

Analysis of Kinetic Results

An important problem in chemical kinetics is to determine how rates depend on the concentrations of reacting substances. It is also important to know how rates are affected by the products of reaction or by added substances, which may be catalysts or inhibitors (Section 1.9). Another problem is to analyze the effect of temperature on reaction rates. The present chapter is concerned with these aspects of chemical kinetics.

As far as reactant concentrations are concerned, there are two main procedures: the differential method and the method of integration. In the *differential method*, rates are measured directly, by determining the slopes of concentration–time curves, and an analysis is made of the way in which the slope depends on the reactant concentration. The *method of integration* involves first making a tentative decision as to what the order of the reaction might be. The differential equation corresponding to that order is integrated, resulting in an expression for concentration as a function of time. A test is then made as to whether the experimental concentration–time results fit the integrated equation; if they do, the right order has been chosen and the rate constant can be obtained readily. If the results do not fit the equation, another order must be chosen. These two methods will now be considered in detail.

2.1 DIFFERENTIAL METHOD

In the differential method, which was first suggested in 1884 by van't Hoff,¹ the procedure is to determine rates by measuring the slopes of concentration–time curves (see Section 1.3). One does this at various concentrations c of a reactant, and if the reaction has an order n with respect to this particular reactant,

$$v = -\frac{dc}{dt} = kc^n$$

(2.1)

A double-logarithmic plot of $\ln v$ versus $\ln c$ gives a straight line of slope n ; the intercept when $\ln c = 0$ is then $\ln k$. If a straight-line plot is not obtained, the rate cannot be represented by Eq. (2.1); that is, the reaction does not have an order with respect to that particular reactant.

The procedure may be applied in two different ways. In one of them, shown schematically in Fig. 2.1a, runs are carried out at different initial concentrations, and initial rates are determined by measuring initial slopes. A double-logarithmic plot then gives the order of reaction (Fig. 2.1b). This procedure, dealing with initial rates, avoids possible complications due to interference by products. Because of this, Letort² referred to the order determined in this way as the *order with respect to concentration*, or the *true order*. The symbol n_c is used to denote this order.

The second procedure involves considering a single run and measuring slopes at various times, corresponding to a number of values of the reactant concentration. This method is illustrated schematically in Fig. 2.2a, and again the logarithms of the rates are plotted against the logarithms of the corresponding reactant concentrations (Fig. 2.2b). The slope is the order; since time is now varying, Letort referred to this order as the *order with respect to time* n_t .

Figure 2.3 shows schematic plots in which the two procedures have been combined. The points at the extremities of the n_t plots correspond to initial conditions and give rise to the n_c plot.

The two orders are not always the same for a given reaction. In the thermal decomposition of acetaldehyde, for example, as discussed further in Section 8.5.4, Letort found that the order with respect to concentration (the true order) is $3/2$, and that the order with respect to time is 2. The fact that the order with respect to time is greater than the order with respect to concentration means that as the reaction proceeds

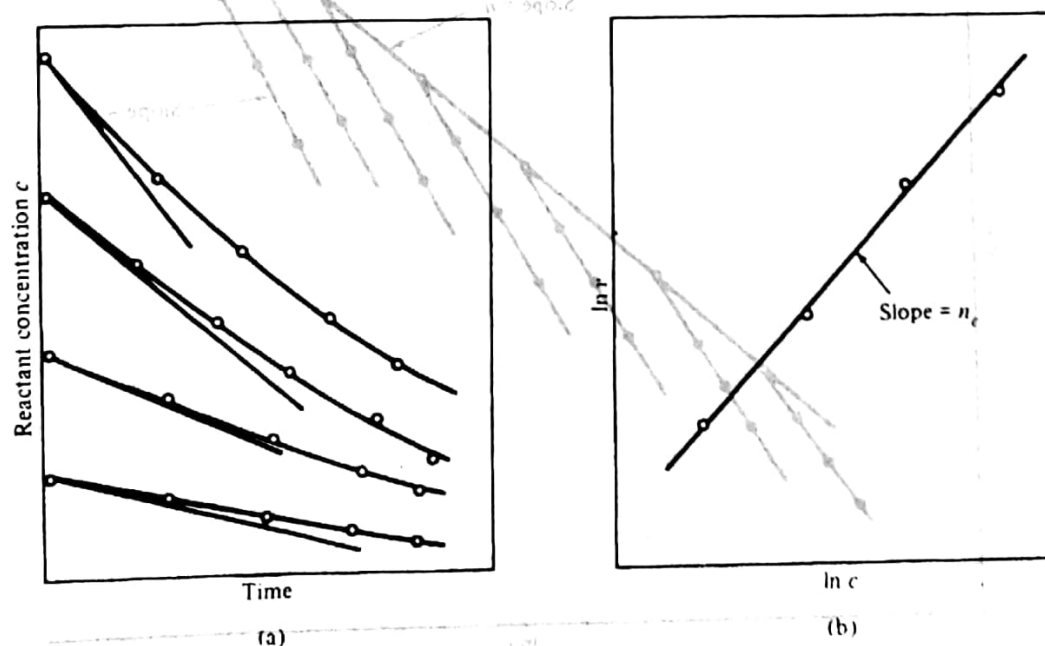


Figure 2.1 (a) Plot of reactant concentrations versus time for various initial concentrations. (b) A plot of $\ln v$ versus $\ln c$.

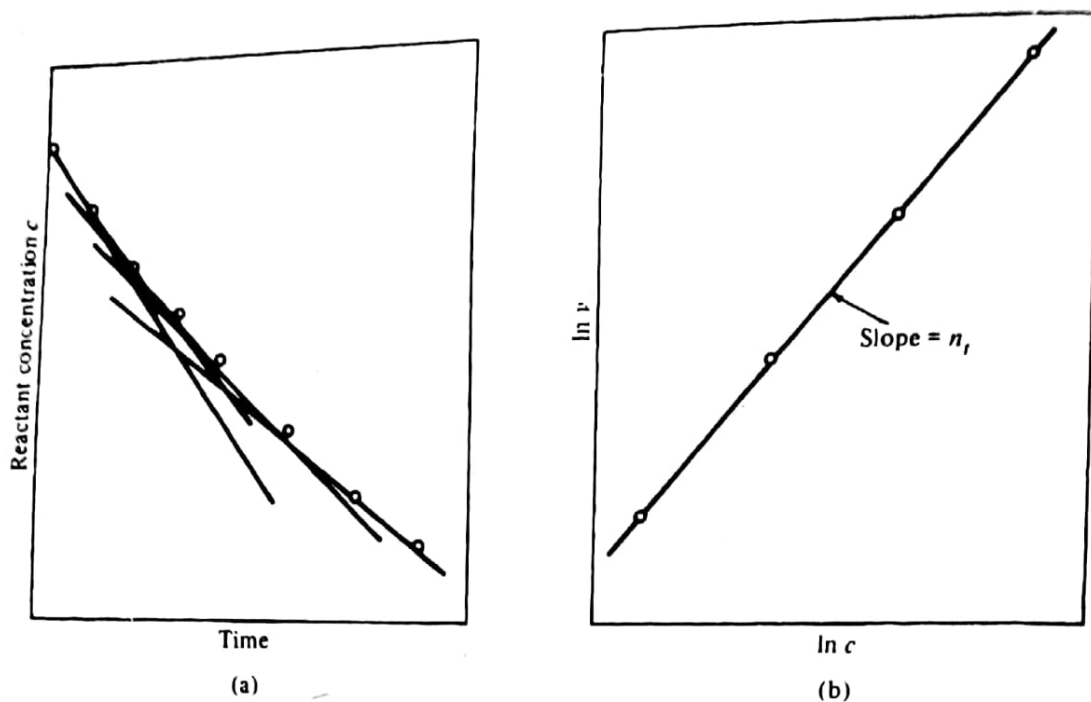


Figure 2.2 (a) A single concentration–time curve, with slopes measured at various reactant concentrations. (b) A plot of $\ln v$ versus $\ln c$.

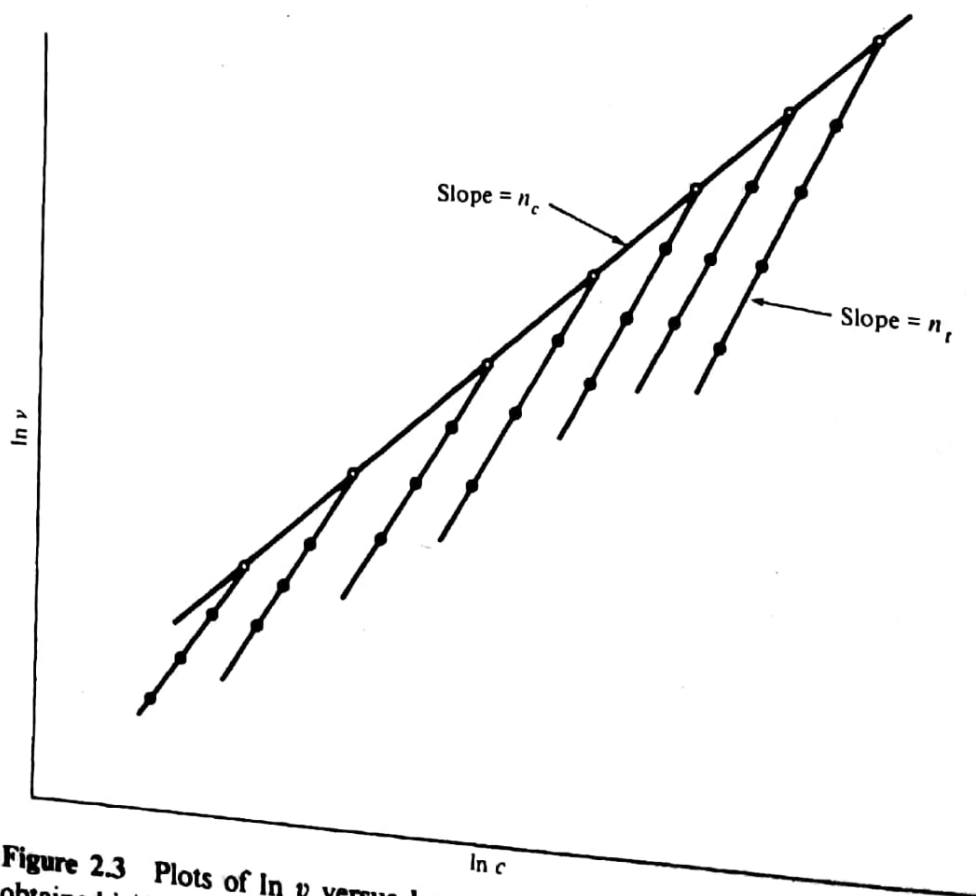


Figure 2.3 Plots of $\ln v$ versus $\ln c$. The closed circles correspond to rates obtained in individual runs; the open circles are the initial rates.

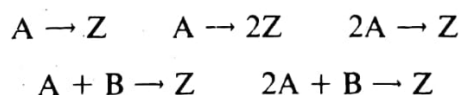
the rate falls off more rapidly than if the true order applied to the time course of the reaction. This abnormally large falling off can only mean that some substance produced in the reaction is acting as an inhibitor. Conversely, if n_t is less than n_c , the rate is falling off less rapidly with time than expected on the basis of the true order. Therefore, some activation by the products of reaction exists, and the reaction is said to be *autocatalytic*.

2.2 METHOD OF INTEGRATION

The method of integration was first used in 1850 by Wilhelmy and some 15 years later was extended by Harcourt and Esson. In this section we discuss only the principles of the method, as applied to a few systems. Table 2.1 gives solutions for some of the simpler cases; many more cases have been treated by Capellos and Bielski.³ Care must be taken with regard to the stoichiometry of the reaction and to the relationships between the different rate constants, as discussed in Section 1.7. The procedure adopted here, which is helpful in avoiding errors, is to focus attention on the consumption of a particular reactant, denoted as A.

2.2.1 First-Order Reactions

A reaction that is first-order with respect to a reactant A and is zero-order with respect to any other reactants may correspond to various stoichiometries, such as



A procedure that covers all these possibilities is as follows. Suppose that at the beginning of the reaction ($t = 0$), with no product present, the concentration of A is a_0 and that at time t the amount of A that has been consumed per unit volume is x ; the concentration of A is then $a_0 - x$, and the rate of consumption of A is $-d(a_0 - x)/dt = dx/dt$. Thus, we can write

$$\frac{dx}{dt} = k_A(a_0 - x) \quad (2.2)$$

where k_A is the first-order rate constant that relates to the consumption of A. This is converted into the rate constant k , which relates to rate of reaction, by use of the stoichiometric coefficients as discussed in Section 1.7. If there is a second reactant B, the rate constant k_B can be related in a similar way.

Separation of the variables x and t in Eq. (2.2) gives

$$\frac{dx}{a_0 - x} = k_A dt \quad (2.3)$$

and integration gives

$$-\ln(a_0 - x) = k_A t - I \quad (2.4)$$

where I is the constant of integration. This constant may be evaluated using the boundary condition that $x = 0$ when $t = 0$; hence,

$$-\ln a_0 = I \quad (2.5)$$

and insertion of this into Eq. (2.4) leads to

$$\ln \left(\frac{a_0}{a_0 - x} \right) = k_A t \quad (2.6)$$

This equation can also be written as

$$x = a_0(1 - e^{-k_A t}) \quad (2.7)$$

and as

$$a_0 - x = a_0 e^{-k_A t} \quad (2.8)$$

This last equation shows that the concentration of reactant, $a_0 - x$, decreases exponentially with time, from an initial value of a_0 to a final value of zero.

The first-order equations can be tested and the constant evaluated using a graphical procedure. It follows from Eq. (2.6) that a plot of $\ln [a_0/(a_0 - x)]$ versus t will give a straight line if the reaction is first order; this is shown schematically in Fig. 2.4a. The rate constant is the slope of this plot. We may also plot $\ln (a_0 - x)$ versus t , as shown in Fig. 2.4b.

2.2.2 Second-Order Reactions

There are two possibilities for second-order reactions: the rate may be proportional to the product of two equal concentrations or to the product of two different ones. The first must occur when a single reactant is involved, as in the process

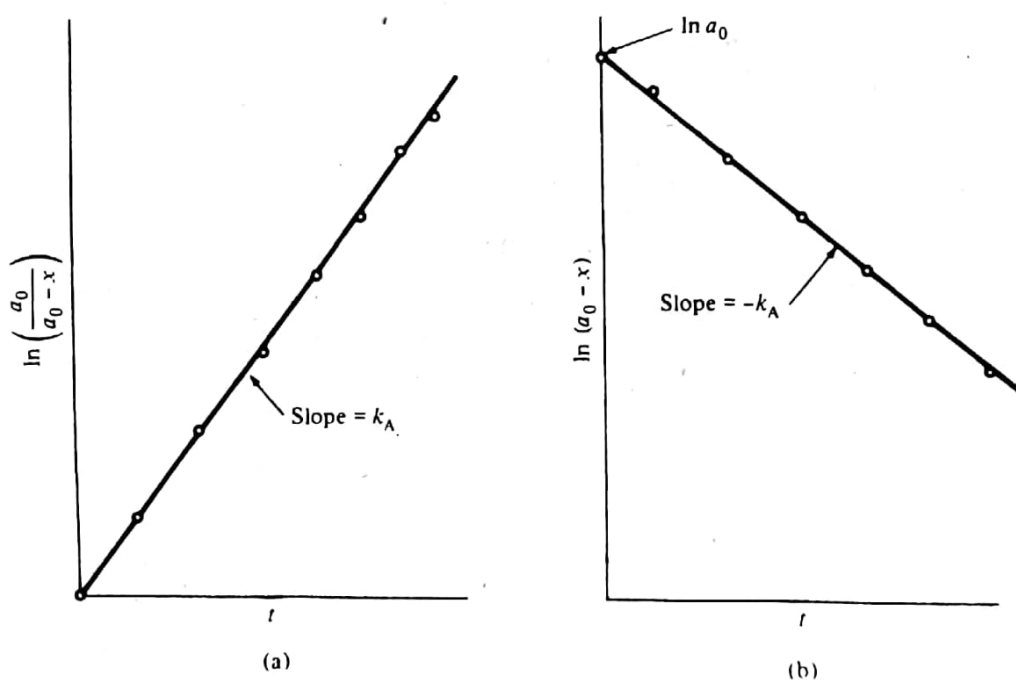
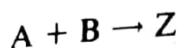


Figure 2.4 Method of integration and analysis of results for a first-order reaction: (a) plot of $\ln [a_0/(a_0 - x)]$ versus t and (b) plot of $\ln (a_0 - x)$ versus t .



It is also found in second-order reactions having the stoichiometry



if the initial concentrations of A and B are the same. §
In such situations the rate may be expressed as

$$\frac{dx}{dt} = k_A(a_0 - x)^2 \quad (2.9)$$

where x is the amount of A that has reacted in unit volume at time t , and a_0 is the initial concentration of A. Separation of the variables leads to

$$\frac{dx}{(a_0 - x)^2} = k_A dt \quad (2.10)$$

which integrates to

$$\frac{1}{a_0 - x} = k_A t + I \quad (2.11)$$

where I is the constant of integration. The boundary condition is that $x = 0$ when $t = 0$; therefore,

$$I = \frac{1}{a_0} \quad (2.12)$$

Hence,

$$\frac{x}{a_0(a_0 - x)} = k_A t \quad (2.13)$$

The variation of x with t is no longer exponential.

Graphical methods can be employed to test this equation and to obtain the rate constant k_A . One procedure is to plot $x/a_0(a_0 - x)$ against t . If the equation is obeyed the points will lie on a straight line passing through the origin (see Fig. 2.5a), and the slope will be k_A . Alternatively, $x/(a_0 - x)$ may be plotted against t (Fig. 2.5b), in which case the slope is $a_0 k_A$.

If the rate is proportional to the product of the concentrations of two different reactants, and these concentrations are not initially the same, the integration proceeds differently. Suppose that the stoichiometry corresponds to $A + B \rightarrow Z$ and that the initial concentrations are a_0 and b_0 ; the rate after an amount x (per unit volume) of A has reacted is

$$\frac{dx}{dt} = k_A(a_0 - x)(b_0 - x) \quad (2.14)$$

§ The procedure must be modified for second-order reactions of different stoichiometries, for example, $A + 2B \rightarrow X$ for which Eq. (2.9) would become

$$\frac{dx}{dt} = k_A(a_0 - x)(a_0 - 2x)$$

See Table 2.1 for this and other cases.

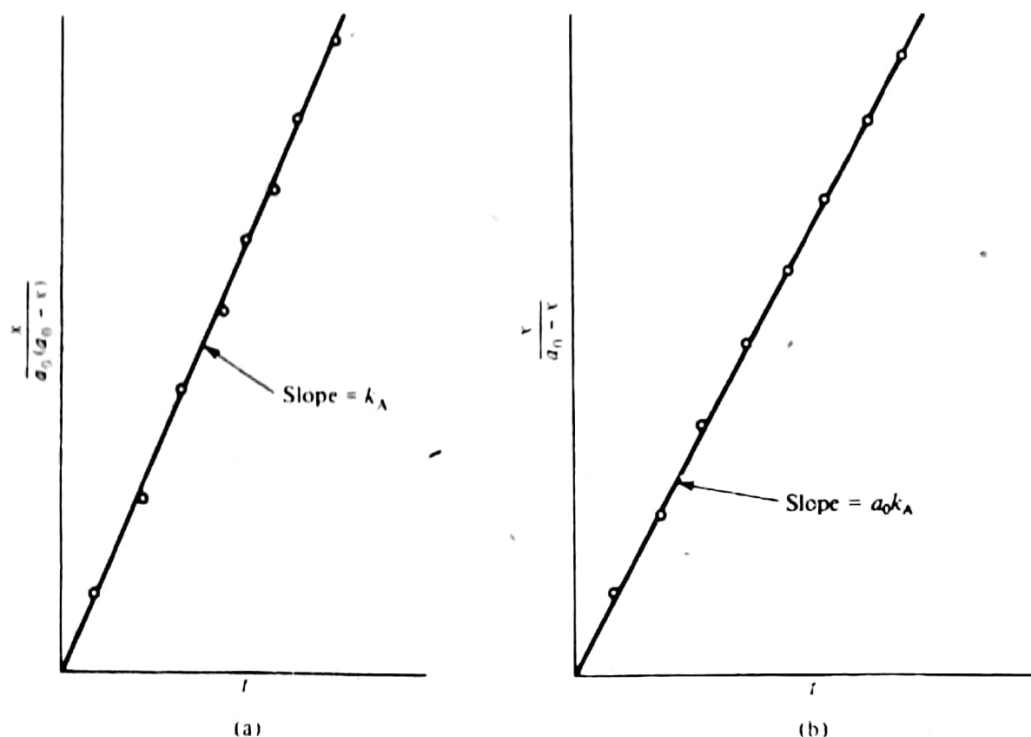


Figure 2.5 Method of integration and analysis of results for a second-order reaction involving a single reactant or two reactants of equal initial concentrations reacting according to the stoichiometry $A + B \rightarrow Z$: (a) plot of $x/a_0(a_0 - x)$ versus t and (b) plot of $x/(a_0 - x)$ versus t .

The result of the integration, with the boundary condition $t = 0$ at $x = 0$, is

$$\frac{1}{a_0 - b_0} \ln \left[\frac{b_0(a_0 - x)}{a_0(b_0 - x)} \right] = k_A t \quad (2.15)$$

This equation can be tested by plotting the left-hand side versus t ; if a straight line is obtained its slope is k_A .

2.2.3 Reactions of the n th Order

Suppose that a reaction is of the n th order and involves a single reactant of concentration a_0 , or reactants of equal concentrations and with stoichiometry $A + B + \dots \rightarrow Z$. If the concentration of A remaining after time t is $a_0 - x$, the rate of consumption of A is

$$v_A \equiv \frac{dx}{dt} = k_A(a_0 - x)^n \quad (2.16)$$

This must be integrated subject to the boundary condition that $x = 0$ when $t = 0$. If n is other than unity, the solution is

$$k_A = \frac{1}{t(n-1)} \left[\frac{1}{(a_0 - x)^{n-1}} - \frac{1}{a_0^{n-1}} \right] \quad (2.17)$$

If n is unity the solution is given by Eq. (2.6).

2.3 ISOLATION METHOD

It was first pointed out by Esson⁴ that if all the reactants except one are present in excess, the apparent order will be the order with respect to the one "isolated" reactant since the concentrations of those in excess will not change very much during the course of the reaction. This method was generalized by Ostwald⁵ as follows. If a reaction is of the α th order with respect to A, of the β th order with respect to B, and of the γ th order with respect to C, and if B and C are in excess of A, the apparent order, determined by any of the methods described above, will correspond to α . The orders β and γ can be determined in a similar way. The method should always be employed in conjunction with other methods of determining the order, since in many cases it does not yield reliable results. Thus, if the reaction under investigation is composite, involving a number of stages, its mechanism may be influenced by the concentration changes, so that different mechanisms may be occurring under the different conditions of isolation.

2.4 HALF-LIFE

For a given reaction the *half-life* $t_{1/2}$ of a particular reactant is defined as the time required for its concentration to reach a value that is half-way between its initial and final values. The value of the half-life is always inversely proportional to the rate constant and in general depends on reactant concentrations. For a first-order reaction the rate equation is Eq. (2.6), and the half-life is obtained by putting x equal to $a_0/2$:

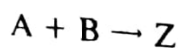
$$\ln \left(\frac{a_0}{a_0 - a_0/2} \right) = k_A t_{1/2} \quad (2.18)$$

and therefore

$$t_{1/2} = \frac{\ln 2}{k_A} \quad (2.19)$$

The half-life is independent of the initial concentration. Since there is only one reactant, the half-life of that reactant may be called the half-life of the *reaction*.

For a second-order reaction involving a single reactant, or two reactants of equal initial concentrations and reacting according to the stoichiometry



the rate equation is Eq. (2.13). Setting $x = a_0/2$ leads to

$$t_{1/2} = \frac{1}{a_0 k_A} \quad (2.20)$$

The half-life is now inversely proportional to the reactant concentration, a fact that may be understood as follows. Suppose that in one reaction system the reactant concentration is 10 times that in another. Ten times as much of it will be consumed when the half-life is reached, but the reaction is proceeding $10^2 = 100$ times as fast; it therefore takes $1/10$ of the time.

So far, the emphasis has been on the half-life of a *reactant*. Sometimes it is legitimate to speak of the half-life of a *reaction*, but care must be taken. No difficulties arise if there is a single reacting substance: the half-life of that substance can be called the half-life of the reaction. The same is true if the stoichiometry is of the type $A + B + \dots \rightarrow \text{products}$ and the initial reactant concentrations are all the same.

If the stoichiometry is of the type $A + B + \dots \rightarrow \text{products}$ but the initial concentrations are different, the half-lives are different for the different reactants, and one should not speak of the half-life of the reaction. In this case, if one of the reactants has more than twice the concentration of another, half of it still will not have been consumed after infinite time.

Other stoichiometries lead to further complications. For example, a reaction may be of stoichiometry $A + 2B \rightarrow Z$ but be first order in both A and B. The rate equations are included in Table 2.1, and if the reactants are present in their stoichiometric ratios (i.e., if $b_0 = 2a_0$), the equations reduce to

$$\begin{aligned} \frac{dx}{dt} &= k_A(a_0 - x)(2a_0 - 2x) \\ &= 2k_A(a_0 - x)^2 = k_B(a_0 - x)^2 \end{aligned} \quad (2.21)$$

Thus, the half-life of A is given by

$$t_{1/2,A} = \frac{1}{k_B a_0} = \frac{1}{k_A b_0} \quad (2.22)$$

and this is also the half-life of B. Note that this half-life is inversely proportional to the reactant concentrations.

This argument can be generalized to show that the concept of the half-life of a reaction is legitimate provided that the reactants are in their stoichiometric ratios. The above example, however, shows that care must be taken in relating the half-life to the

TABLE 2.2 EXPRESSIONS FOR REACTION HALF-LIVES

Order	Half-life $t_{1/2}$	Order	Half-life $t_{1/2}$
Single reacting substance A		Reactants in their stoichiometric ratios; $A + \dots \rightarrow Z$	
0	$\frac{a_0}{2k_A}$	0	$\frac{a_0}{2k_A}$
1	$\frac{\ln 2}{k_A}$	1 ($v_A = k_A[A]$)	$\frac{\ln 2}{k_A}$
2	$\frac{1}{k_A a_0}$	2 ($v_A = k_A[A][B]$)	$\frac{1}{k_B a_0} = \frac{1}{k_A b_0}$
3	$\frac{3}{2k_A a_0^2}$	3 ($v_A = k_A[A][B][C]$)	$\frac{3}{2k_A b_0 c_0}$
n	$\frac{2^{n-1} - 1}{k_A(n-1)a_0^{n-1}}$		

concentrations and rate constants. If the reactants are not in their stoichiometric ratio the concept of half-life of the reaction has no meaning; again, the reactant half-lives depend on the concentrations of all reactants. Some expressions for reaction half-lives are given in Table 2.2.

Since the half-lives of first-order reactions are independent of concentration, they may be quoted in place of rate constants. This is often done, for example, with radioactive decay. When the rate constant is used for a radionuclide, it is known as the *decay constant*. Unlike the rate constants for chemical processes, such decay constants are independent of temperature.

Even for reactions of different orders, half-lives provide a convenient way of making an approximate comparison of rates. For example, if two reactions are of different orders, their rate constants have different units, and it is not immediately obvious which reaction will have the higher rate under the experimental conditions. However, if the half-lives are given at the appropriate reactant concentrations, the rates can be compared.