completion, and under such conditions the concentration of  $\text{OCl}^-$  does affect the rate of the reaction because the concentration of  $\text{OCl}^-$  determines the rate at which the active sites on the solid become occupied.

For a reaction in which a reactant disappears in a zero-order process, we can write

$$-\frac{d[\text{A}]}{dt} = k[\text{A}]^0 = k \quad (1.29)$$

because  $[\text{A}]^0 = 1$ . Therefore, we can write the equation as

$$-d[\text{A}] = k dt \quad (1.30)$$

so that the rate law in integral form becomes

$$-\int_{[\text{A}]_0}^{[\text{A}]} d[\text{A}] = k \int_0^t dt \quad (1.31)$$

Integration of this equation between the limits of  $[\text{A}]_0$  at zero time and  $[\text{A}]$  at some later time,  $t$ , gives

$$[\text{A}] = [\text{A}]_0 - kt \quad (1.32)$$

which shows that a plot of  $[\text{A}]$  versus time should be linear with a slope of  $-k$  and an intercept of  $[\text{A}]_0$ . Figure 1.5 shows such a graph for a process that follows a zero-order rate law, and the slope of the line is  $-k$ , which has the units of  $\mathbf{M} \text{ time}^{-1}$ .

As in the previous cases, we can determine the half-life of the reaction because after one half-life,  $[\text{A}] = [\text{A}]_0/2$ . Therefore,

$$\frac{[\text{A}]_0}{2} = [\text{A}]_0 - kt_{1/2} \quad (1.34)$$

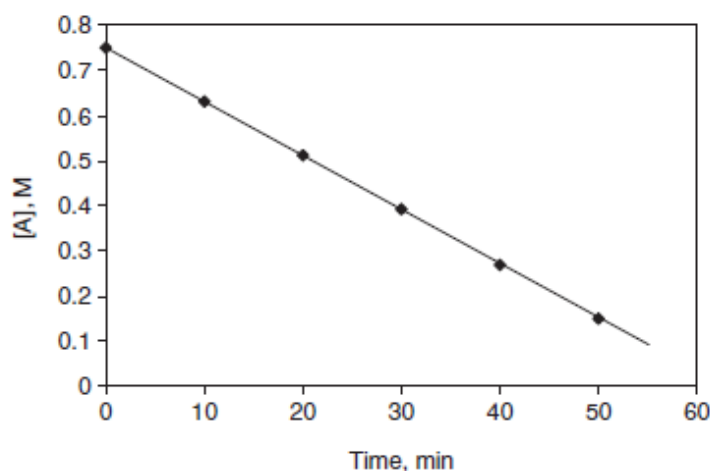


FIGURE 1.5 A zero-order rate plot for a reaction where  $[A]_o = 0.75 \text{ M}$  and  $k = 0.012 \text{ mol/l}$ .

so that

$$t_{1/2} = \frac{[A]_o}{2k} \quad (1.35)$$

In this case, we see that the half-life is directly proportional to  $[A]_o$ , the initial concentration of A.

#### 1.2.4 Nth-Order Reaction

If a reaction takes place for which only one reactant is involved, a general rate law can be written as

$$-\frac{d[A]}{dt} = k[A]^n \quad (1.36)$$

If the reaction is not first-order so that  $n$  is not equal to 1, integration of this equation gives

$$\frac{1}{[A]^{n-1}} - \frac{1}{[A]_o^{n-1}} = (n-1)kt \quad (1.37)$$

From this equation, it is easy to show that the half-life can be written as

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k[A]_o^{n-1}} \quad (1.38)$$

In this case,  $n$  may have either a fraction or integer value.

## PROBLEMS

1. For the reaction  $A \rightarrow \text{products}$ , the following data were obtained.

Time, hrs	[A], M	Time, hrs	[A], M
0	1.24	6	0.442
1	0.960	7	0.402
2	0.775	8	0.365
3	0.655	9	0.335
4	0.560	10	0.310
5	0.502		

- (a) Make appropriate plots or perform linear regression using these data to test them for fitting zero-, first-, and second-order rate laws. Test all three even if you happen to guess the correct rate law on the first trial. (b) Determine the rate constant for the reaction. (c) Using the rate law that you have determined, calculate the half-life for the reaction. (d) At what time will the concentration of A be 0.380?

2. For the reaction  $X \rightarrow Y$ , the following data were obtained.

Time, min	[X], M	Time, min	[X], M
0	0.500	60	0.240
10	0.443	70	0.212
20	0.395	80	0.190
30	0.348	90	0.171
40	0.310	100	0.164
50	0.274		

- (a) Make appropriate plots or perform linear regression using these data to determine the reaction order. (b) Determine the rate constant for the reaction. (c) Using the rate law you have determined, calculate

the half-life for the reaction. (d) Calculate how long it will take for the concentration of X to be 0.330 M.

- . If the half-life for the reaction



is the same when the initial concentration of  $\text{C}_2\text{H}_5\text{Cl}$  is 0.0050 M and 0.0078 M, what is the rate law for this reaction?