Measurement techniques

Chemical method = Follow the progress of reaction

Physical method = Follow the change of property of the system

35.4 Reaction Mechanism

Reaction mechanism=Collection of individual elementary steps for the overall reaction
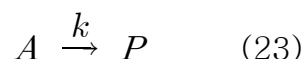
→Order of reaction

Mechanism is verified only by the rate equation determined by experiment.

35.5 Integrated Rate Law Expression

35.1.1 First-order Reaction

Consider the following reaction:

$$A \xrightarrow{k} P \qquad (23)$$

If the reaction is first order, rate law becomes:

$$R=k[A] \qquad (24)$$

Regardless of order of reaction, R can be written as:

$$R=-\frac{d[A]}{dt} \qquad (25)$$

Then

$$\frac{d[A]}{dt}=-k[A] \qquad (26)$$

Eq (26) is called differential rate eq.

Separation of variables and integration gives:

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \int_0^t -kdt$$

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

$$[A] = [A]_0 e^{-kt} \tag{27a}$$

►Exponential decay of reactant concentration w/ time.
Taking natural logarithm gives:

$$\ln[A] = \ln[A]_o - k\, t \tag{28}$$

►ln[A] vs t plot: A straight line of slope of -k and intercept $\ln[A]_o$. See Figure 4 for (27a) and (28). If the experimental data lie on the curve the reaction is said to follow the first order kinetics.
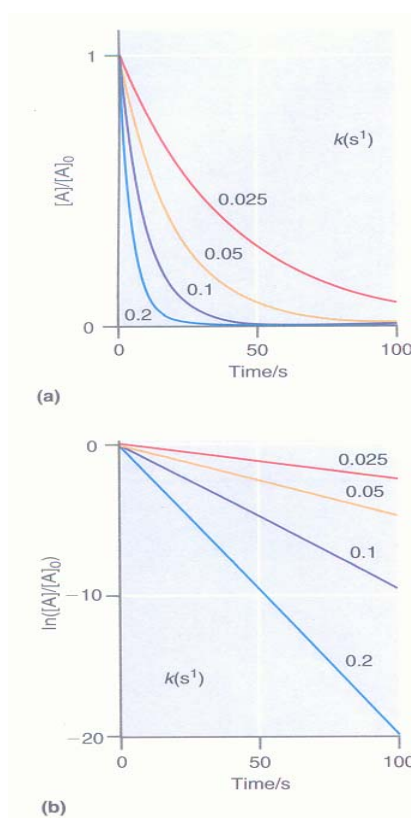

FIGURE 35.4

Reactant concentration as a function of time for a first-order chemical reaction as given by Equation (35.27). **(a)** Plots of [A] as a function of time for various rate constants k. The rate constant of a given curve is provided in the figure. **(b)** The natural log of reactant concentration as a function of time for a first-order chemical reaction as given by Equation (35.28).

The concentration of product $[P]$ can be given as:

$$[P] + [A] = [A]_0$$
$$[P] = [A]_0 - [A]$$
$$[P] = [A]_0(1 - e^{-kt}) \qquad (27b)$$

35.5.2 Half-life and First Order Reactions

Half-life$=t_{1/2}$ =time for $[M]_o \rightarrow [M]_o/2$

Plug $[A] = [A]_o/2$ in (28): $\qquad \ln[A] = \ln[A]_o - k\,t \quad (28)$

$$-kt_{1/2} = \ln\left(\frac{[A]_o/2}{[A]_o}\right) = -\ln 2$$
$$t_{1/2} = \frac{\ln 2}{k} \qquad (29)$$

This is one way to determine the rate constant k.

EXAMPLE PROBLEM 35.3

The decomposition of N_2O_5 is an important process in tropospheric chemistry. The half-life for the first-order decomposition of this compound is 2.05×10^4 s. How long will it take for a sample of N_2O_5 to decay to 60% of its initial value?

Solution

Using Equation (35.29), the rate constant for the decay reaction is determined using the half-life as follows:

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{2.05 \times 10^4 \text{ s}} = 3.38 \times 10^{-5} \text{ s}^{-1}$$

The time at which the sample has decayed to 60% of its initial value is then determined using Equation (35.27a):

$$[N_2O_5] = 0.6[N_2O_5]_0 = [N_2O_5]_0 e^{-(3.38 \times 10^{-5} \text{ s}^{-1})t}$$
$$0.6 = e^{-(3.38 \times 10^{-5} \text{ s}^{-1})t}$$
$$\frac{-\ln(0.6)}{3.38 \times 10^{-5} \text{ s}^{-1}} = t = 1.51 \times 10^4 \text{ s}$$

Scan EXAMPLE 35.3

EXAMPLE PROBLEM 35.4

Carbon-14 is a radioactive nucleus with a half-life of 5760 years. Living matter exchanges carbon with its surroundings (for example, through CO_2) so that a constant level of ^{14}C is maintained, corresponding to 15.3 decay events per minute. Once living matter has died, carbon contained in the matter is not exchanged with the surroundings, and the amount of ^{14}C that remains in the dead material decreases with time due to radioactive decay. Consider a piece of fossilized wood that demonstrates 2.4 ^{14}C decay events per minute. How old is the wood?

Solution

The ratio of decay events yields the amount of ^{14}C present currently versus the amount that was present when the tree died:

$$\frac{[^{14}C]}{[^{14}C]_0} = \frac{2.40 \text{ min}^{-1}}{15.3 \text{ min}^{-1}} = 0.157$$

The rate constant for isotope decay is related to the half-life as follows:

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{5760 \text{ years}} = \frac{\ln 2}{1.82 \times 10^{11} \text{ s}} = 3.81 \times 10^{-12} \text{ s}^{-1}$$

With the rate constant and ratio of isotope concentrations, the age of the fossilized wood is readily determined:
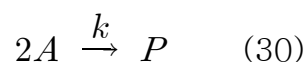
$$\frac{[^{14}C]}{[^{14}C]_0} = e^{-kt}$$

$$\ln\left(\frac{[^{14}C]}{[^{14}C]_0}\right) = -kt$$

$$-\frac{1}{k}\ln\left(\frac{[^{14}C]}{[^{14}C]_0}\right) = -\frac{1}{3.81 \times 10^{-12} \text{ s}}\ln(0.157) = t$$

$$4.86 \times 10^{11} \text{ s} = t$$

This time corresponds to an age of roughly 15,400 years.

Scan EXAMPLE 35.4

35.5.3 Second -order Reaction

Consider the following elementary second order reaction:

$$2A \xrightarrow{k} P \qquad (30)$$

All dimerization reactions in polymer : 2 Monomers → Dimer

Type I= Single reactant like (30)

Type II=Two reactants (A and B)

For type I,

$$R = k[A]^2 \qquad (31)$$

According to (8) $\qquad R = \dfrac{1}{\nu_i}\dfrac{dM_i}{dt} \qquad (8)$

$$R = -\frac{1}{2}\frac{d[A]}{dt} \qquad (32)$$

From {31) and (32)

$$-\frac{d[A]}{dt} = 2k[A]^2 \qquad (33)$$

Let 2k=k_{eff} (Effective rate constant). Separation of variables and integration (33) give:

$$-\int_{[A]_0}^{[A]}\frac{d[A]}{[A]^2} = \int_0^t k_{eff}dt$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k_{eff}t$$

$$\frac{1}{[A]} = \frac{1}{[A]_0} + k_{eff}t \qquad (34)$$

See Figure 5 for [A]/[A]$_o$ for various K_{eff} and for the plot of Eq (34).
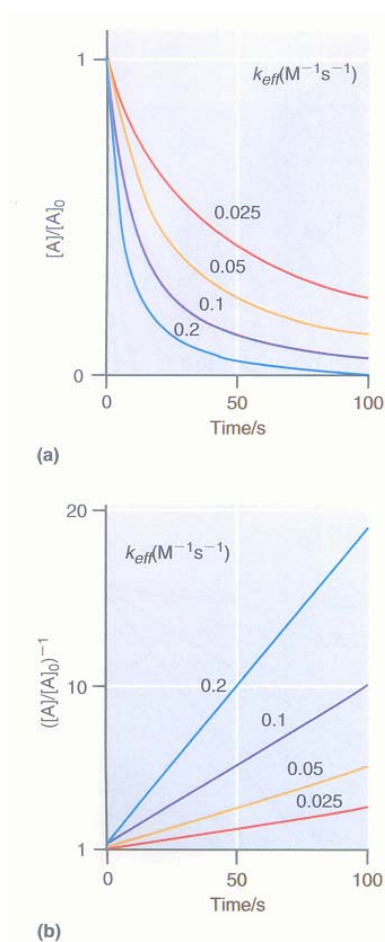
FIGURE 35.5

Reactant concentration as a function of time for a type I second-order chemical reaction. **(a)** Plots of [A] as a function of time for various rate constants. The rate constant of a given curve is provided in the figure. **(b)** The inverse of reactant concentration as a function of time as given by Equation (35.34).

Figure 5

35.5.4 Half-life and Reaction of Second Order (Type I)

Plug [A]=[A]$_0$/2 in (34):
$$\frac{1}{[A]}=\frac{1}{[A]_0}+k_{eff}t \qquad (34)$$

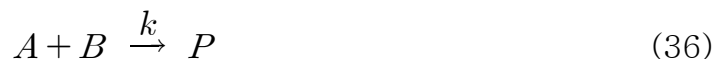$$t_{1/2} = \frac{1}{k_{eff}[A]_0} \qquad (35)$$

$$< Rf : For\ the\ first\ order\ reaction\ \ t_{1/2} = \frac{\ln 2}{k} \qquad (29) >$$

The half-life for the second order reaction is inversely proportional to the initial concentration.

35.5.5 Half-life and Reaction of Second Order (Type II)

Second-order reactions of type Ⅱ involve two different reactants, A and B, as follows:

$$A + B \xrightarrow{k} P \tag{36}$$

Assuming first order in both A and B, the reaction rate is

$$R = k[A][B] \tag{37}$$

In addition, the reaction rate wrt the reactant concentrations is

$$R = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} \tag{38}$$

Notice that the loss rate for the reactants is equal such that

$$[A]_0 - [A] = [B]_0 - [B]$$
$$[B]_0 - [A]_0 + [A] = [B]$$
$$\triangle + [A] = [B] \tag{39}$$

Equation (39) provides a definition for [B] in terms of [A] and the difference in initial concentration, $[B]_0 - [A]_0 \equiv \triangle$ (Constant). Then

$$\frac{d[A]}{dt} = -k[A][B] = -k[A](\triangle + [A])$$
$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A](\triangle + [A])} = -\int_0^t k\, dt \tag{40}$$

Next, solution to the integral involving [A] is given by a formula:

$$\int \frac{dx}{x(c+x)} = -\frac{1}{c}\ln\left(\frac{c+x}{x}\right)$$

Using this formula, the integrated rate law expression becomes

$$-\frac{1}{\triangle} \ln\left(\frac{\triangle + [A]}{[A]}\right) \Big|_{[A]_0}^{[A]} = -kt$$

$$\frac{1}{\triangle}\left[\ln\left(\frac{\triangle + [A]}{[A]}\right) - \ln\left(\frac{\triangle + [A]_0}{[A]_0}\right)\right] = kt$$

$$\frac{1}{\triangle}\left[\ln\left(\frac{[B]}{[A]}\right) - \ln\left(\frac{[B]_0}{[A]_0}\right)\right] = kt$$

$$\frac{1}{[B]_0 - [A]_0} \ln\left(\frac{[B]/[B]_0}{[A]/[A]_0}\right) = kt \qquad (41)$$

See this eq is not applicable for $[B]_0 = [A]_0$. This case reduces to the type I with $k_{eff}=k$.

35.6 Numerical Solution

When the integrated rate law can not be solved a numerical method is applied. Typical one is Euler's method for numerical integration.

$$A \xrightarrow{k} P \qquad (42)$$

$$\frac{d[A]}{dt} = -k[A] \qquad (43)$$

$$\frac{\triangle[A]}{\triangle t} = -k[A]$$

$$\triangle[A] = -\triangle t(k[A]) \qquad (44)$$

$$[A]_{t+\triangle t} = [A]_t + \triangle[A]$$
$$= [A]_t + \triangle t(-k[A]_t)$$
$$= [A]_t - k\triangle t[A]_t \qquad (45)$$

The process is continued until the entire concentration profile is obtained. (See Figure 7 for numerical approximation for the first order reaction)
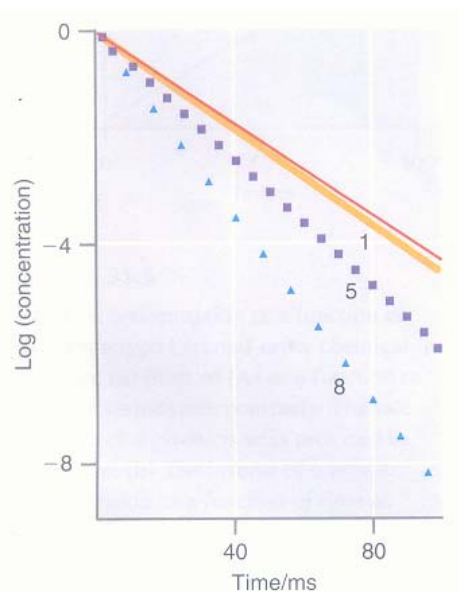
FIGURE 35.7

Comparison of the numerical approxima-
tion method to the integrated rate law ex-
pression for a first-order reaction. The rate
constant for the reaction is 0.1 M s^{-1}. The
time evolution in reactant concentration
determined by the integrated rate law ex-
pression of Equation (35.27) is shown as
the solid red line. Comparison to three nu-
merical approximations is given, and the
size of the time step (in ms) employed for
each approximation is indicated. Notice
the improvement in the numerical approx-
imation as the time step is decreased.

Figure 7

35.7 Sequential First-order Reaction

$$A \xrightarrow{k_A} I \xrightarrow{k_I} P \qquad (46)$$

$$\frac{d[A]}{dt} = -k_A[A] \qquad (47)$$

$$\frac{d[I]}{dt} = k_A[A] - k_I[I] \qquad (48)$$

$$\frac{d[P]}{dt} = k_I[I] \qquad (49)$$

$$[A]_0 \neq 0 \qquad [I]_0 = 0 \qquad [P]_0 = 0 \qquad (50)$$

$$[A] = [A]_0 e^{-k_A t} \tag{51}$$

$$\frac{d[I]}{dt} = k_A[A] - k_I[I]$$

$$\rightarrow \frac{d[I]}{dt} + k_I[I] = k_A[A]_0 e^{-k_A t} \tag{52}$$

Eq (52) is a first order linear differential eq. of the form:

$$\frac{dy}{dx} + P(x)y = Q(x)$$

General solution take the form :

$$y = e^{-\int P(x)dx}[\int Qe^{\int P(x)dx}dx + C]$$

$P = k_I$

$Q = k_A[A]_0 e^{-k_A t}$

Then

$$[I] = \frac{k_A}{k_I - k_A}(e^{-k_A t} - e^{-k_I t})[A]_0 \tag{53}$$

The [P] is readily determined using the initial conditions, $[A]_0$.

$$[A]_0 = [A] + [I] + [P]$$
$$[P] = [A]_0 - [A] - [I] \tag{54}$$

Then

$$[P] = (\frac{k_A e^{-k_I t} - k_I e^{-k_A t}}{k_I - k_A} + 1)[A]_0 \tag{55}$$

See Figure 8 for the concentration profiles with different k.

FIGURE 35.8

Concentration profiles for a sequential reaction in which the reactant (A, blue line) forms an intermediate (I, orange line) that undergoes subsequent decay to form the product (P, red line) where (a) $k_A = 2k_I = 0.1\ s^{-1}$ and (b) $k_A = 8k_I = 0.4\ s^{-1}$. Notice that both the maximal amount of I in addition to the time for the maximum is changed relative to the first panel. (c) $k_A = 0.025k_I = 0.0125\ s^{-1}$. In this case, very little intermediate is formed, and the maximum in [I] is delayed relative to the first two examples.
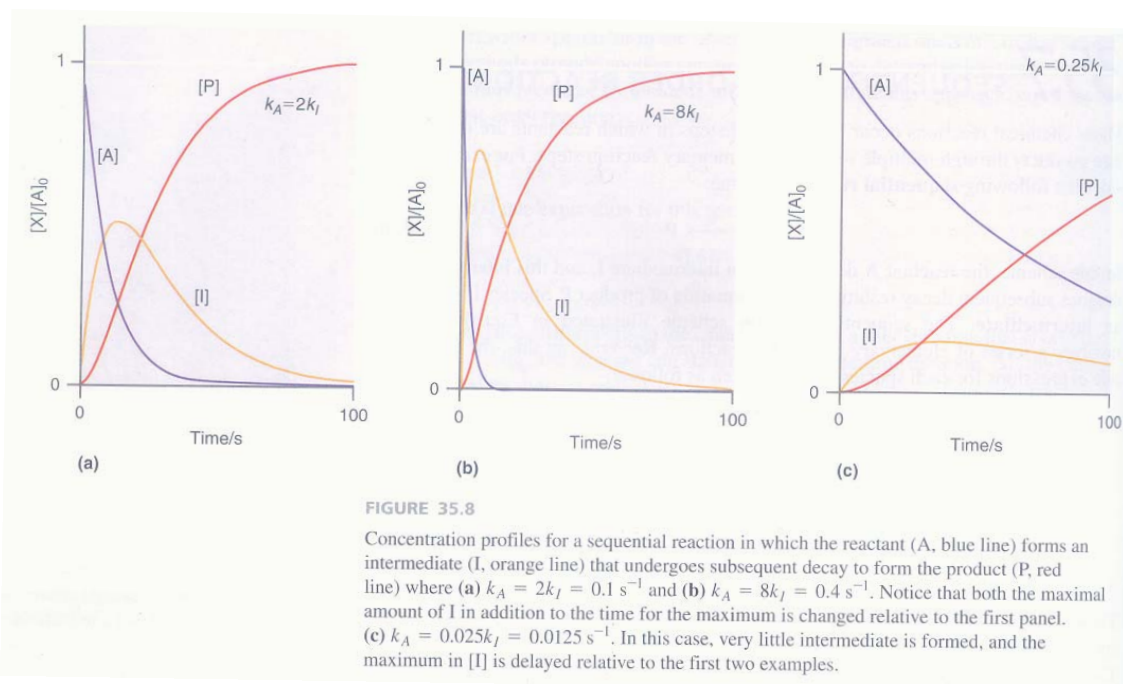
Figure 8

35.7.1 Maximum Intermediate Concentration

Letting

$$\left(\frac{d[I]}{dt}\right)_{t=t_{\max}} = 0 \qquad (56)$$

where

$$[I] = \frac{k_A}{k_I - k_A}(e^{-k_A t} - e^{-k_I t})[A]_0 \qquad (53)$$

Then the time at which [I] is maximum is obtained as:

$$t_{\max} = \frac{1}{k_A - k_I}\ln\left(\frac{k_A}{k_I}\right) \qquad (57)$$

The $t_{\max}$ depends only on the rate constants.

EXAMPLE 35.5

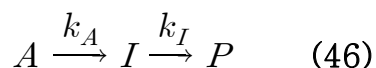Determine the time at which [I] is at a maximum for $k_A = 2k_I = 0.1\ s^{-1}$.

<u>Solution</u>

This is the first example illustrated in Figure 35.8 where $k_A = 0.1\,s^{-1}$ and $k_I = 0.05\,s^{-1}$. Using these rate constants and Equation (35.57), $t_{\max}$ is determined as follows:

$$t_{\max} = \frac{1}{k_A - k_I}\ln\left(\frac{k_A}{k_I}\right) = \frac{1}{0.1\,s^{-1} - 0.05\,s^{-1}}\ln\left(\frac{0.1\,s^{-1}}{0.05\,s^{-1}}\right) = 13.9\,s$$

35.7.2 Rate Determining Step

Consider

$$A \xrightarrow{k_A} I \xrightarrow{k_I} P \qquad (46)$$

Two limiting situations can occur: $k_A \gg k_I$ and $k_A \ll k_I$.

When $k_A \gg k_I$, then Eq 55 becomes

$$\lim_{k_A \to \infty}[P] = \lim_{k_A \to \infty}\left(\left(\frac{k_A e^{-k_I t} - k_I e^{-k_A t}}{k_I - k_A}+1\right)[A]_0\right) = (1 - e^{-k_I t})[A]_0 \quad (58)$$

When $k_A \ll k_I$, then Eq 55 becomes

$$\lim_{k_I \to \infty}[P] = \lim_{k_I \to \infty}\left(\left(\frac{k_A e^{-k_I t} - k_I e^{-k_A t}}{k_I - k_A}+1\right)[A]_0\right) = (1 - e^{-k_A t})[A]_0 \quad (59)$$

The time dependence of [P] is identical to the first order decay. See Figure 9 for the two limiting cases.
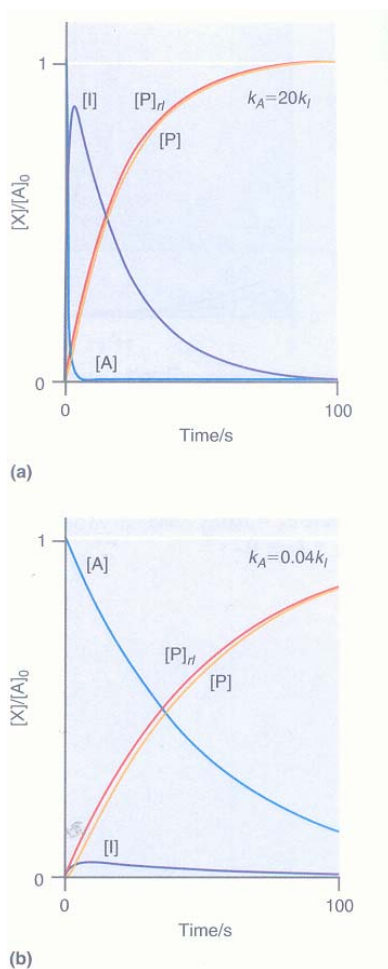
FIGURE 35.9

Rate-limiting step behavior in sequential reactions. (a) $k_A = 20k_I = 1 \text{ s}^{-1}$ such that the rate-limiting step is the decay of intermediate I. In this case, the reduction in [I] is reflected by the appearance of [P]. The time evolution of [P] predicted by the sequential mechanism is given by the orange line, and the corresponding evolution assuming rate-limiting step behavior, $[P]_{rl}$, is given by the red curve. (b) The opposite case from part (a) in which $k_A = 0.04k_I = 0.02 \text{ s}^{-1}$ such that the rate-limiting step is the decay of reactant A.

Figure 9

35.7.3 The Steady State Approximation

SS assumption in radical polymerization

$\text{Decomposition}: I \rightarrow 2R \quad R_d = \dfrac{d[R]}{dt} = -2\dfrac{d[I]}{dt} = 2fk_d[I]$

$\text{Initiation}: \; R + M \rightarrow M_1 \bullet \;\; \text{At SS for } R, \; \dfrac{d[R]}{dt} = 0, \, viz. \, R_i = k_i[R][M] = R_d$

$\text{Propagation}: M_n \bullet + M \rightarrow M_{n+1} \bullet \quad R_p = k_p[M_n \bullet][M]$

$\text{Termination by coupling}: M_n \bullet + M_m \bullet \rightarrow M_{m+n} \quad R_t = k_t[M \bullet]^2$

$\text{At steady state,} \; \dfrac{d[M \bullet]}{dt} = 0$
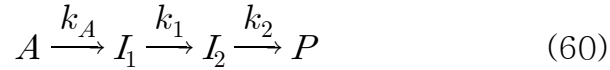
$R_i = R_t, \; i.e., 2fk_d[I] = k_t[M \bullet]^2$

$\therefore \; [M \bullet] = \left(\dfrac{2fk_d[I]}{k_t}\right)^{\frac{1}{2}}$

$R_p = -\dfrac{d[M]}{dt} = k_p[M \bullet][M] = k_p\left(\dfrac{2fk_d[I]}{k_t}\right)^{\frac{1}{2}}[M]$

Rate of propagation is the rate of polymerization since most monomers are consommed in this step.

Consider the following sequential reactions:

$$A \xrightarrow{k_A} I_1 \xrightarrow{k_1} I_2 \xrightarrow{k_2} P \qquad (60)$$

$$\dfrac{d[A]}{dt} = -k_A[A] \qquad (61)$$

$$\dfrac{d[I_1]}{dt} = k_A[A] - k_1[I_1] \qquad (62)$$

$$\dfrac{d[I_2]}{dt} = k_1[I_1] - k_2[I_2] \qquad (63)$$

$$\dfrac{d[P]}{dt} = k_2[I_2] \qquad (64)$$

See Figure 10 for numerical simulations.

The intermediate concentrations change very slowly so that

$$\dfrac{d[I]}{dt} = 0 \qquad \text{(SS)} \qquad (65)$$

$$\frac{d[I_1]_{ss}}{dt} = 0 = k_A[A] - k_1[I_1]_{ss}$$

$$[I_1]_{ss} = \frac{k_A}{k_1}[A] = \frac{k_A}{k_1}[A]_0 e^{-k_A t} \qquad (66)$$

$$\frac{d[I_2]_{ss}}{dt} = 0 = k_1[I_1]_{ss} - k_2[I_2]_{ss}$$

$$[I_2]_{ss} = \frac{k_1}{k_2}[I_1]_{ss} = \frac{k_A}{k_2}[A]_0 e^{-k_A t} \qquad (67)$$

$$\frac{d[P]_{ss}}{dt} = k_2[I_2] = k_A[A]_0 e^{-k_A t} \qquad (68)$$

Integration of this eq gives (Apply IC: @ t=0, [P]=0):

$$[P]_{ss} = [A]_0 (1 - e^{-k_A t}) \qquad (69)$$

Under SS, [P] follows first order kinetics (See (27b)).

Consider the variation of $[I_1]$(66) with time.

$$\frac{d[I_1]_{ss}}{dt} = \frac{d}{dt}\left(\frac{k_A}{k_1}[A]_0 e^{-k_A t}\right) = -\frac{k_A^2}{k_1}[A]_0 e^{-k_A t} \qquad (70)$$

Under SS (70)=0. That is, $k_1 >> k_A{}^2[A]_o,$ so that k_1 is sufficiently large such that [I] is small all the time. Same is true for $[I_2]$ where $k_2 >> k_A{}^2[A]_o$ (See 67).

See Figure 11 for the comparison of numerical solution and SS concentration profiles.
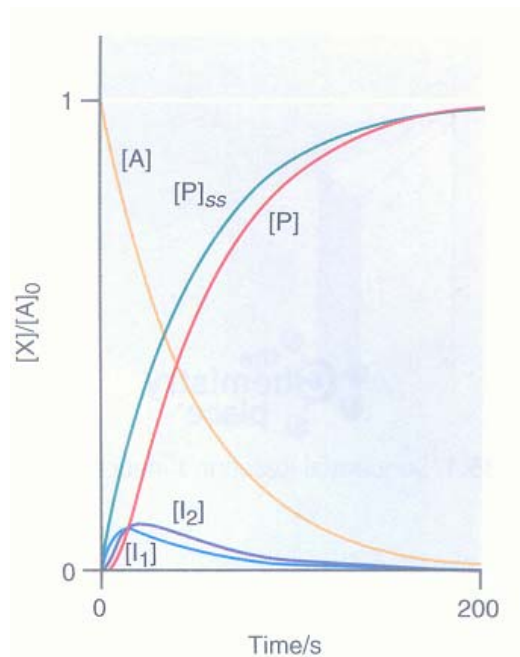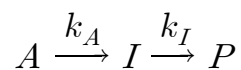
FIGURE 35.11

Comparison of the numerical and steady-state concentration profiles for the sequential reaction scheme presented in Equation (35.44) where $k_A = 0.02 \text{ s}^{-1}$ and $k_1 = k_2 = 0.2 \text{ s}^{-1}$. Curves corresponding to the steady-state approximation are indicated by the subscript ss.

Figure 11

EXAMPLE 35.6

Consider the following sequential reaction scheme:

$$A \xrightarrow{k_A} I \xrightarrow{k_I} P$$

Assuming that only reactant A is present at t=0, what is the expected time dependence of [P] using the steady-state approximation?

Solution

The differential rate expressions for this reaction were provided in

Eqs (47), (48), and (49):

$$\frac{d[A]}{dt} = -k_A[A] \qquad (47)$$

$$\frac{d[I]}{dt} = k_A[A] - k_I[I] \qquad (48)$$

$$\frac{d[P]}{dt} = k_I[I] \qquad (49)$$

Applying the steady-state approximation to the differential rate expression for I and substituting in the integrated expression for [A] of Equation (51) yield

$$\frac{d[I]}{dt} = 0 = k_A[A] - k_I[I]$$

$$[I] = \frac{k_A}{k_I}[A] = \frac{k_A}{k_I}[A]_0 e^{-k_A t}$$

Substituting the preceding expression for [I] (66 for [I]$_1$) into the differential rate expression for the product and integrating yield

$$\frac{d[P]}{dt} = k_I[I] = \frac{k_A}{k_I}(k_I[A]_0 e^{-k_A t}) \qquad [I_1]_{ss} = \frac{k_A}{k_1}[A] = \frac{k_A}{k_1}[A]_0 e^{-k_A t} \quad (66)$$

$$\int_0^{[P]} d[P] = k_A[A]_0 \int_0^t e^{-k_A t} dt$$

$$[P] = k_A[A]_0 [\frac{1}{k_A}(1 - e^{-k_A t})]$$

$$[P] = [A]_0(1 - e^{-k_A t})$$

This expression for [P] is identical to that derived in the limit that the decay of A is the rate-limiting step in the sequential reaction [Equation (59)].

35.8 Parallel Reactions

$$A \overset{k_B \nearrow B}{\underset{k_C \searrow C}{}} \tag{71}$$

$$\frac{d[A]}{dt} = -k_B[A] - k_C[A] = -(k_b + k_c)[A] \tag{72}$$

$$\frac{d[B]}{dt} = k_B[A] \tag{73}$$

$$\frac{d[C]}{dt} = k_c[A] \tag{74}$$

Integrating (72) yields (IC: at t=0, [A]=[A]ₒ)

$$[A] = [A]_0 e^{-(k_B + k_C)t} \tag{75}$$

(75)→(73) and (74) and integrate

$$[B] = \frac{k_B}{k_B + k_C}[A]_0(1 - e^{-(k_B + k_C)t}) \tag{76}$$

$$[C] = \frac{k_C}{k_B + k_c}[A]_0(1 - e^{-(k_B + k_C)t}) \tag{77}$$

$$\frac{[B]}{[C]} = \frac{k_B}{k_C} \tag{78}$$

The yield is the probability that a given product will be formed:

$$\Phi_i = \frac{k_i}{\sum\limits_n k_n} \tag{79}$$

where

$$\sum\limits_i \Phi_i = 1 \tag{80}$$

Assume $k_B = 2k_C$ in Figure 12

$$\Phi_C = \frac{k_C}{k_B + k_C} = \frac{k_C}{(2k_C) + k_C} = \frac{1}{3} \tag{81}$$

Then

$$\Phi_B = \frac{2}{3}$$

Figure 12 reveals that [B]=2[C], consistent with the calculated yield.