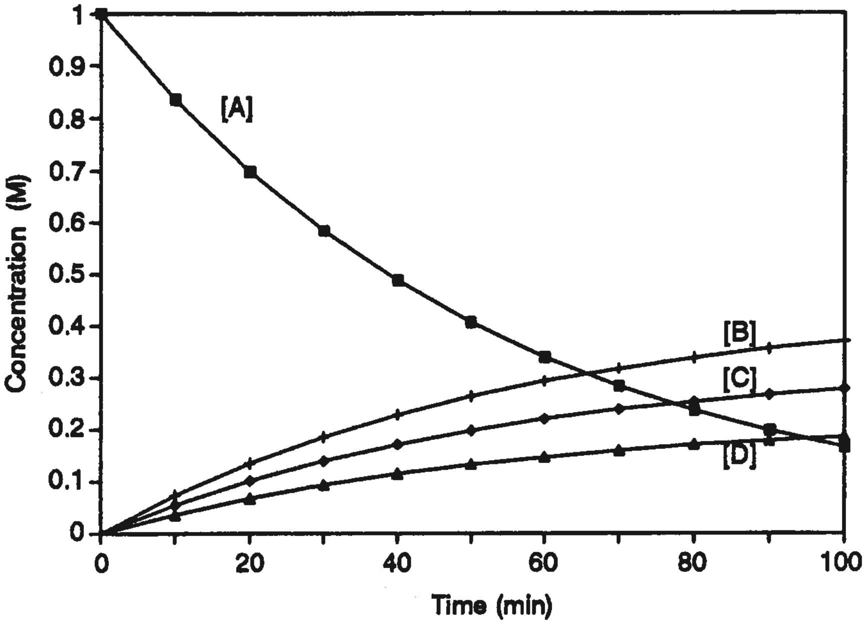


Figure 2.2 Concentration of reactant and products for parallel first-order reactions.

2.4 SERIES FIRST-ORDER REACTIONS

It is by no means uncommon for a chemical reaction to take place in steps.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{2.51}$$

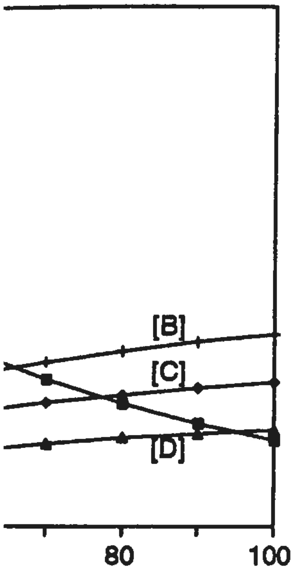
In this case, B is known as an *intermediate* because it is not the final product. A similar situation is very common in nuclear chemistry where a nuclide decays to a daughter, which is also radioactive and undergoes decay. For simplicity, only the case of first-order reactions will be treated here.

The rate of disappearance of A can be written as

$$-\frac{d[A]}{dt} = k_1[A] \tag{2.52}$$

The change in concentration of B with time is

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \tag{2.53}$$



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where the term $k_1[\mathrm{A}]$ represents the formation of B from A, and the term $-k_2[\mathrm{B}]$ represents the reaction of B to form C. The rate of formation of C can be expressed as

$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{B}] \tag{2.54}$$

If the stoichiometry as shown in Eq. (2.51) is followed, it is obvious that

$$[\mathrm{A}] + [\mathrm{B}] + [\mathrm{C}] = [\mathrm{A}]_o \tag{2.55}$$

Eq. (2.52) can be integrated immediately to give

$$[\mathrm{A}] = [\mathrm{A}]_o \exp(-k_1 t) \tag{2.56}$$

Substituting for [A] in Eq. (2.53) gives

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}]_o \exp(-k_1 t) - k_2[\mathrm{B}] \tag{2.57}$$

which can be written as

$$\frac{d[\mathrm{B}]}{dt} + k_2[\mathrm{B}] - k_1[\mathrm{A}]_o \exp(-k_1 t) = 0 \tag{2.58}$$

This is a linear differential equation with constant coefficients. If we assume a solution of the form

$$[\mathrm{B}] = u \exp(-k_2 t)$$

then

$$\frac{d[\mathrm{B}]}{dt} = -uk_2 \exp(-k_2 t) + \exp(-k_2 t)\frac{du}{dt}$$

Substituting the right-hand side of this equation for d[B]/dt in Eq. (2.58), we obtain

$$-uk_2 \exp(-k_2 t) + \exp(-k_2 t)\frac{du}{dt} = k_1[\mathrm{A}]_o \exp(-k_1 t) - uk_2 \exp(-k_2 t)$$

which simplifies to

$$\exp(-k_2 t)\frac{du}{dt} = k_1[\mathrm{A}]_o \exp(-k_1 t)$$

Dividing both sides of this equation by $\exp(-k_2 t)$ gives

$$\frac{du}{dt} = k_1[\mathrm{A}]_o \exp(-(k_1 - k_2)t) \tag{2.59}$$

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Integration of this equation yields

$$u = \frac{k_1}{k_2 - k_1}[\mathrm{A}]_o \exp(-(k_1 - k_2)\mathrm{t}) + \mathrm{C} \qquad \textbf{(2.60)}$$

where C is a constant. Having assumed a solution of the form

$$[\mathrm{B}] = u \exp\left(-k_2\mathrm{t}\right)$$

we obtain

$$[\mathrm{B}] = u \exp(-k_2\mathrm{t}) = \frac{k_1[\mathrm{A}]_o}{k_2 - k_1}\exp(-k_1\mathrm{t}) + \mathrm{C}\cdot\exp(-k_2\mathrm{t}) \qquad \textbf{(2.61)}$$

If we let $[\mathrm{B}]_o$ be the concentration of B present at $\mathrm{t} = 0$, Eq. (2.61) reduces to

$$[\mathrm{B}]_o = \frac{k_1[\mathrm{A}]_o}{k_2 - k_1} + \mathrm{C}$$

so that the final equation for the concentration of B is

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]_o}{k_2 - k_1}(\exp(-k_1\mathrm{t}) - \exp(-k_2\mathrm{t})) + [\mathrm{B}]_o \exp(-k_2\mathrm{t}) \qquad \textbf{(2.62)}$$

The first term on the right-hand side of Eq. (2.62) gives the reaction of B produced by disappearance of A, while the second term gives the reaction of any B initially present. If, as is usual, $[\mathrm{B}]_o = 0$, Eq. (2.62) reduces to

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]_o}{k_2 - k_1}(\exp(-k_1\mathrm{t}) - \exp(-k_2\mathrm{t})) \qquad \textbf{(2.63)}$$

If this result and that shown for [A] in Eq. (2.56) are substituted into Eq. (2.55), we obtain

$$[\mathrm{C}] = [\mathrm{A}]_o\left[1 - \frac{1}{k_2 - k_1}(k_2 \exp(-k_1\mathrm{t}) - k_1 \exp(-k_2\mathrm{t}))\right] \qquad \textbf{(2.64)}$$

A number of interesting cases can arise depending on the relative magnitudes of k_1 and k_2. Figure 2.3 shows the unlikely case where $k_1 = 2k_2$. This case is unlikely because the intermediate, B, is usually more reactive than A, as shown in Figure 2.4 where $k_2 = 2k_1$. In this case, it is apparent that there is a less rapid decrease in [A] and a slower buildup of B in the system. Because of the particular relationship chosen for the rate constants ($k_1 = 2k_2$ and $k_2 = 2k_1$), production of C is unchanged in the two cases. Figure 2.5 shows the case where $k_2 = 10k_1$ as

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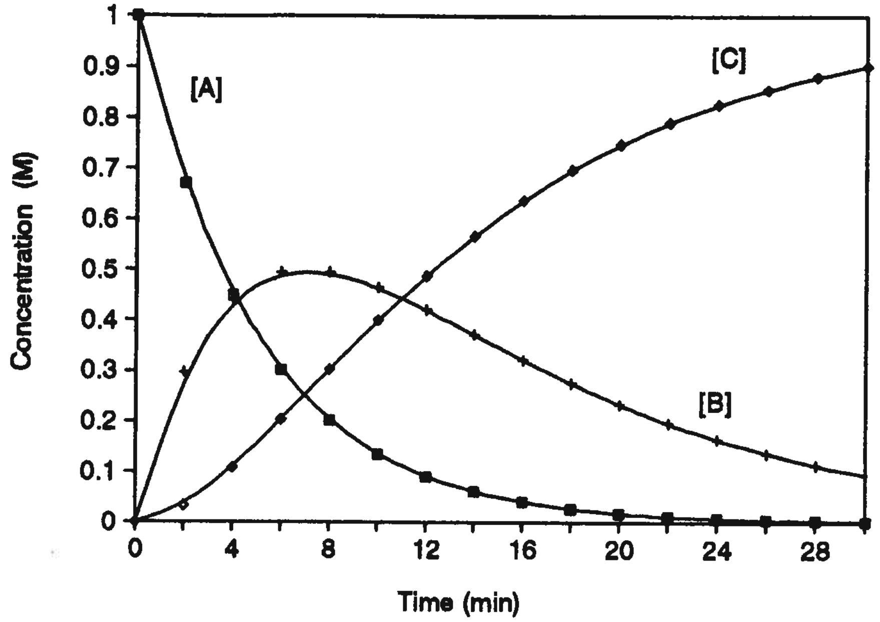

Figure 2.3 Series first-order reactions where $[A]_o = 1.00$ M, $k_1 = 0.200$ and $k_2 = 0.100$ min^{-1}.

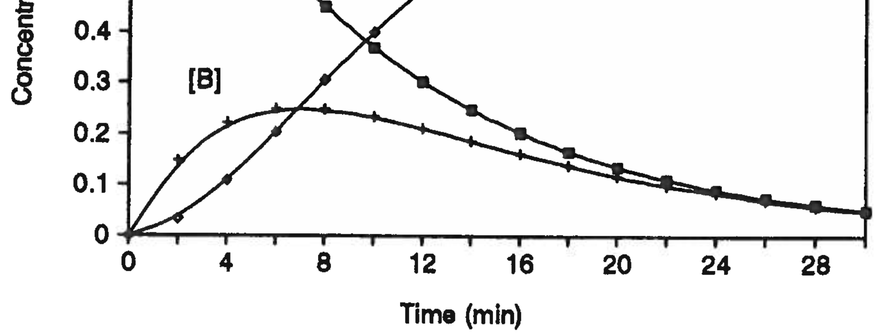

Figure 2.4 Series first-order reactions where $[A]_o = 1.00$ M, $k_1 = 0.100$ and $k_2 = 0.200$ min^{-1}.

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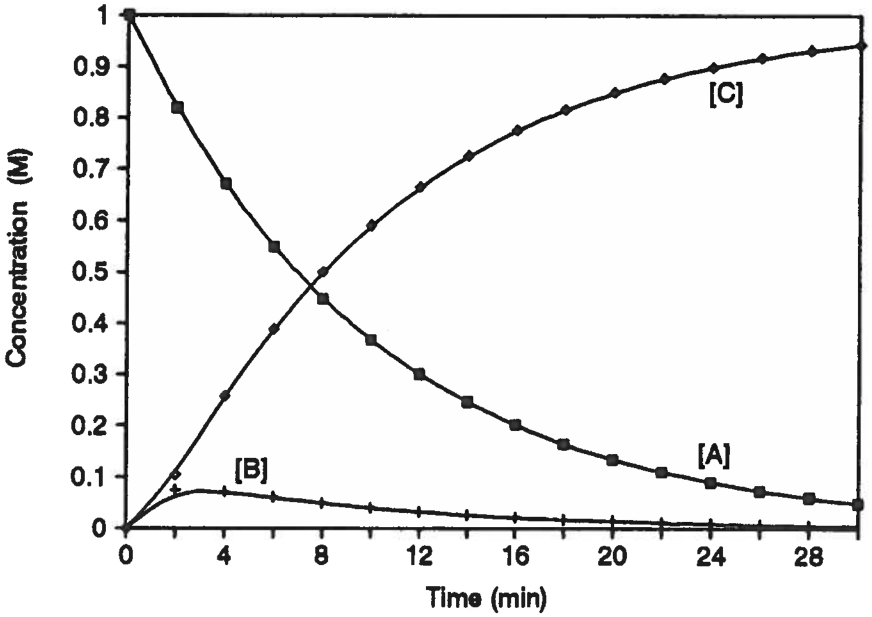


Figure 2.5 Series first-order reactions where $[A]_o = 1.00$ M, $k_1 = 0.100$ and $k_2 = 1.00$ min^{-1}.

a realistic example of a system with a reactive intermediate. In this case, the concentration of B is always low, which is more likely for an intermediate. Further, over a large extent of reaction, [B] is essentially a constant. When $k_2 > k_1$, there is a low and essentially constant concentration of intermediate, B. Therefore, d[B]/dt is essentially 0, which can be shown as follows. For this system of first-order reactions,

$$[A] + [B] + [C] = [A]_o$$

which, because [B] is nearly 0, is approximated by

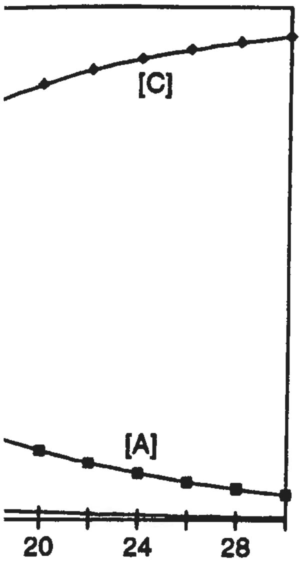
$$[A] + [C] = [A]_o$$

Taking the derivatives with respect to time,

$$\frac{d[A]}{dt} + \frac{d[B]}{dt} + \frac{d[C]}{dt} = 0$$

and

$$\frac{d[A]}{dt} + \frac{d[C]}{dt} = 0$$



M, $k_1 = 0.100$ and $k_2 = 1.00$ min^{-1}.

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Therefore d[B]/dt = 0, and [B] remains constant throughout most of the reaction. For the case where $k_2 = 10k_1$ and $[A]_o = 1.00$ **M** (shown in Figure 2.5), [B] never goes above 0.076 **M** and it varies only from 0.076 to 0.033 **M** from t = 2 min to t = 12 min where [A] varies from 0.819 to 0.301 **M** and [C] varies from 0.105 **M** to 0.666 **M**. The approximation of considering the concentration of the intermediate to be essentially constant is called the *steady-state approximation*.

It is clear from Figures 2.3 through 2.5 that [B] goes through a maximum as expected. The time necessary to reach that maximum concentration of B, t_m, can easily be calculated. At that time, d[B]/dt = 0. If Eq. (2.63) is differentiated with respect to time,

$$\frac{d[B]}{dt} = \frac{-k_1k_1[A]_o}{k_2 - k_1}\exp(-k_1t) + \frac{k_1k_2[A]_o}{k_2 - k_1}\exp(-k_2t) = 0 \qquad \textbf{(2.65)}$$

Therefore,

$$\frac{k_1k_1[A]_o}{k_2 - k_1}\exp(-k_1t) = \frac{k_1k_2[A]_o}{k_2 - k_1}\exp(-k_2t)$$

Cancelling like terms from both sides of the equation gives

$$k_1\exp(-k_1t) = k_2\exp(-k_2t)$$

which can be written as

$$k_1/k_2 = \exp(-k_2t)/\exp(-k_1t) = \exp(-k_2t)(\exp(k_1t)) = \exp((k_1 - k_2)t)$$

Taking the logarithm of both sides of the equation gives

$$\ln(k_1/k_2) = (k_1 - k_2)t$$

which yields the time to reach the maximum in the [B] curve,

$$t_m = \frac{\ln(k_1/k_2)}{k_1 - k_2} \qquad \textbf{(2.66)}$$

Although several other cases of series of reactions have been described mathematically, we will leave these discussions to more advanced books. The basic principles have been adequately demonstrated here.

2.5 REVERSIBLE REACTIONS

Many reactions do not proceed to completion, and the extent of reversibility must be considered from the early stages. The first-order case is the simplest.

Principles of Chemical Kinetics

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