Chapter 21 The Rates of Chemical Reactions

The concentration of reactants and products = *f* (time)

The methods of monitoring the concentrations

1. Pressure change

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

- the pressure of the system increases during the course of the reaction
- inappropriate for the reactions that leave the overall pressure unchanged, and for reactions in solution

2. Spectroscopy

$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

By monitoring the intensity of absorption of visible light by the bromine, the progress of the reaction can be monitored.

3. Polarimetry

   When the optical activity of a mixture changes in the course of reaction, it can be monitored by measuring the angle of optical rotation.

4. Electrochemical methods

   When a reaction changes the number or nature of ions present in a solution, its course may be followed by monitoring the conductivity of the solution.

5. Miscellaneous methods

   e.g., mass spectrometry and chromatography

   In order to employ these techniques, a small amount of the reaction mixture is bled from the reacting system at a series of times after the initiation of the reaction, and then analyzed.

Three ways of applying these analytical techniques

1. Real time analysis: the composition of the system is analyzed while the reaction is in progress. (See Figure 21.1.)

2. Quenching: the reaction is frozen after it has been allowed to proceed for a certain time, and then the composition is analyzed by any suitable techniques.

3. Flow method: the reaction continues as the thoroughly mixed solutions flow through the outlet tube, and observation of the composition at different positions (e.g. IR) is equivalent to observing the reaction mixture at different times after mixing. (See Figure 21.2.)

The rates of reactions

$A+B\rightarrow$Products, P

where [A], [B], [P]: the concentrations of the species, A, B, and P.

The rate of reaction (see Figure 21.3)

$$\frac{d[\mathrm{P}]}{dt}=-\frac{d[\mathrm{A}]}{dt}=-\frac{d[\mathrm{B}]}{dt}$$

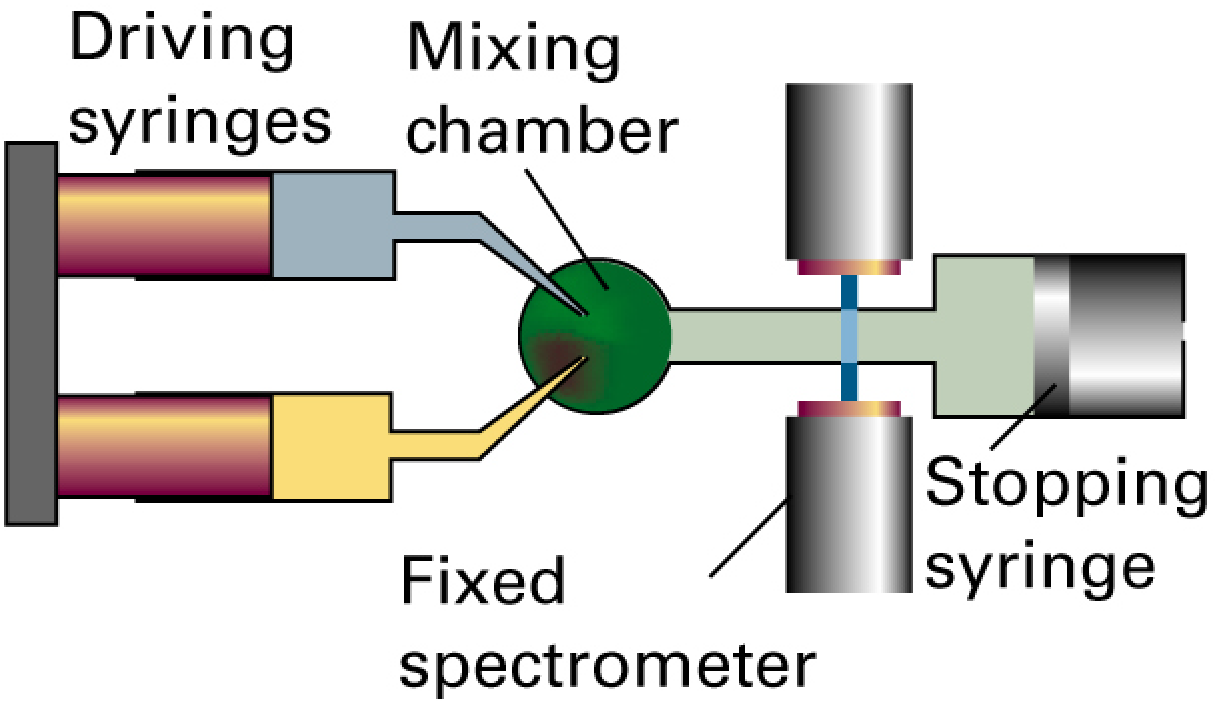


Figure 21.1
In the stopped-flow technique, the reagents are driven quickly into the mixing chamber by the driving syringes and then the time dependence of the concentrations is monitored.

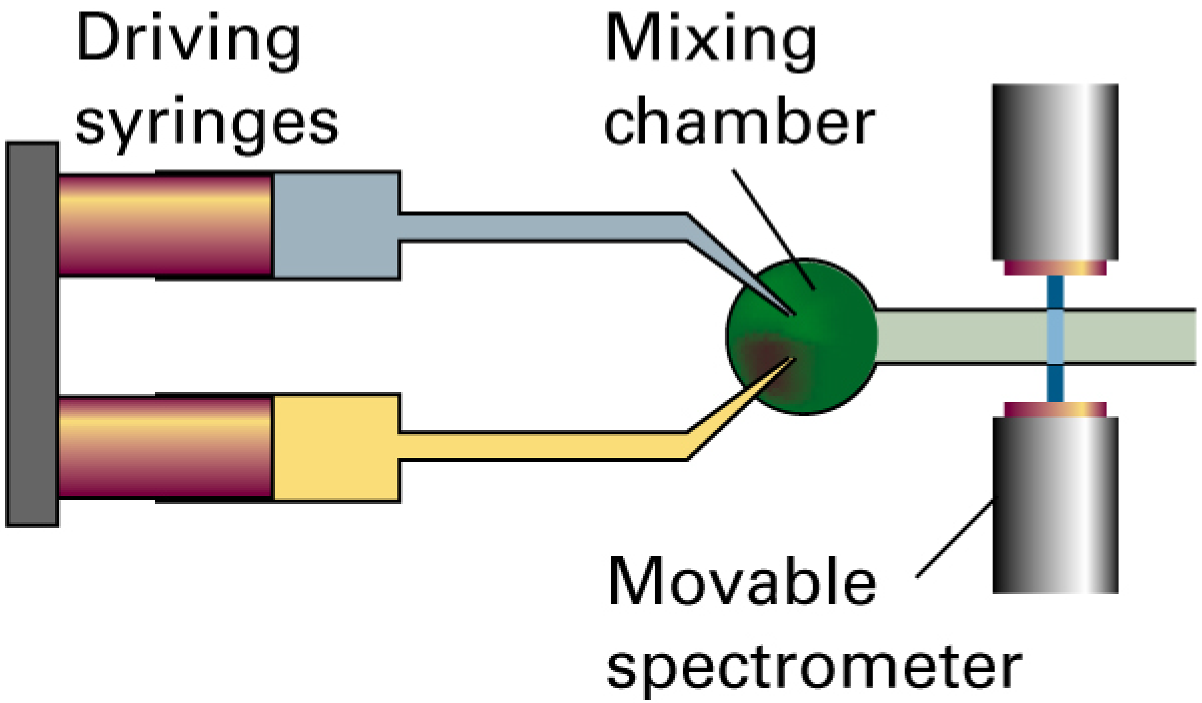


Figure 21.2
The arrangement used in the flow technique for studying reaction rates. The reactants are injected into the mixing chamber at a steady rate. The location of the spectrometer corresponds to different times after initiation.

$$\mathrm{A} + 2\mathrm{B} \rightarrow 3\mathrm{C} + \mathrm{D}$$

$$v = -\frac{d[\mathrm{A}]}{dt} = -\frac{1}{2}\frac{d[\mathrm{B}]}{dt} = \frac{1}{3}\frac{d[\mathrm{C}]}{dt} = \frac{d[\mathrm{D}]}{dt}$$

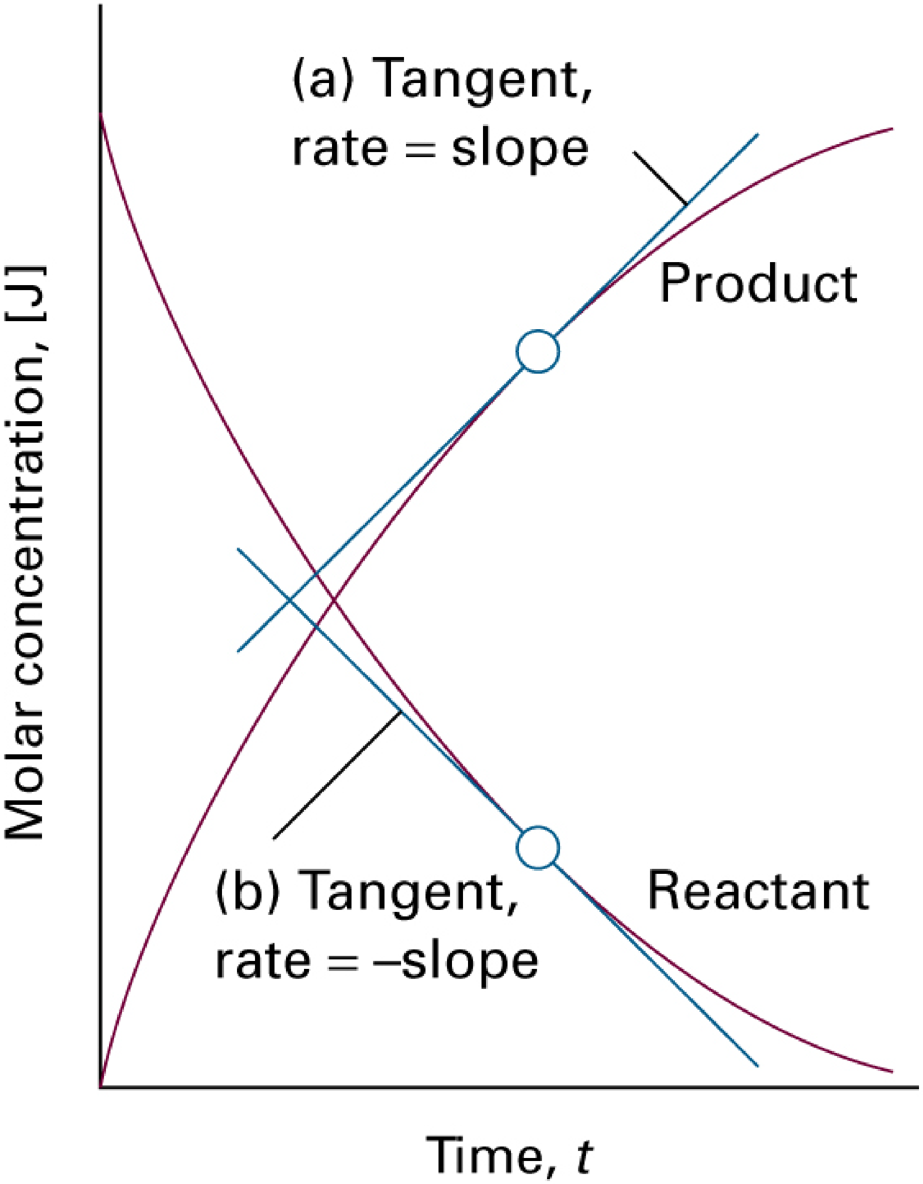


Figure 21.3
The definition of (instantaneous) rate as the slope of the tangent drawn to the curve showing the variation of concentration with time. For negative slopes, the sign is changed when reporting the rate, so all reaction rates are positive.

Determination of the rate law

A direct method for determining the rate law from the raw kinetic data giving the concentration as a function of time is from the measurement of initial slopes.

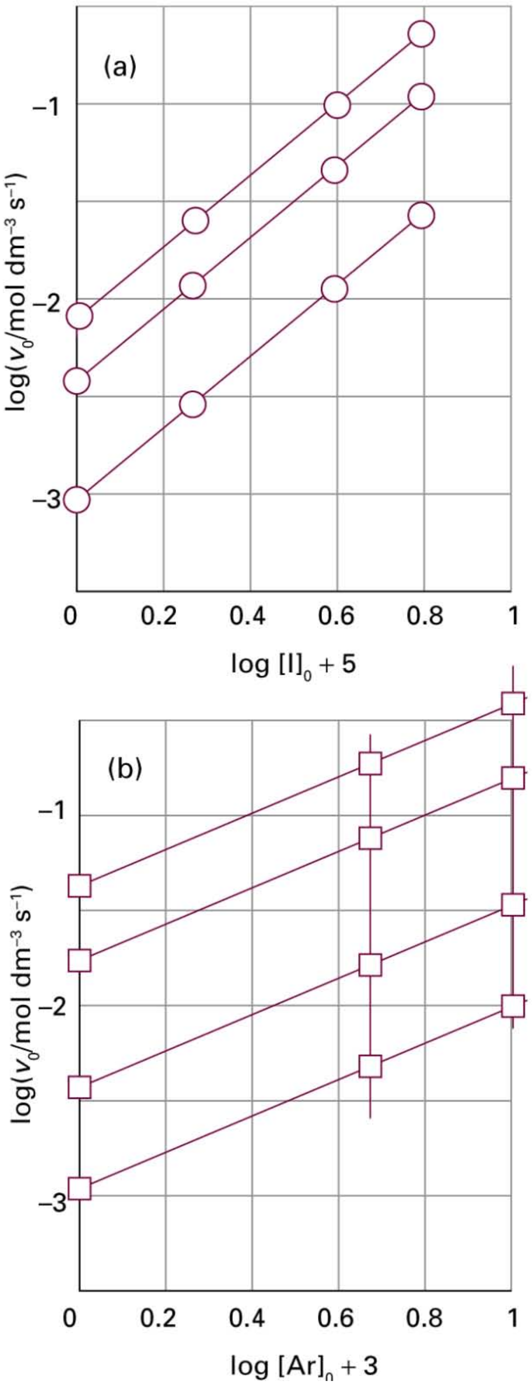
The reaction between A and B: **A + B → Product, P**

$$v = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^a[\mathrm{B}]^b$$

$$-\left(\frac{d[\mathrm{A}]}{dt}\right)_{\text{initial}} = k[\mathrm{A}]_0^a[\mathrm{B}]_0^b$$

$$\log\left\{-\left(\frac{d[\mathrm{A}]}{dt}\right)_{\text{initial}}\right\} = \log k + a\log[\mathrm{A}]_0 + b\log[\mathrm{B}]_0$$

A plot of the initial rate against various concentrations of A and B gives the orders *a* and *b* from the slopes, and log *k* from the intercept. (See Figure 21.4.) Unfortunately, the initial slope might not reveal the full rate law. Integration will give and expression for the actual concentrations at any time.



The reaction between A and B

$$2\mathrm{I}(g)+\mathrm{Ar}(g)\rightarrow \mathrm{I}_2(g)+\mathrm{Ar}(g)$$

$$v=k[\mathrm{I}]_0^2[\mathrm{Ar}]_0$$

$$-\frac{d[\mathrm{A}]}{dt}=k[\mathrm{A}]^a[\mathrm{B}]^b$$

$$-\left(\frac{d[\mathrm{A}]}{dt}\right)_{\text{initial}}=k[\mathrm{A}]_0^a[\mathrm{B}]_0^b$$

$$\log\left\{-\left(\frac{d[\mathrm{A}]}{dt}\right)_{\text{initial}}\right\}=\log k+a\log[\mathrm{A}]_0$$

$$+b\log[\mathrm{B}]_0$$

Figure 21.4
The plot of log v_0 against (a) log$[\mathrm{I}]_0$ for a given $[\mathrm{Ar}]_0$, and (b) log$[\mathrm{Ar}]_0$ for a given $[\mathrm{I}]_0$.

A+2B → 3C+D

$$v = -\frac{d[\mathrm{A}]}{dt} = -\frac{1}{2}\frac{[\mathrm{B}]}{dt} = \frac{1}{3}\frac{d[\mathrm{C}]}{dt} = \frac{d[\mathrm{D}]}{dt}$$

The ambiguity in the definition of rate is avoided if we define the rate of reaction v as

$$v = \frac{1}{v_J}\frac{d[J]}{dt}$$

where v_J is the stoichiometric constant of substance J.

The first order reaction

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

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

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t}\left(-\frac{d[\mathrm{A}]}{[\mathrm{A}]}\right) = \int_0^t k_1 dt$$

$$-\left(\ln[\mathrm{A}]_t - \ln[\mathrm{A}]_0\right) = k_1 t$$

$$\ln\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -k_1 t$$

$$\therefore [\mathrm{A}]_t = [\mathrm{A}]_0 \exp(-k_1 t)$$

$$[\mathrm{A}]_t = [\mathrm{A}]_0 \exp(-k_1 t)$$

(1) The concentration of A falls exponentially with time with a rate determined by k_1. (See Figure 21.5.)

(2) If $\ln \dfrac{[\mathrm{A}]_t}{[\mathrm{A}]_0}$ is plotted against t, the slope of the straight line is $-k_1$. (See Figure 21.6.)

The second order reaction

(i) **A+A → Products, P**

$$-\frac{d[\mathrm{A}]}{dt} = k_2[\mathrm{A}]^2$$

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t}\left(-\frac{d[\mathrm{A}]}{[\mathrm{A}]^2}\right) = \int_0^t k_2 dt$$

$$\therefore \frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0} = k_2 t$$

$$[\mathrm{A}]_t = \frac{[\mathrm{A}]_0}{1 + k_2 t[\mathrm{A}]_0}$$

When $\dfrac{1}{[\mathrm{A}]_t}$ is plotted against t, a straight line should be obtained and the slope is second-order rate coefficient k_2. (See Figure 21.7)

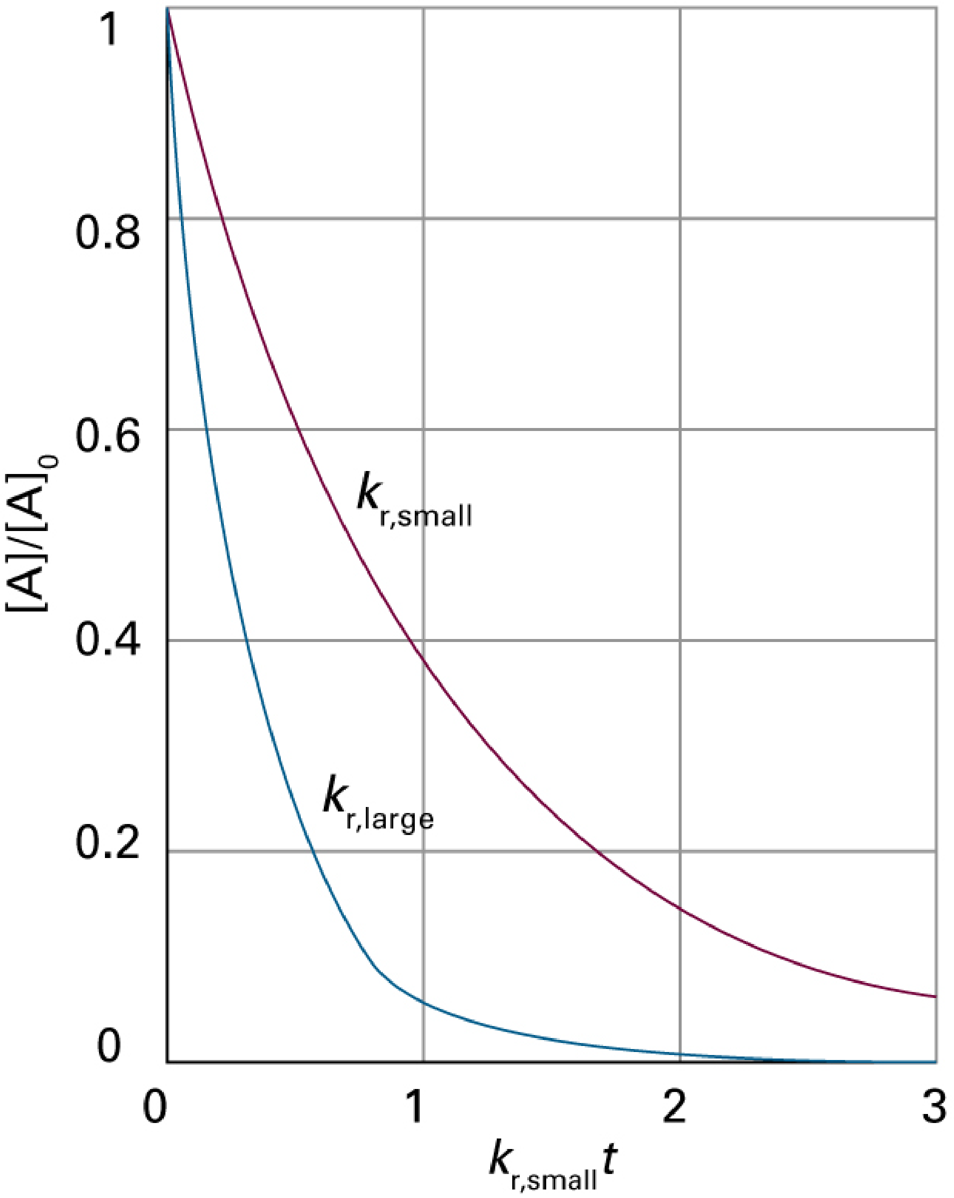


Figure 21.5
The exponential decay of the reactant in a first-order reaction. The larger the rate constant, the more rapid the decay: here $k_{\mathrm{large}} = 3k_{\mathrm{small}}$.

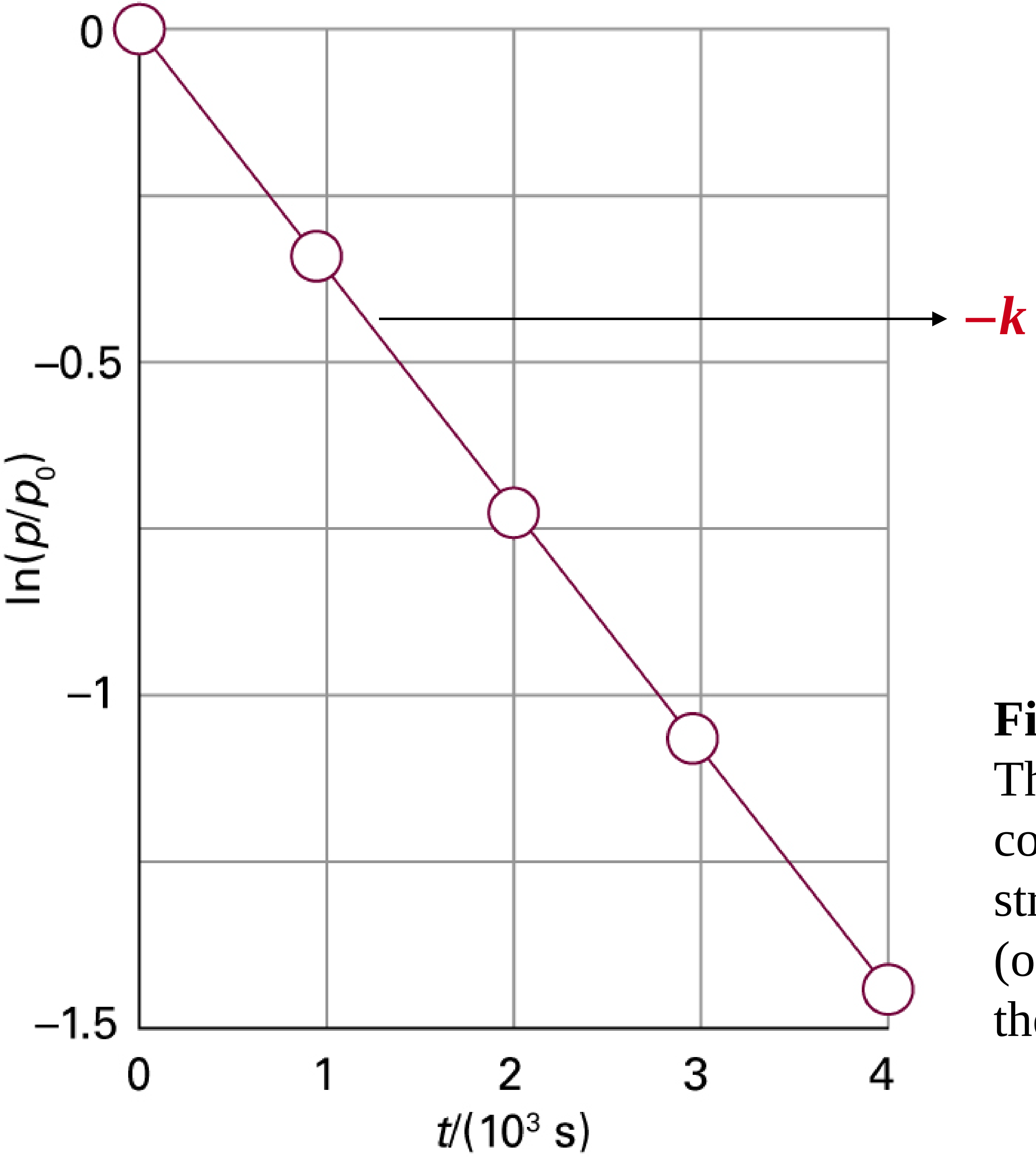
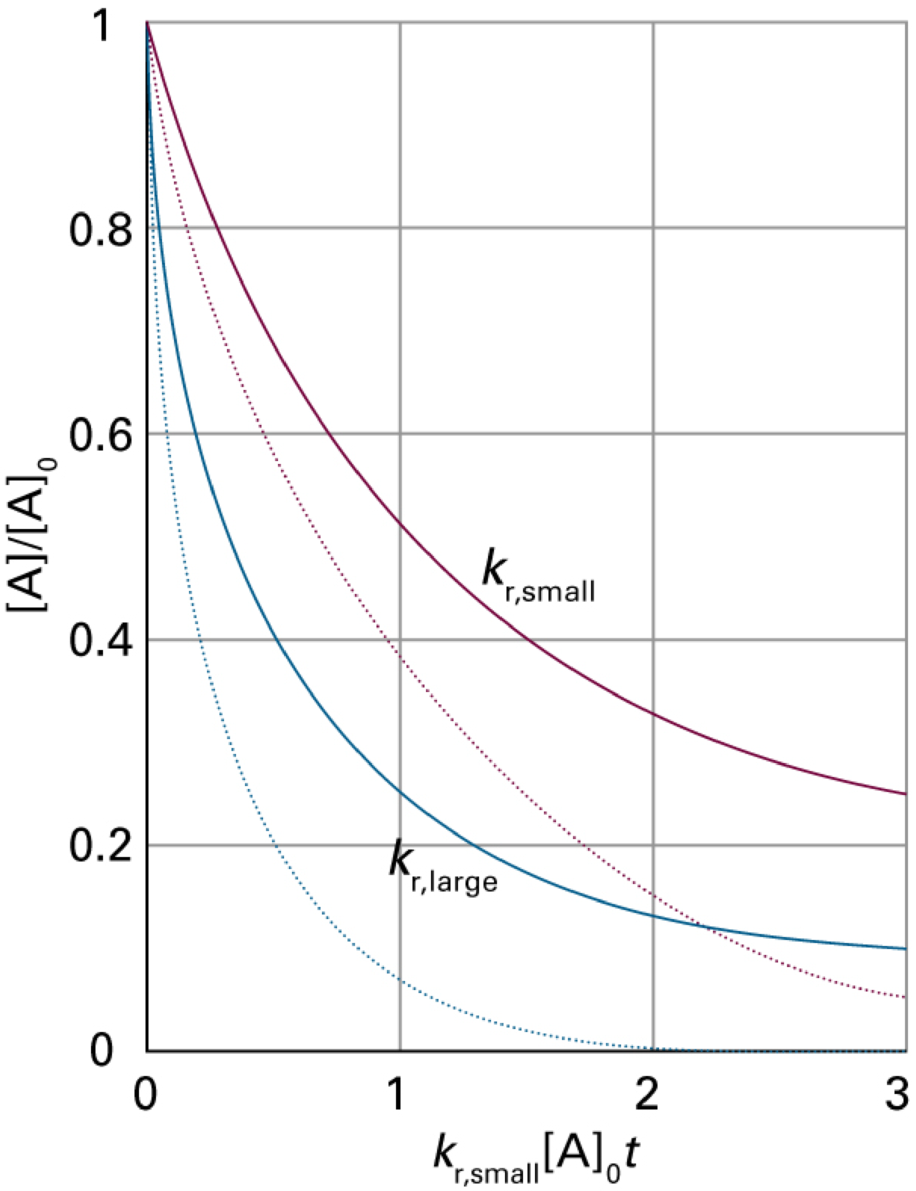
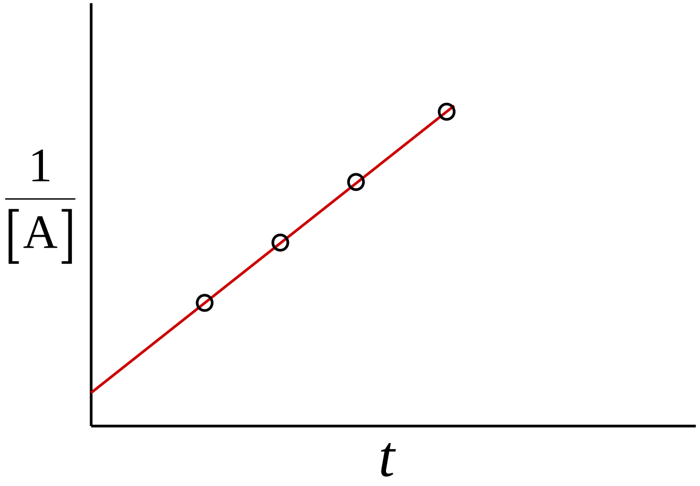


Figure 21.6
The determination of the rate constant of a first-order reaction: a straight line is obtained when ln [A] (or, as here, ln *p*) is plotted against *t*; the slope gives *k*.





$$\frac{1}{[A]} - \frac{1}{[A]_0} = k_2 t$$

2nd-order reaction

Figure 21.7
The variation with time of the concentration of a reactant in a second-order reaction. The dotted line is the corresponding decay in a first-order reaction with the same initial rate. For this illustration, $k_{\mathrm{large}} = 3k_{\mathrm{small}}$.

(ii) **A+B → Product, P**

$$-\frac{d[\mathrm{A}]}{dt}=k_2[\mathrm{A}][\mathrm{B}]$$

If the initial concentration of A and B are $[\mathrm{A}]_0$ and $[\mathrm{B}]_0$, then when the concentration of A drops $[\mathrm{A}]_0 - x$, the concentration of B drops to $[\mathrm{B}]_0 - x$, because every molecule of A that disappears entails the disappearance of one molecule of B.

$$-\frac{d[\mathrm{A}]}{dt}=k_2[\mathrm{A}][\mathrm{B}]=k_2\left([\mathrm{A}]_0-x\right)\left([\mathrm{B}]_0-x\right)$$

Since $\dfrac{d[\mathrm{A}]}{dt}=\dfrac{d\left([\mathrm{A}]_0-x\right)}{dt}=-\dfrac{dx}{dt}$,

$$\frac{dx}{dt}=k_2\left([\mathrm{A}]_0-x\right)\left([\mathrm{B}]_0-x\right)$$

$$k_2 t = \int_0^{x_t} \frac{dx}{([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x)}$$

$$= \int_0^{x_t} \left\{ \frac{-1}{[\mathrm{A}]_0 - [\mathrm{B}]_0} \right\} \left\{ \frac{1}{([\mathrm{A}]_0 - x)} - \frac{1}{([\mathrm{B}]_0 - x)} \right\} dx$$

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

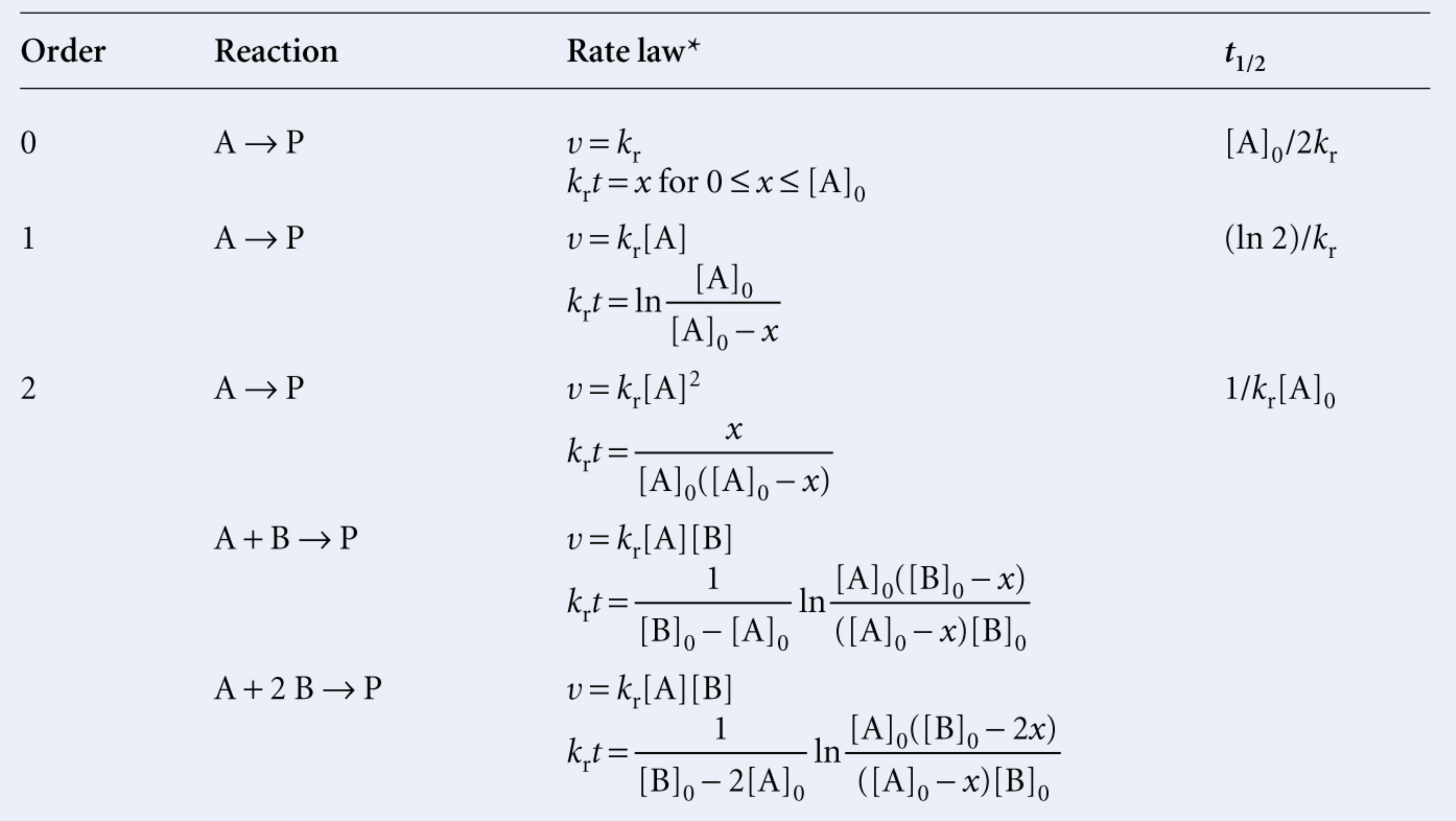
$$[\mathrm{A}]_t = [\mathrm{A}]_0 - x_t, \ [\mathrm{B}]_t = [\mathrm{B}]_0 - x_t$$

$$\boldsymbol{k_2 t = \left\{ \frac{1}{[\mathrm{A}]_0 - [\mathrm{B}]_0} \right\} \ln \left\{ \frac{[\mathrm{A}]_t [\mathrm{B}]_0}{[\mathrm{A}]_0 [\mathrm{B}]_t} \right\}}$$

When the right-hand side of this expression is plotted against t, a straight line is obtained and the rate coefficient k_2 can be determined from its slope.

The integrated rate expression rapidly become complicated, but they can often be simplified by Ostwald's isolation method. This depends on the approximation that when a reactant is present in large excess its concentration is hardly changed during the course of the reaction.

Table 21.1 Integrated rate laws



Order	Reaction	Rate law*	$t_{1/2}$
0	$A \rightarrow P$	$v = k_r$ $k_r t = x$ for $0 \leq x \leq [A]_0$	$[A]_0/2k_r$
1	$A \rightarrow P$	$v = k_r[A]$ $k_r t = \ln \dfrac{[A]_0}{[A]_0 - x}$	$(\ln 2)/k_r$
2	$A \rightarrow P$	$v = k_r[A]^2$ $k_r t = \dfrac{x}{[A]_0([A]_0 - x)}$	$1/k_r[A]_0$
	$A + B \rightarrow P$	$v = k_r[A][B]$ $k_r t = \dfrac{1}{[B]_0 - [A]_0} \ln \dfrac{[A]_0([B]_0 - x)}{([A]_0 - x)[B]_0}$	
	$A + 2\,B \rightarrow P$	$v = k_r[A][B]$ $k_r t = \dfrac{1}{[B]_0 - 2[A]_0} \ln \dfrac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	

Order	Reaction	Rate law*	$t_{1/2}$
	$\mathrm{A} \rightarrow \mathrm{P}$ with autocatalysis	$v = k_{\mathrm{r}}[\mathrm{A}][\mathrm{P}]$ $k_{\mathrm{r}}t = \frac{1}{[\mathrm{A}]_0 + [\mathrm{P}]_0} \ln \frac{[\mathrm{A}]_0([\mathrm{P}]_0 + x)}{([\mathrm{A}]_0 - x)[\mathrm{P}]_0}$	
3	$\mathrm{A} + 2\,\mathrm{B} \rightarrow \mathrm{P}$	$v = k_{\mathrm{r}}[\mathrm{A}][\mathrm{B}]^2$ $k_{\mathrm{r}}t = \frac{2x}{(2[\mathrm{A}]_0 - [\mathrm{B}]_0)([\mathrm{B}]_0 - 2x)[\mathrm{B}]_0}$ $+ \frac{1}{(2[\mathrm{A}]_0 - [\mathrm{B}]_0)^2} \ln \frac{[\mathrm{A}]_0([\mathrm{B}]_0 - 2x)}{([\mathrm{A}]_0 - x)[\mathrm{B}]_0}$	
$n \geq 2$	$\mathrm{A} \rightarrow \mathrm{P}$	$v = k_{\mathrm{r}}[\mathrm{A}]^n$ $k_{\mathrm{r}}t = \frac{1}{n-1}\left\{\frac{1}{([\mathrm{A}]_0 - x)^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right\}$	$\frac{2^{n-1} - 1}{(n-1)k_{\mathrm{r}}[\mathrm{A}]_0^{n-1}}$

* $x = [\mathrm{P}]$ and $v = \mathrm{d}x/\mathrm{d}t$.

(i) $$-\frac{d[\mathrm{A}]}{dt}=k_2[\mathrm{A}][\mathrm{B}]$$

If B is in large excess, the concentration [B] is virtually constant, $[\mathrm{B}]\approx[\mathrm{B}]_0$, and may be absorbed into the rate coefficient to give a new coefficient $k_1{}' = k_2[\mathrm{B}]_0$.

$$\therefore -\frac{d[\mathrm{A}]}{dt}\cong k_1^{'}[\mathrm{A}]$$

pseudo-first-order rate law

(ii) $$\frac{d[\mathrm{P}]}{dt}=k_3[\mathrm{A}]^2[\mathrm{B}]$$

By having the component A in large, the rate can be tuned into a pseudo-first-order law.

$$\frac{d[\mathrm{P}]}{dt}=k_1^{'}[\mathrm{B}]$$

Half-lives

A simple indication of the rate of a chemical reaction is the time it takes for the concentration of a reagent to fall to half its initial value: this is called the half-life of the reaction, and is denoted $t_{1/2}$.

In general, the half-life depends on the initial concentration in a characteristic way for reactions of different orders, and so its measurement gives a guide to the order.

For a first-order reaction,

$$[\mathrm{A}]_0 \rightarrow \frac{1}{2}[\mathrm{A}]_0 \ \text{ at } t_{1/2}$$

$$\ln \frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -k_1 t$$

$$-k_1 t_{1/2} = \ln \frac{\frac{1}{2}[\mathrm{A}]_0}{[\mathrm{A}]_0} = -\ln 2$$

$$\therefore t_{1/2} = \frac{\ln 2}{k_1}$$

Two significant points of $t_{1/2}$ of first order reaction

(i) $t_{1/2}$ may readily be determined from a plot of the time dependence of $[\mathrm{A}]_t$, and so this is very rapid method of measuring the first-order rate coefficient.

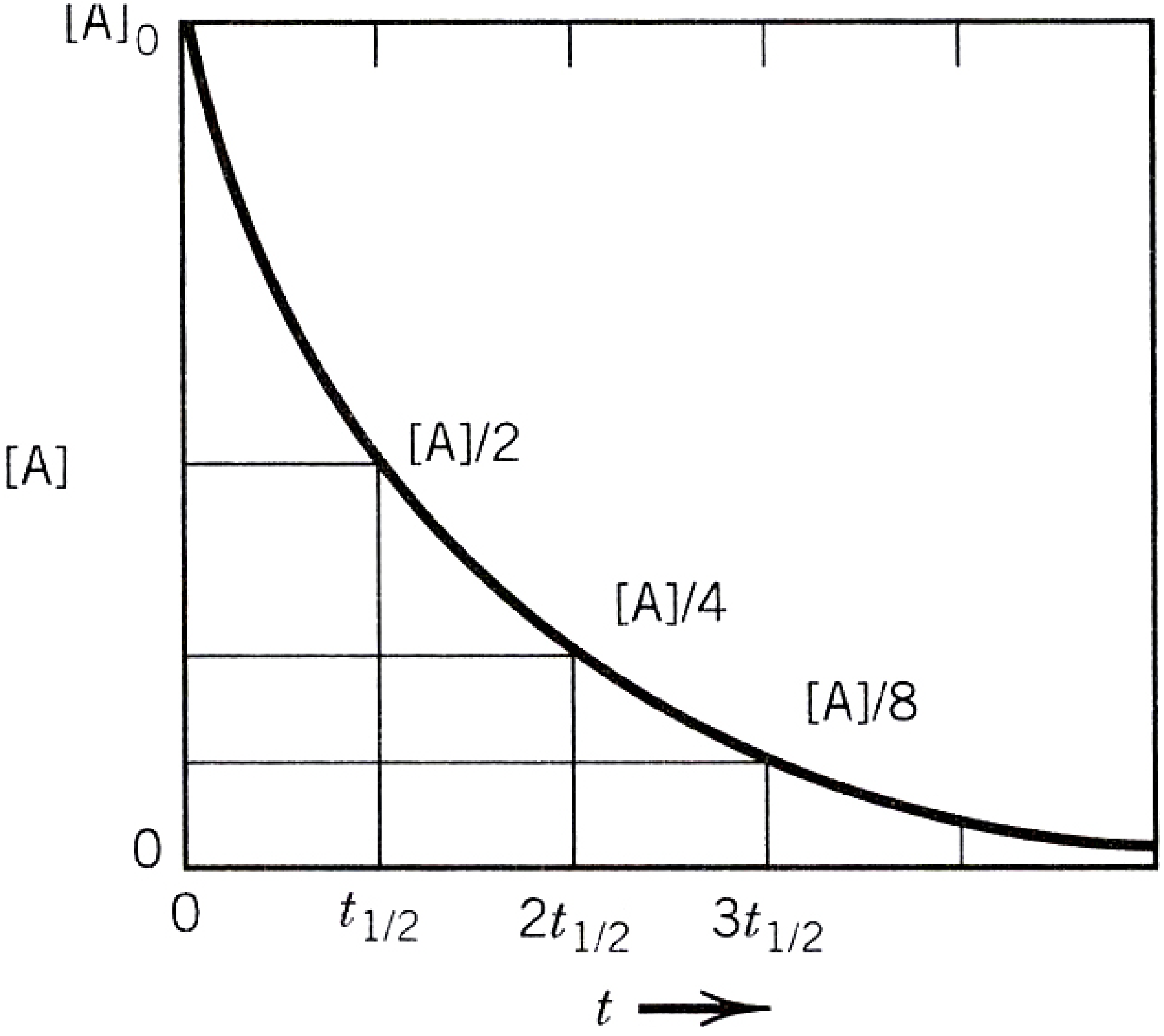
(ii) $t_{1/2}$ of a first-order reaction is independent of the concentration (Figure 21.8), thus if the concentration at arbitrary stage of the reaction is [A]', the concentration will have fallen to $\frac{1}{2}[\mathrm{A}]'$ after a further interval of ln $2/k_1$.

In the case of second-order reaction,

$$\frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0} = k_2 t$$

$$\frac{2}{[\mathrm{A}]_0} - \frac{1}{[\mathrm{A}]_0} = k_2 t_{1/2} \qquad \therefore t_{1/2} = \frac{1}{k_2[\mathrm{A}]_0}$$

The value of $t_{1/2}$ clearly depends on the initial concentration. If $t_{1/2}$ is determined for a series of different initial concentration, a plot of its value against $1/[\mathrm{A}]_0$ should be straight line so that the second-order rate coefficient can be determined from its slope (see Figure 21.9).

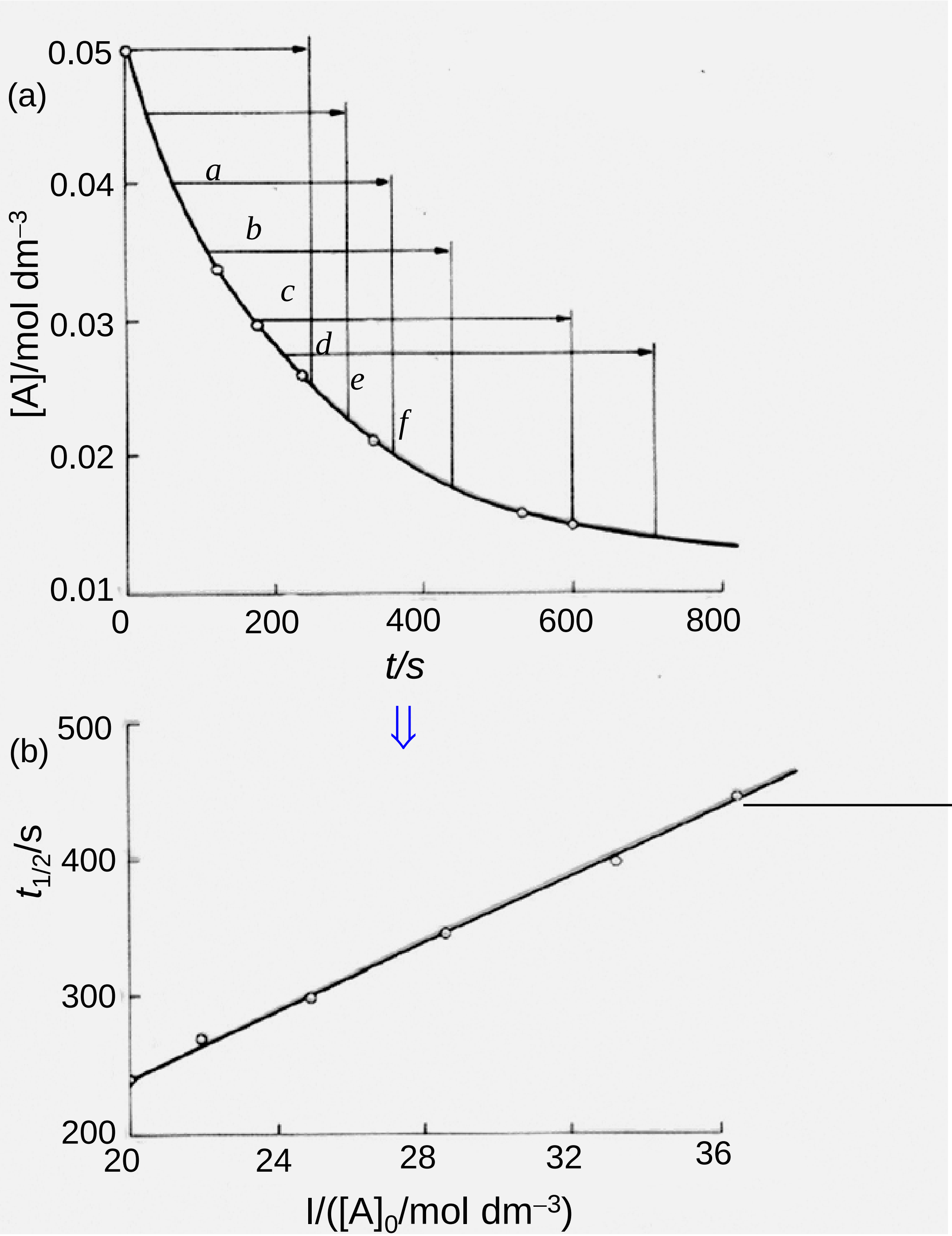


$$t_{1/2} = \frac{\ln 2}{k_1}$$

Figure 21.8

For a first-order reaction, one-half of the reactant disappears in $t_{1/2}$ independent of the initial concentration.

$$t_{1/2} = \frac{1}{k_2[A]_0}$$



$$\frac{1}{k_2}$$

Figure 21.9
Determination of the rate-coefficient of a second-order reaction.

The temperature dependence of the rates of simple reactions

The rates of most reactions increase as the temperature is raised. A good rule of thumb is that the rate doubles for every 10 *K* increase in temperature.

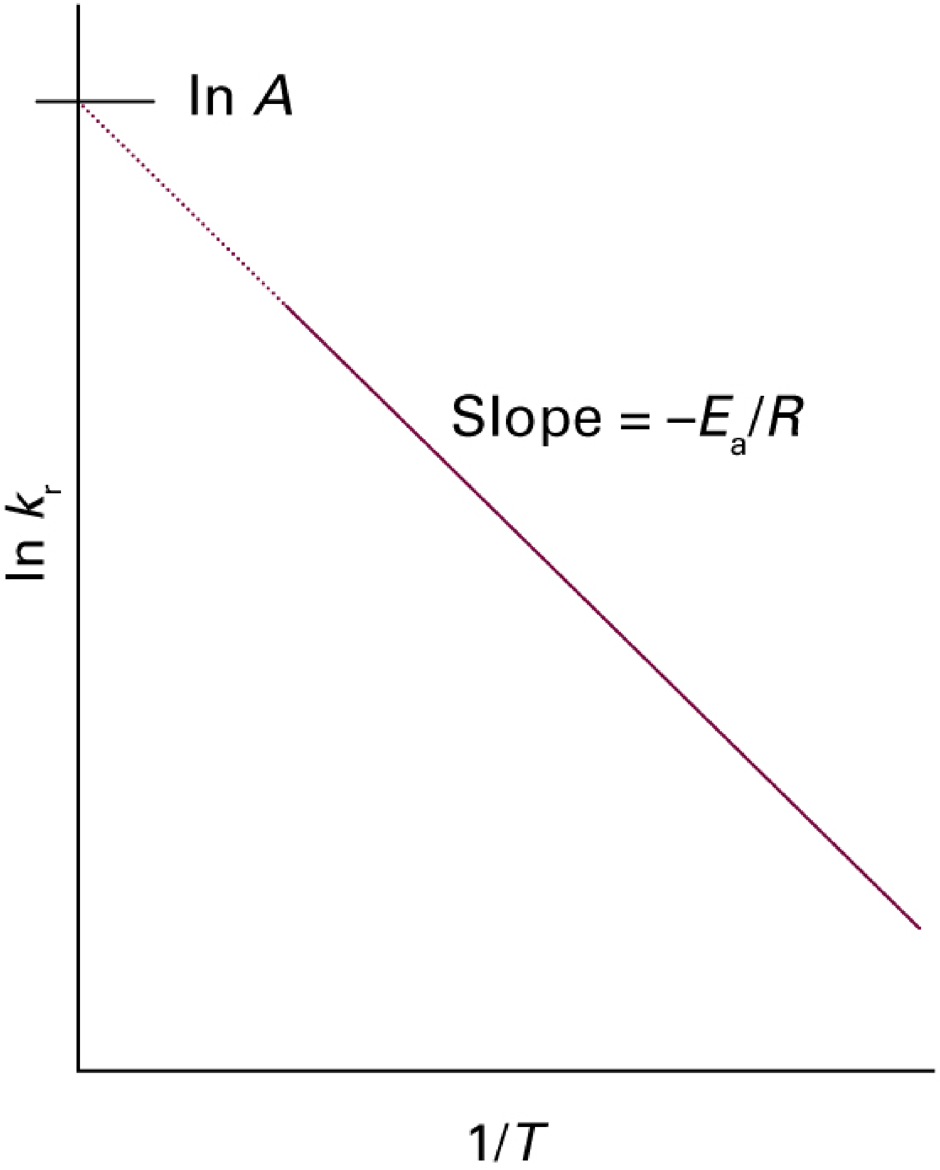
The temperature dependence of the rate coefficient has been found to fit the expression proposed by Arrhenius:

$$k_2 = A\exp\left(-\frac{E_a}{RT}\right)$$

where A and E_a are the pre-exponential factor (independent of temperature) and the activation energy (determined from a plot of $\ln k_2$ against $1/T$). (See Figure 21.10)

$$\ln k_2 = \ln A - \frac{E_a}{RT}$$

Once the activation energy of a reaction has been determined it is a simple matter to predict how the rate will respond to a change of temperature.



$$\ln k_2 = \ln A - \frac{E_a}{RT}$$

Figure 21.10
A plot of ln *k* against $1/T$ is a straight line when the reaction follows the behavior described by the Arrhenius equation. The slope gives $-E_a/R$ and the intercept at $1/T = 0$ gives ln *A*.

Consider a bimolecular reaction. There are two criteria to fulfill in order to have a reaction.

First, the molecules must come together. In a gas we call this a collision, in a liquid we call it an encounter.

Z: the rate at which these collisions occur per unit volume, collision frequency.

$$Z_{\mathrm{AB}} = \pi d^2 \left(\frac{8kT}{\pi\mu} \right)^{\frac{1}{2}} \left(\frac{\mathrm{N_A N_B}}{V^2} \right)$$

If the occurrence of a collision were the only factor for a reaction, all gas phase reactions at 1 *atm* pressure would be complete in about 10^{-9} *s*, which is contrary to the facts.

However, in order to react, the molecules must collide with enough energy. If we suppose that the molecules must collide with at least an energy E_a for reaction to ensue, the collision frequency must be multiplied by the proportion of molecules colliding with at least the kinetic energy E_a along the line of approach.

This proportion is given by the Boltzmann distribution, and $\exp(-E_a/RT)$ for a system at a temperature T.

$$\text{rate} = Z \exp\left(-\frac{E_a}{RT}\right)$$

The collision frequency itself is temperature dependent, whereas the experimental results seem to demand that the pre-exponential factor Z is temperature independent. In fact, the exponential temperature dependence is much stronger than the square-root dependence of Z, and it is very difficult experimental problem to detect deviations from the exponential form.

e.g. typical activation energies = 50~100 kJ/mol

10 K rise in temperature → the rate doubles, but collision

$$\text{frequency}: \left(\frac{308K}{298K}\right)^{\frac{1}{2}} \cong 1.02$$

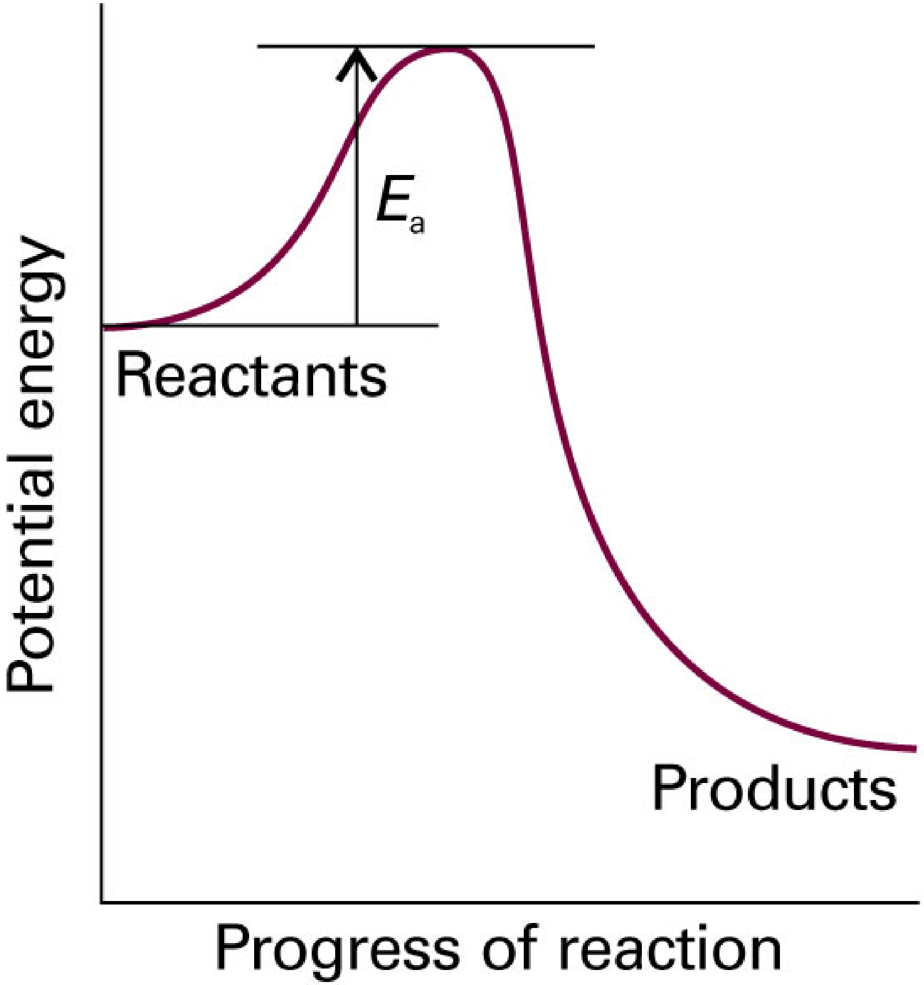


Figure 21.12 A potential energy profile for an exothermic reaction. The height of the barrier between the reactants and products is the activation energy of the reaction.

Reactions moving toward equilibrium

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B}$$

Assume both forward and backward reactions are first-order:

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{B}]$$

If the initial amount of A is $[\mathrm{A}]_0$, and if initially there is no B present, then $[\mathrm{A}]+[\mathrm{B}]=[\mathrm{A}]_0$ at all times:

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}\left([\mathrm{A}]_0 - [\mathrm{A}]\right) = -\left(k_1 + k_{-1}\right)[\mathrm{A}] + k_{-1}[\mathrm{A}]_0$$

The solution of this first-order differential equation is (see Figure 21.13)

$$[\mathrm{A}]_t = [\mathrm{A}]_0 \left\{ \frac{k_{-1} + k_1 \exp\left[-\left(k_1 + k_{-1}\right)t\right]}{k_1 + k_{-1}} \right\}$$

If $k_{-1} = 0$ (no reverse reaction), the equation becomes

$$[\mathrm{A}]_t = [\mathrm{A}]_0 \exp\left(-k_1 t\right)$$

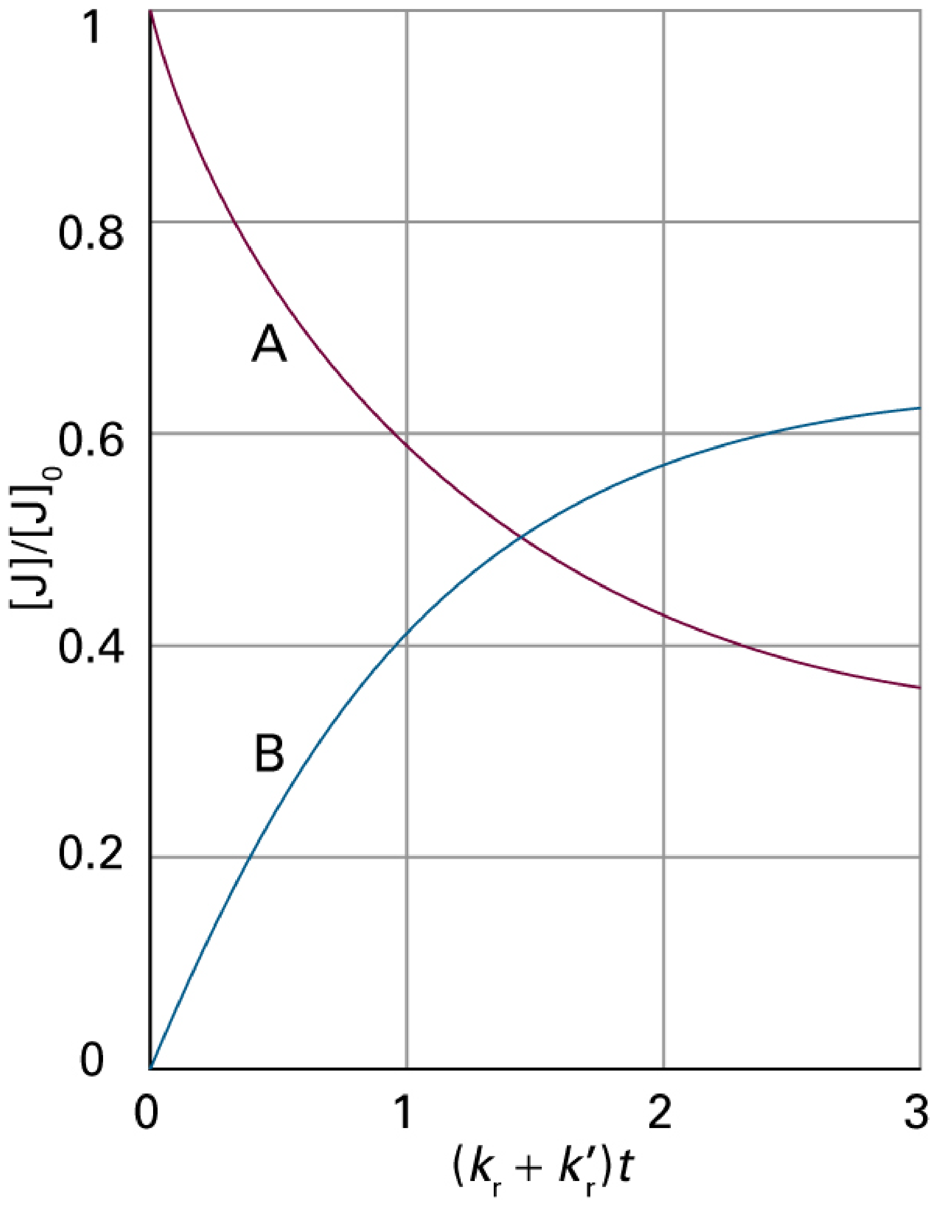


Figure 21.13
The approach of concentrations to their equilibrium values as predicted by the equation for a reaction $A \rightleftarrows B$ that is first-order in each direction, and for which $k_1 = 2k_{-1}$.

What is the final state of the system?

$t \to \infty$

$$[\mathrm{A}]_\infty = \frac{k_{-1}[\mathrm{A}]_0}{k_{-1}+k_1}\ , \qquad [\mathrm{B}]_\infty = [\mathrm{A}]_0 - [\mathrm{A}]_\infty = \frac{k_1[\mathrm{A}]_0}{k_{-1}+k_1}$$

$$K = \frac{[\mathrm{B}]_\infty}{[\mathrm{A}]_\infty} = \frac{k_1}{k_{-1}}$$

The same type of calculation for the simple bimolecular, second-order reaction,

$$\mathbf{A + B \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C + D}$$

$$K = \left\{\frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}\right\}_e = \frac{[\mathrm{C}]_\infty[\mathrm{D}]_\infty}{[\mathrm{A}]_\infty[\mathrm{B}]_\infty} = \frac{k_2}{k_{-2}}$$

Note that we emphasize simple reaction: the conclusion that ***$K=k_n/k_{-n}$*** is valid for a simple, one-step reaction but is not necessarily valid for a general second-order reaction that is the consequence of several steps.

Relaxation methods

The term relaxation denotes the return of a system to equilibrium. It is used in chemical kinetics to indicate that an externally applied influence has shifted the equilibrium position of a reaction, normally suddenly, and that the reaction is adjusting to the equilibrium composition characteristic of new conditions.

1. Temperature jump
2. Pressure-jump technique

Consider $\mathbf{A} \underset{k_b}{\overset{k_a}{\rightleftarrows}} \mathbf{B}$

$$x = x_0 e^{-\frac{t}{\tau}}, \quad \frac{1}{\tau} = k_a + k_b$$

where x_0 is the departure from equilibrium immediately after the temperature jump and x is the departure from equilibrium at the new temperature after a time t.

$$k_a[\mathrm{A}]_{eq} = k_b[\mathrm{B}]_{eq}$$

We write the deviation of [A] from its new equilibrium value as *x*, so $[\mathrm{A}]=[\mathrm{A}]_{eq}+x$ and $[\mathrm{B}]=[\mathrm{B}]_{eq}-x$. The concentration of A then changes as follows:

$$\frac{d[\mathrm{A}]}{dt} = -k_a[\mathrm{A}] + k_b[\mathrm{B}]$$

$$= -k_a([\mathrm{A}]_{eq}+x) + k_b([\mathrm{B}]_{eq}-x)$$

$$= -(k_a+k_b)x$$

Because of $d[\mathrm{A}]/dt = dx/dt$,

$$\frac{dx}{dt} = -(k_a+k_b)x$$

$$\frac{dx}{x} = -(k_a+k_b)dt \Rightarrow \ln\frac{x}{x_0} = -(k_a+k_b)t$$

$$x = x_0 e^{-(k_a+k_b)t} = x_0 e^{-\frac{t}{\tau}}, \text{ where } \frac{1}{\tau} = k_a + k_b$$

Since $\boldsymbol{K \approx k_a/k_b}$, its value may be combined with the relaxation time measurement to find the individual k_a and k_b.

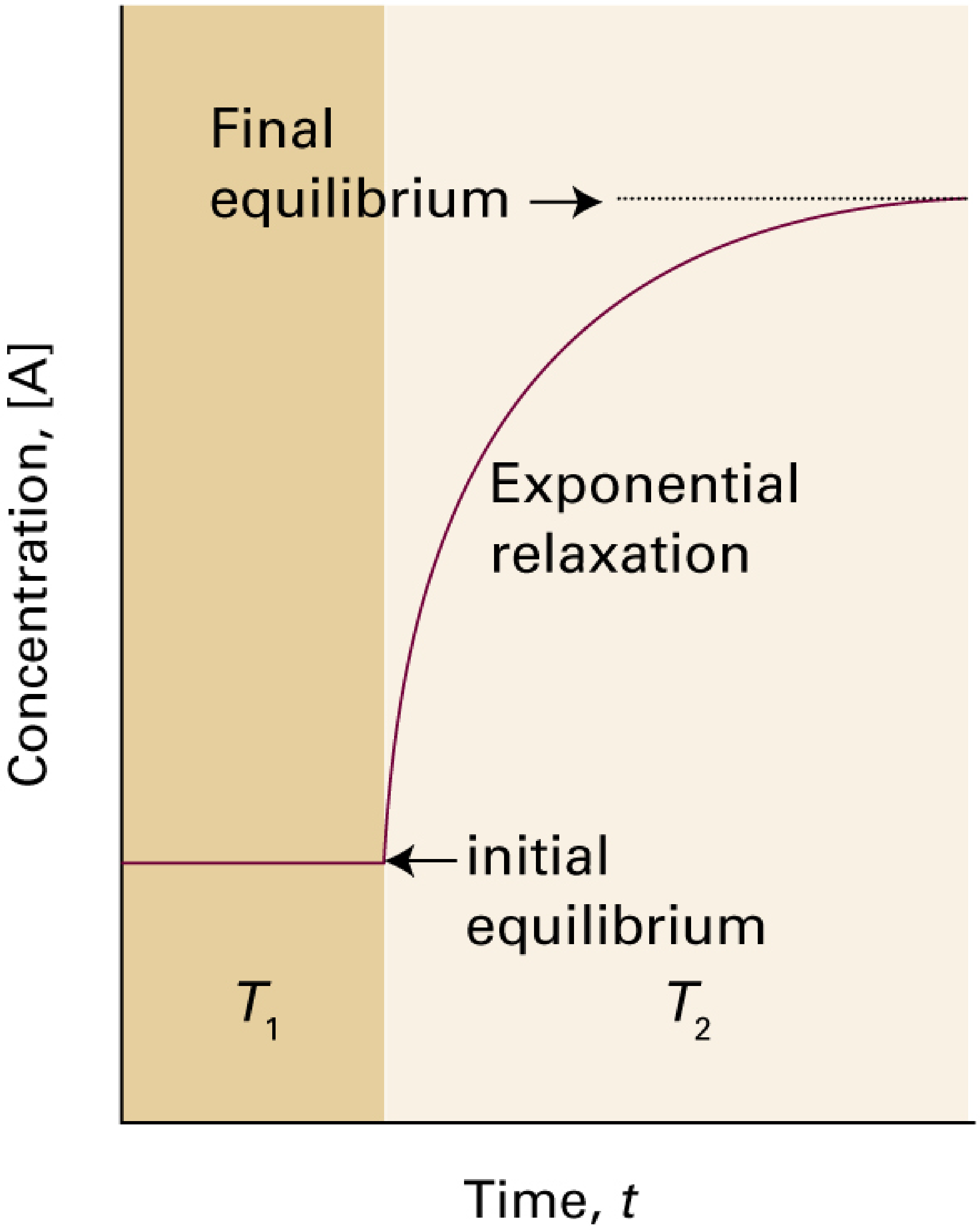


Figure 21.20
The relaxation to the new equilibrium composition when a reaction initially at equilibrium at a temperature T_1 is subjected to a sudden change of temperature, which takes it to T_2.

Consecutive reactions and the steady state

$$\mathbf{A} \xrightarrow{k_1} \mathbf{B} \xrightarrow{k_1^{'}} \mathbf{C}$$

e.g. $${}^{239}_{92}\mathrm{U} \xrightarrow{\beta} {}^{239}_{93}\mathrm{Np} \xrightarrow{\beta} {}^{239}_{94}\mathrm{Pu}$$

23.5 min 2.35days

half-lives

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] , \qquad \frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_1^{'}[\mathrm{B}] , \qquad \frac{d[\mathrm{C}]}{dt} = k_1^{'}[\mathrm{B}]$$

We suppose that only A is present initially, and that its concentration is then $[\mathrm{A}]_0$.

$$[\mathrm{A}]_t = [\mathrm{A}]_0 \exp(-k_1 t)$$

If this result is inserted into the equation for B and the condition $[\mathrm{B}]_0=0$ imposed, we arrived at

$$[\mathrm{B}]_t = [\mathrm{A}]_0 \left\{ \frac{k_1}{k_1^{'} - k_1} \right\} \left(e^{-k_1 t} - e^{-k_1^{'} t} \right)$$

$$[\mathrm{A}]_t + [\mathrm{B}]_t + [\mathrm{C}]_t = [\mathrm{A}]_0$$

$$[\mathrm{C}]_t = [\mathrm{A}]_0 - [\mathrm{A}]_t - [\mathrm{B}]_t = [\mathrm{A}]_0 \left\{ 1 + \left(\frac{1}{k_1 - k_1^{'}} \right) \right\} \left(k_1^{'} e^{-k_1 t} - k_1 e^{-k_1^{'} t} \right)$$

The solution for [B]

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_1^{'}} C$$

$$\frac{d[\mathrm{A}]}{dt} = -k[\mathrm{A}] \qquad (1)$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_1^{'}[\mathrm{B}] \qquad (2)$$

$$\frac{d[\mathrm{C}]}{dt} = k_1^{'}[\mathrm{B}] \qquad (3)$$

$$[\mathrm{A}] = [\mathrm{A}]_0 \exp(-k_1 t) \qquad (4)$$

$(4) \rightarrow (2)$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}]_0 \exp(-k_1 t) - k_1^{'}[\mathrm{B}] \qquad (5)$$

Let $Y = [\mathrm{B}]e^{k_1' t}$

$$\frac{dY}{dt} = e^{k_1' t}\frac{d[\mathrm{B}]}{dt} + [\mathrm{B}]k_1' e^{k_1' t}$$

$$\therefore e^{-k_1' t}\frac{dY}{dt} = \frac{d[\mathrm{B}]}{dt} + k_1'[\mathrm{B}] \tag{6}$$

Rearranging eq (5)

$$\frac{d[\mathrm{B}]}{dt} + k_1'[\mathrm{B}] = k_1[\mathrm{A}]_0 \exp(-k_1 t) \tag{7}$$

From eqs (6) and (7)

$$e^{-k_1' t}\frac{dY}{dt} = k_1[\mathrm{A}]_0 \exp(-k_1 t)$$

$$\frac{dY}{dt} = k_1[\mathrm{A}]_0 e^{(k_1' - k_1)t}$$

$$dY = k_1[\mathrm{A}]_0 e^{(k_1' - k_1)t} dt$$

$$Y_t - Y_0 = \frac{k_1[\mathrm{A}]_0}{k_1' - k_1} e^{(k_1' - k_1)t} - \frac{k_1[\mathrm{A}]_0}{k_1' - k_1}$$

$$[\mathrm{B}]e^{k_1' t} - 0 = \frac{k_1[\mathrm{A}]_0}{k_1' - k_1} e^{(k_1' - k_1)t} - \frac{k_1[\mathrm{A}]_0}{k_1' - k_1}$$

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]_0}{k_1' - k_1}\left(e^{-k_1 t} - e^{-k_1' t}\right)$$

(i) The three equations for [A], [B] and [C] indicate how to analyze a reaction scheme consisting of two consecutive first-order reactions: the proposed mechanism has to be confirmed by checking that these equations are obeyed. If they are obeyed, the values of the rate coefficients can be obtained.

(ii) The “rate-determining step”

If $k_1' >> k_1$, whenever B molecules is formed it decays quickly into C.

$$[\mathrm{C}]_t = [\mathrm{A}]_0 \left\{ 1 + \left(\frac{1}{k_1 - k_1'} \right) \left(k_1' e^{-k_1 t} - k_1 e^{-k_1' t} \right) \right\}$$

$$\cong [\mathrm{A}]_0 \left\{ 1 + \left(\frac{k_1'}{k_1 - k_1'} \right) e^{-k_1 t} \right\} \approx [\mathrm{A}]_0 \left(1 - e^{-k_1 t} \right)$$

The formation of C is seen to depend only on the smaller rate coefficient, as anticipated. For this reason, the step with the slowest rate is called the rate-determining step of the reaction.

If $k_1' << k_1$,

$$[\mathrm{C}]_t \approx [\mathrm{A}]_0 \left(1 - e^{-k_1' t} \right)$$

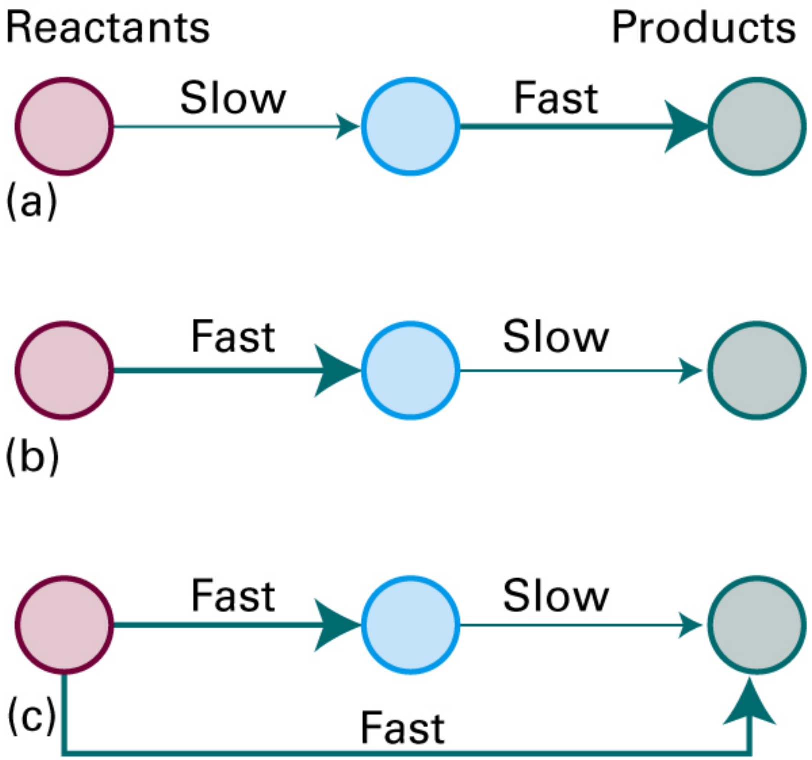


Figure 21.15 In these diagrams of reaction schemes, heavy arrows represent fast steps and light arrows represent slow steps. (a) The first step is rate determining; (b) the second step is rate-determining; (c) although one step is slow, it is not rate-determining step because there is a fast route that circumvents it.

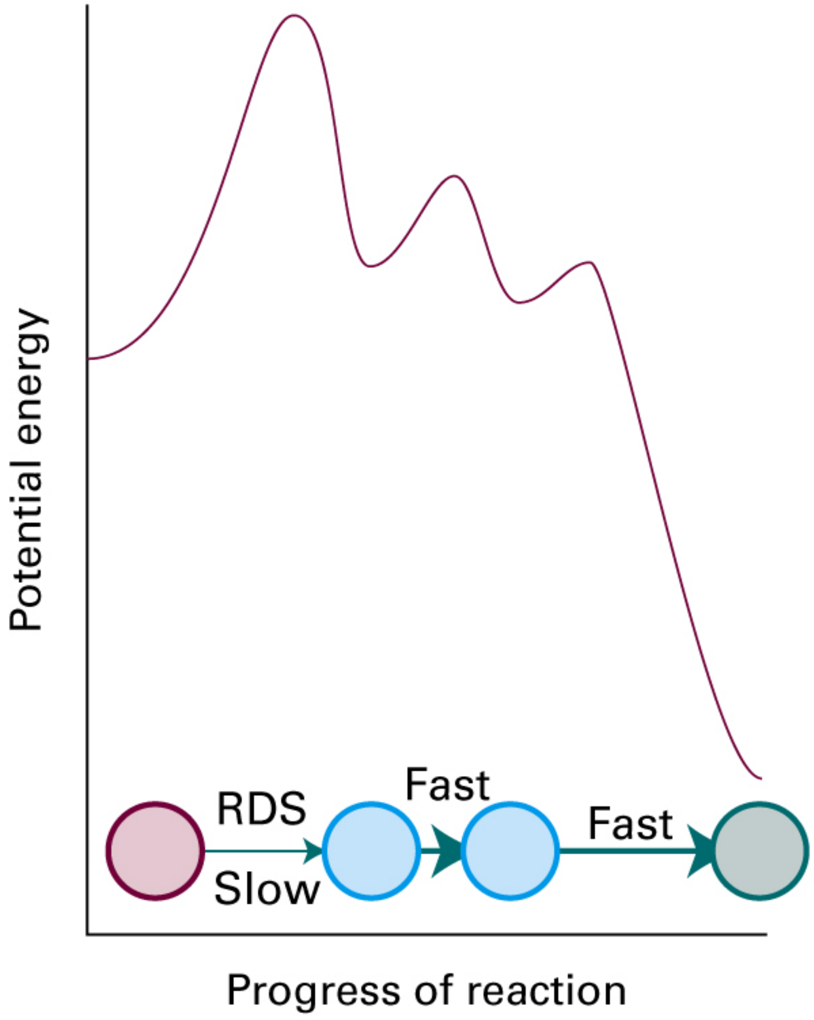


Figure 21.16 the reaction profile for a mechanism in which the first step (RDS) is rate-determining.

(iii) The third point established by the calculation is the rapidity with which sets of kinetic equations develop mathematical complexity.

Can an approximation be found, based on the present exact solution, which will lead to much simpler equations?

The steady-state approximation assumes that during the major part of the reaction, the concentrations and rates of change of all reaction intermediates are constant and small.

$$\mathbf{A} \xrightarrow{k_a} \mathbf{I} \xrightarrow{k_b} \mathbf{P}$$

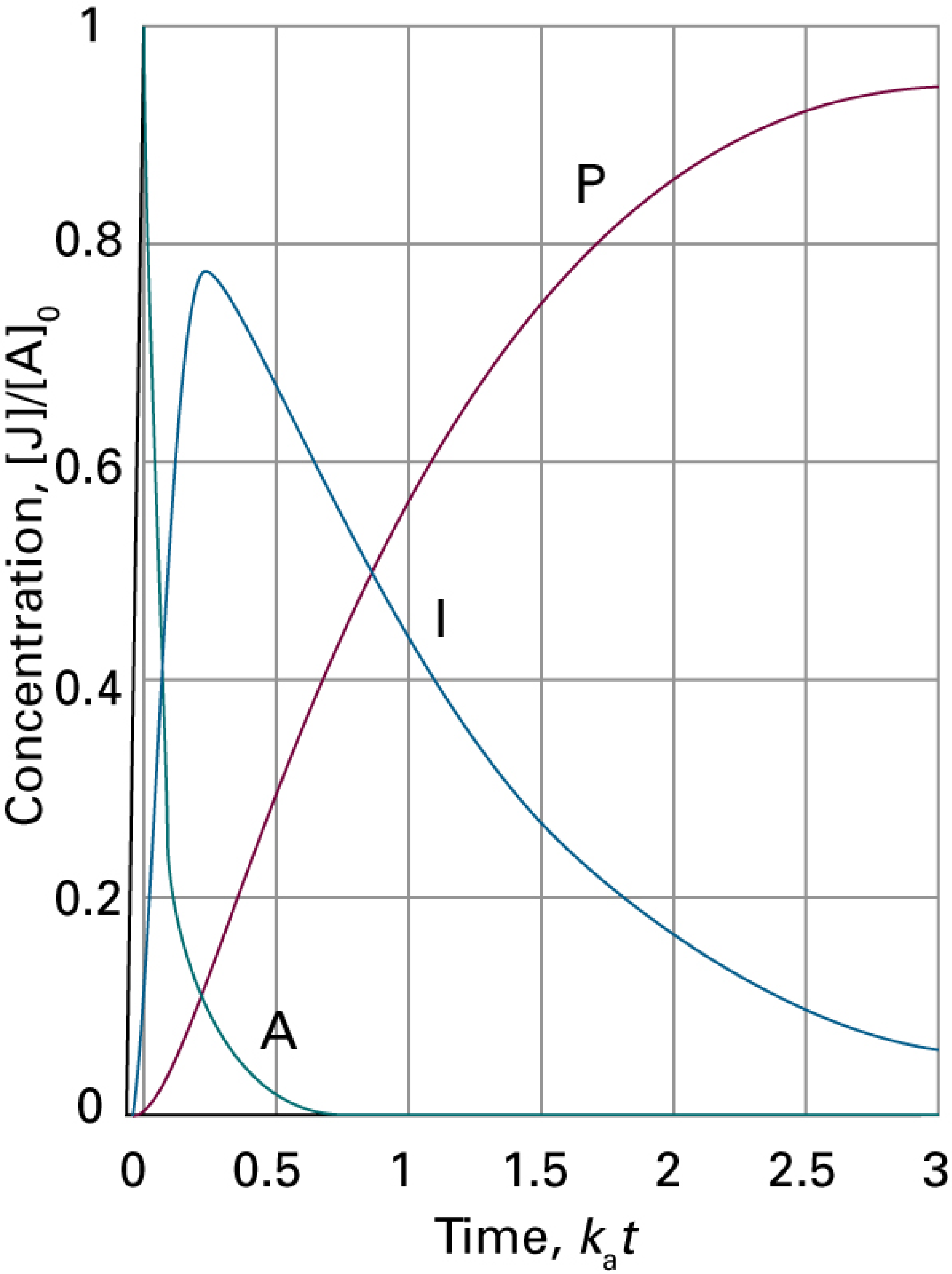


Figure 21.13
The concentrations of A, I, and P in the consecutive reaction scheme A→I→P. The curves are plots with $k_a = 10k_b$. If the intermediate I is in fact the desired product, it is important to be able to predict when its concentration is greatest.

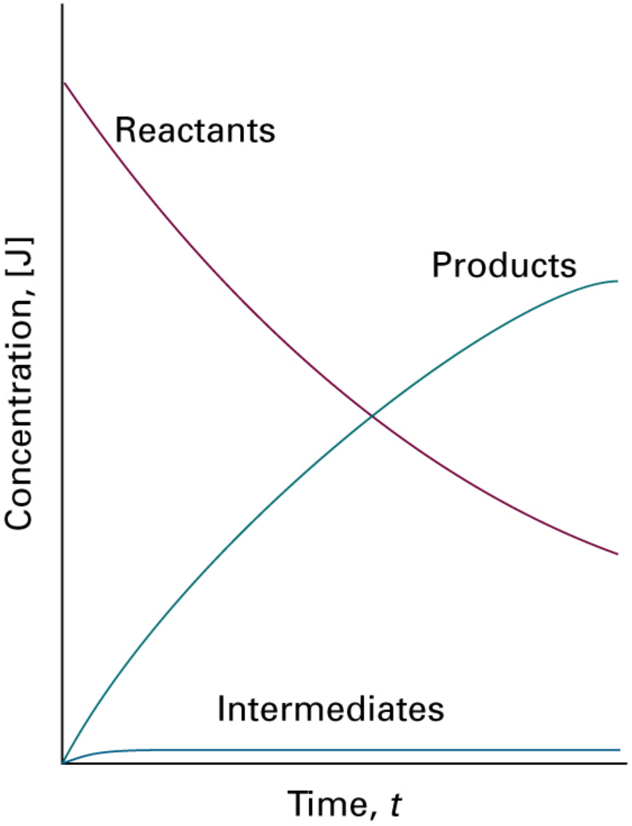


Figure 21.14
The basis of the steady-state approximation. It is supposed that the concentrations of intermediates remain small and hardly change during most of the course of the reaction.

$$\mathbf{A} \xrightarrow{k_1} \mathbf{B} \xrightarrow{k_1'} \mathbf{C}$$

$$[\mathrm{A}] = [\mathrm{A}]_0\, e^{-k_1 t}, \qquad [\mathrm{B}] = \frac{k_1 [\mathrm{A}]_0}{k_1' - k_1}\left(e^{-k_1 t} - e^{-k_1' t}\right)$$

$$\frac{[\mathrm{B}]}{[\mathrm{A}]} = \frac{k_1}{k_1' - k_1}\left(1 - e^{\left(k_1 - k_1'\right)t}\right)$$

$$\text{If } k_1' >> k_1, \qquad \frac{[\mathrm{B}]}{[\mathrm{A}]} = \frac{k_1\left(1 - e^{-k_1' t}\right)}{k_1'}$$

$$k_1' t >> 1, \qquad \frac{[\mathrm{B}]}{[\mathrm{A}]} = \frac{k_1}{k_1'}, \qquad \therefore [\mathrm{B}] = \frac{k_1}{k_1'}[\mathrm{A}] << [\mathrm{A}]$$

$$\frac{d[\mathrm{B}]}{dt} = \frac{k_1}{k_1'}\frac{d[\mathrm{A}]}{dt} << \frac{d[\mathrm{A}]}{dt}$$

$$\therefore \frac{d[\mathrm{B}]}{dt} \approx 0$$

For example,

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_1^{'}} \mathrm{C}$$

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}], \qquad \frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_1^{'}[\mathrm{B}] \approx 0$$

$$\therefore [\mathrm{B}] = \frac{k_1}{k_1^{'}}[\mathrm{A}]$$

Since $\dfrac{d[\mathrm{C}]}{dt} = k_1^{'}[\mathrm{B}]$,

$$\frac{d[\mathrm{C}]}{dt} = k_1^{'}[\mathrm{B}] = k_1[\mathrm{A}]$$

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t}$$

$$\therefore \frac{d[\mathrm{C}]}{dt} = k_1[\mathrm{A}]_0 e^{-k_1 t}$$

$$[\mathrm{C}] = k_1[\mathrm{A}]_0 \int_0^t e^{-k_1 t} dt = [\mathrm{A}]_0 (1 - e^{-k_1 t})$$

$$\mathbf{A} \xrightarrow{k_a} \mathbf{I} \xrightarrow{k_b} \mathbf{P}$$

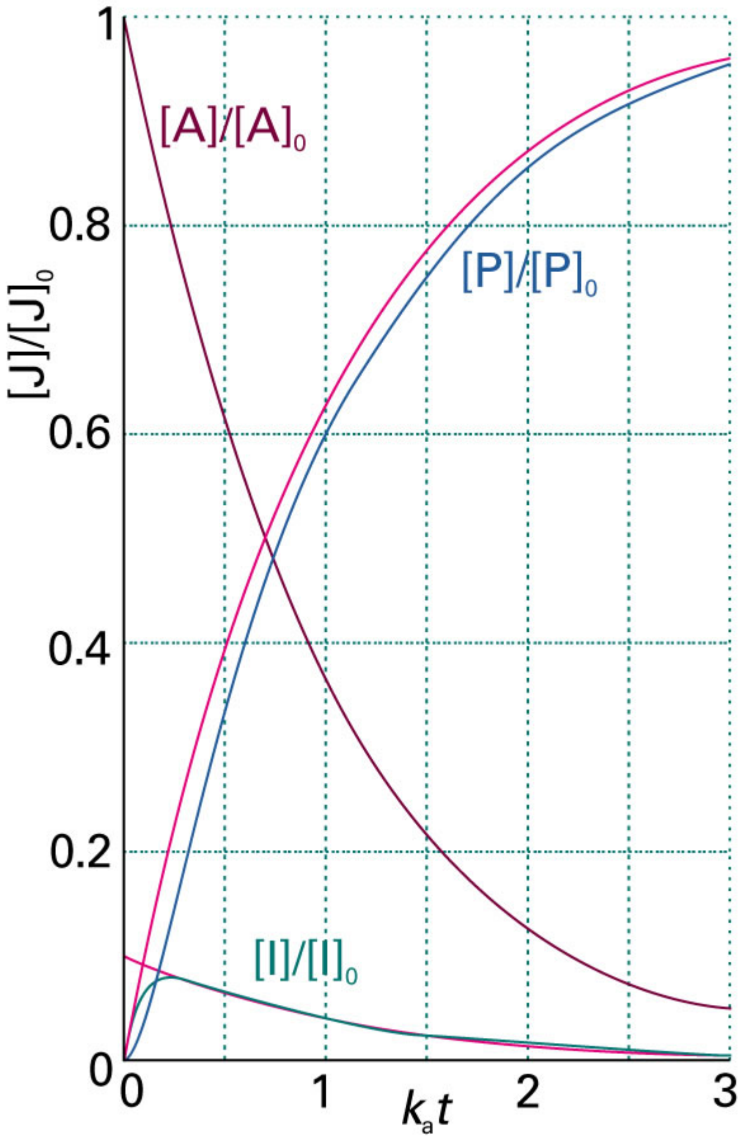


Figure 21.17 A comparison of the exact result for the concentrations of a consecutive reaction and the concentrations obtained by using the steady-state approximation (red lines) for k_b=20k_a. (The curve for [A] is unchanged.)

Another type of consecutive reaction

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_2}{\rightleftarrows}} (\mathrm{AB}) \xrightarrow{k_1} \mathrm{C}$$

Suppose that the intermediate (AB) falls apart into C only very slowly in comparison with the rates at which it both forms from and decays back into A and B.

$$\frac{d[(\mathrm{AB})]}{dt} = k_2[\mathrm{A}][\mathrm{B}] - k_{-1}[(\mathrm{AB})]$$

the steady-state approximation

$$k_2[\mathrm{A}][\mathrm{B}] - k_{-1}[(\mathrm{AB})] \approx 0$$

$$[(\mathrm{AB})] = \frac{k_2}{k_{-1}}[\mathrm{A}][\mathrm{B}]$$

$$[(\mathrm{AB})] = K[\mathrm{A}][\mathrm{B}]$$

$$\frac{d[\mathrm{C}]}{dt} = k_1 K[\mathrm{A}][\mathrm{B}]$$

Therefore the reaction has overall second-order kinetics.

An example of a consecutive reaction with pre-equilibrium

$$2\mathrm{NO} + \mathrm{O_2} \xrightarrow{k_3} 2\mathrm{NO_2}$$

(1) The reaction is third-order. This would require the simultaneous collision of three molecules, and such events are rare.

(2) The reaction rate decreases with increasing temperature.

A mechanism that accounts for the rate law and the temperature dependence is a pre-equilibrium.

$$\mathrm{NO} + \mathrm{NO} \rightleftharpoons \mathrm{N_2O_2} \qquad K = \frac{[\mathrm{N_2O_2}]}{[\mathrm{NO}]^2}$$

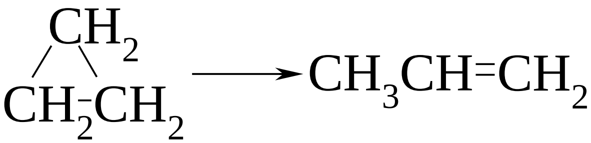
$$\mathrm{N_2O_2} + \mathrm{O_2} \xrightarrow{k_2} 2\mathrm{NO_2} \quad \text{bimolecular reaction}$$

$$\frac{d[\mathrm{NO_2}]}{dt} = 2k_2[\mathrm{N_2O_2}][\mathrm{O_2}] = 2k_2K[\mathrm{NO}]^2[\mathrm{O_2}]$$

This is a third-order rate law, as required by experiment, and the third-order rate coefficient can be identified as $k_3=2k_2K$.

The reason for the anomalous temperature dependence of the rate is that the equilibrium between NO and N_2O_2 shifts to the left (K decreases) as the temperature is raised (K decreases with temperature because the dimerization reaction is exothermic) although k_2 probably behaves normally and increases with temperature.

The unimolecular reactions



Rate=k[cyclopropane]

Lindemann-Hinshelwood mechanism

$$\mathrm{A}+\mathrm{A}\xrightarrow{k_a}\mathrm{A}^*+\mathrm{A} \qquad \frac{d[\mathrm{A}^*]}{dt}=k_a[\mathrm{A}]^2$$

$$\mathrm{A}^*+\mathrm{A}\xrightarrow{k_a'}2\mathrm{A} \qquad \frac{d[\mathrm{A}^*]}{dt}=-k_a'[\mathrm{A}^*][\mathrm{A}]$$

$$\mathrm{A}^*\xrightarrow{k_b}\mathrm{P} \qquad \frac{d[\mathrm{P}]}{dt}=k_b[\mathrm{A}^*],\quad \frac{d[\mathrm{A}^*]}{dt}=-k_b[\mathrm{A}^*]$$

If the unimolecular step is slow enough to be the rate-determining step, the overall reaction will have the first-order kinetics.

$$\frac{d[\mathrm{A}^*]}{dt}=k_a[\mathrm{A}]^2-k_a'[\mathrm{A}^*][\mathrm{A}]-k_b[\mathrm{A}^*]\cong 0 \qquad \therefore[\mathrm{A}^*]=\frac{k_a[\mathrm{A}]^2}{k_b+k_a'[\mathrm{A}]}$$

$$\therefore\frac{d[\mathrm{P}]}{dt}=k_b[\mathrm{A}^*]=\frac{k_ak_b[\mathrm{A}]^2}{k_b+k_a'[\mathrm{A}]} \qquad (*)$$

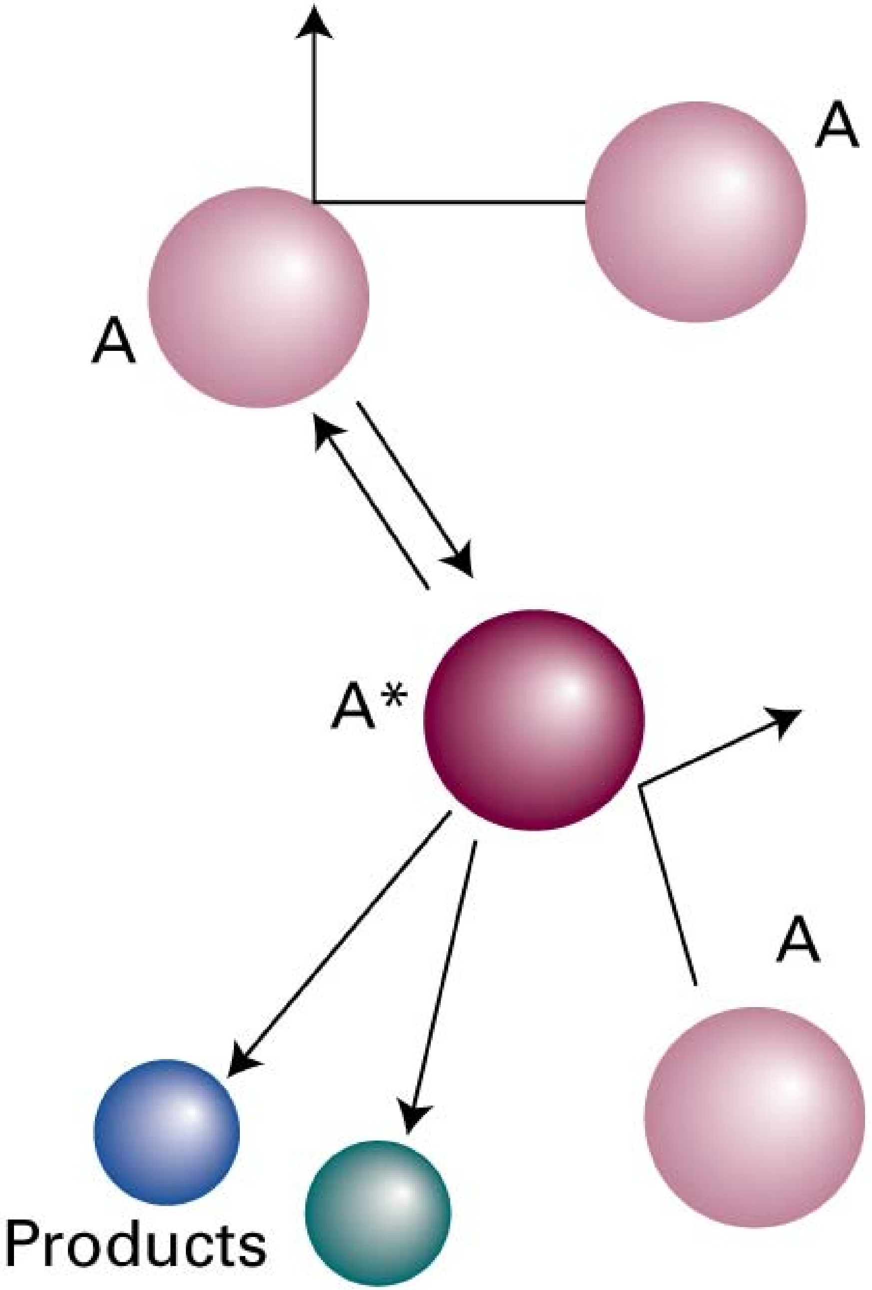


Figure 21.21
A representation of the Lindemann-Hinshelwood mechanism of unimolecular reactions. The species A is excited by collision with A, and the excited A molecule (A^*) may either be deactivated by a collision with A or go on to decay by a unimolecular process to form products.

$$\frac{d[\mathrm{P}]}{dt}=\frac{k_a k_b[\mathrm{A}]^2}{k_b+k_a^{'}[\mathrm{A}]} \qquad (*)$$

If $k_a^{'}[\mathrm{A}^*][\mathrm{A}] >> k_b[\mathrm{A}^*]$, or $k_a^{'}[\mathrm{A}] >> k_b$, then $\frac{d[P]}{dt}=k[\mathrm{A}]$,

where $k=\frac{k_a k_b}{k_a^{'}}$

If $k_a^{'}[\mathrm{A}] << k_b$,

$$\therefore \frac{d[\mathrm{P}]}{dt}=k_a[\mathrm{A}]^2 \qquad \text{from eq } (*)$$

The Lindemann-Hinshelwood mechanism can be tested because it predicts that as the concentration (and therefore the partial pressure) of A is reduced the reaction should switch to overall second-order kinetics. The physical reason for the change of order is that at low pressures the rate-determining step is the bimolecular formation of A*.

$$\frac{d[\mathrm{P}]}{dt} = k_b[\mathrm{A}^*] = \frac{k_a k_b [\mathrm{A}]^2}{k_b + k_a^{'}[\mathrm{A}]} \qquad (*)$$

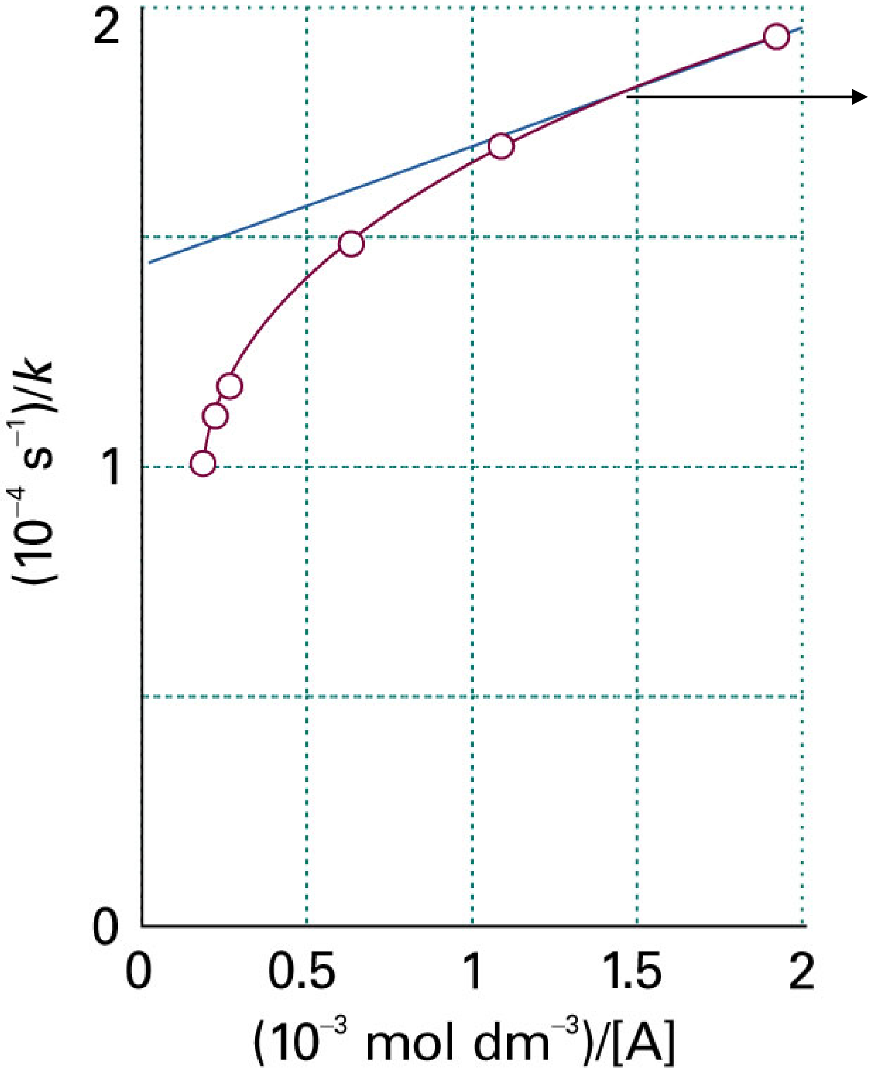
Equation (*) can be written

$$\frac{d[\mathrm{P}]}{dt} = k[\mathrm{A}], \quad \text{where } k = \frac{k_a k_b [\mathrm{A}]}{k_b + k_a^{'}[\mathrm{A}]}$$

The expression for the effective rate-constant can be rearranged to

$$\frac{1}{k} = \frac{1}{k_a[\mathrm{A}]} + \frac{k_a^{'}}{k_a k_b}$$

Hence, a test of the theory is to plot 1/*k* against 1/[A], and to expect a straight line.



$$\frac{1}{k} = \frac{1}{k_a[\mathrm{A}]} + \frac{k_a'}{k_a k_b}$$

Figure 21.22
The pressure-dependence of the unimolecular isomerization of *tran*-$C_2H_2D_2$ showing a pronounced departure from the straight line predicted by the Lindemann-Hinshelwood mechanism.

The kinetics of complex reactions

Chain reactions

Many reactions in the gas phase proceed through a series of steps involving free radicals.

$$\cdot CH_3 + CH_3CH_3 \longrightarrow CH_4 + \cdot CH_2CH_3$$

The radicals produced, in this case the ethyl radical $\cdot CH_2CH_3$, can go on to react either by producing yet another radical by attack on a molecule, or by meeting and combining with another free radical. This sequence of reactions, of radicals producing radicals, is the basis of the name chain reaction.

Four steps of chain reactions

1. Initiation step: the step that the radicals are formed from ordinary molecules

   - A Lindemann-type process, where the molecule pick up enough energy by collision with other molecules, and then falls apart in a subsequent unimolecular step

     e.g. $\mathrm{Cl_2} \longrightarrow 2\mathrm{Cl}\cdot$

   - By the absorption of a photon

     $\mathrm{Cl_2} + h\nu \longrightarrow 2\mathrm{Cl}\cdot$

2. Propagation step: the attacks of the free radical on other molecules
3. Inhibition step: the step that a radical attacks a product
4. Termination step: dimerization or some reaction with the walls of the containing vessel

Example 1

$$\mathrm{H_2} + \mathrm{Br_2} \longrightarrow 2\mathrm{HBr}$$

empirical rate law: $$\frac{d[\mathrm{HBr}]}{dt} = \frac{k[\mathrm{H_2}][\mathrm{Br_2}]^{\frac{3}{2}}}{[\mathrm{Br_2}] + k'[\mathrm{HBr}]}$$

The mechanism that has been proposed:

Initiation: $\mathrm{Br_2} \xrightarrow{k_\mathrm{a}} 2\mathrm{Br}\cdot$

Propagation: $\mathrm{Br}\cdot + \mathrm{H_2} \xrightarrow{k_\mathrm{b}} \mathrm{HBr} + \mathrm{H}\cdot$

$\mathrm{H}\cdot + \mathrm{Br_2} \xrightarrow{k_\mathrm{c}} \mathrm{HBr} + \mathrm{Br}\cdot$

Inhibition: $\mathrm{H}\cdot + \mathrm{HBr} \xrightarrow{k_\mathrm{d}} \mathrm{H_2} + \mathrm{Br}\cdot$

Termination: $\mathrm{Br}\cdot + \mathrm{Br}\cdot \xrightarrow{k_\mathrm{e}} \mathrm{Br_2}$

$$\frac{d[\mathrm{HBr}]}{dt} = k_\mathrm{b}[\mathrm{Br}\cdot][\mathrm{H}_2] + k_\mathrm{c}[\mathrm{H}\cdot][\mathrm{Br}_2] - k_\mathrm{d}[\mathrm{H}\cdot][\mathrm{HBr}]$$

the steady state approximation

$$\frac{d[\mathrm{H}\cdot]}{dt} = k_\mathrm{b}[\mathrm{Br}\cdot][\mathrm{H}_2] - k_\mathrm{c}[\mathrm{H}\cdot][\mathrm{Br}_2] - k_\mathrm{d}[\mathrm{H}\cdot][\mathrm{HBr}] \approx 0$$

$$\frac{d[\mathrm{Br}\cdot]}{dt} = 2k_\mathrm{a}[\mathrm{Br}_2] - k_\mathrm{b}[\mathrm{Br}\cdot][\mathrm{H}_2] + k_\mathrm{c}[\mathrm{H}\cdot][\mathrm{Br}_2] + k_\mathrm{d}[\mathrm{H}\cdot][\mathrm{HBr}]$$

$$-2k_\mathrm{e}[\mathrm{Br}\cdot]^2 \approx 0$$

These two simultaneous equations may be solved for [H•] and [Br•] and the result substituted into the equation for $d[\mathrm{HBr}]/dt$.

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{2k_\mathrm{b}(k_\mathrm{a}/k_\mathrm{e})^{\frac{1}{2}}[\mathrm{H}_2][\mathrm{Br}_2]^{\frac{3}{2}}}{[\mathrm{Br}_2] + \frac{k_\mathrm{d}}{k_\mathrm{c}}[\mathrm{HBr}]}$$

$$k = 2k_\mathrm{b}\left(\frac{k_\mathrm{a}}{k_\mathrm{e}}\right)^{\frac{1}{2}}, \quad k' = \frac{k_\mathrm{d}}{k_\mathrm{c}}$$

Example 2 $CH_3CH_3 \longrightarrow CH_2{=}CH_2 + H_2$

empirical rate law: $$\frac{d\left[\mathrm{CH_2{=}CH_2}\right]}{dt} = k_1\left[\mathrm{CH_3CH_3}\right]$$

The reaction sequence is known as the Rice-Herzfeld mechanism.

Initiation: $\mathrm{CH_3CH_3} \xrightarrow{k_a} 2\mathrm{CH_3}\cdot$

Propagation: $\mathrm{CH_3}\cdot + \mathrm{CH_3CH_3} \xrightarrow{k_b} \mathrm{CH_4} + \mathrm{CH_3CH_2}\cdot$

$$\mathrm{CH_3CH_2}\cdot \xrightarrow{k_c} \mathrm{CH_2{=}CH_2} + \mathrm{H}\cdot$$

$$\mathrm{H}\cdot + \mathrm{CH_3CH_3} \xrightarrow{k_d} \mathrm{H_2} + \mathrm{CH_3CH_2}\cdot$$

Termination: $\mathrm{H}\cdot + \mathrm{CH_3CH_2}\cdot \xrightarrow{k_e} \mathrm{CH_3CH_3}$

$$\frac{d\left[\mathrm{CH_2{=}CH_2}\right]}{dt} = \left(\frac{k_a k_c k_d}{k_e}\right)^{\frac{1}{2}}\left[\mathrm{CH_3CH_3}\right]$$

Assignment: Prove the above relation.

Polymerization

Addition polymerization of ethylene, propylene, styrene etc.

1. Initiation

$\mathrm{I} \xrightarrow{k_d} 2\mathrm{R}\cdot$: Rate determining step

$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{k_i} \mathrm{M}\cdot$

2. Propagation

$$\mathrm{M}\cdot + \mathrm{M} \xrightarrow{k_p} \mathrm{M}_2\cdot$$

$$\mathrm{M}_2\cdot + \mathrm{M} \longrightarrow \mathrm{M}_3\cdot$$

$$\vdots$$

$$\mathrm{M}_{n\text{-}1}\cdot + \mathrm{M} \longrightarrow \mathrm{M}_n\cdot$$

3. Termination

$$\mathrm{M}_n\cdot + \mathrm{M}_m\cdot \xrightarrow{k_\mathrm{t}} \mathrm{M}_{n+m}$$

$$\left(\frac{d[\mathrm{M}\cdot]}{dt}\right)_i = 2\,f\,k_d[\mathrm{I}]$$

f : the initiator efficiency factor

$$-\left(\frac{d[\mathrm{M}\cdot]}{dt}\right)_t = 2k_t[\mathrm{M}\cdot]^2$$

at the steady state

$$2\,fk_{\mathrm{d}}[\mathrm{I}] = 2k_{\mathrm{t}}[\mathrm{M}\cdot]^2$$

$$\therefore [\mathrm{M}\cdot] = \left(\frac{f\,k_{\mathrm{d}}}{k_{\mathrm{t}}}[\mathrm{I}]\right)^{\frac{1}{2}}$$

the propagation rate (the rate at which the monomer is consumed)

$$-\frac{d[\mathrm{M}]}{dt} = k_{\mathrm{p}}[\mathrm{M}\cdot][\mathrm{M}] = k_{\mathrm{p}}\left(\frac{f\,k_{\mathrm{d}}}{k_{\mathrm{t}}}\right)^{\frac{1}{2}}[\mathrm{I}]^{\frac{1}{2}}[\mathrm{M}]$$

The kinetic chain length (ν) is defined as the ratio of the rate of propagation to the rate of initiation. It is also defined as the ratio of the number of monomer units consumed per active center produced in the initiation step.

$$\nu = \frac{k_\mathrm{p}\left(\dfrac{f\,k_\mathrm{d}}{k_\mathrm{t}}\right)^{\frac{1}{2}}[\mathrm{I}]^{\frac{1}{2}}[\mathrm{M}]}{2\,f\,k_\mathrm{d}[\mathrm{I}]} = \frac{k_\mathrm{p}[\mathrm{M}]}{2\left(f\,k_\mathrm{d}k_\mathrm{t}[\mathrm{I}]\right)^{\frac{1}{2}}}$$

Step polymerization: e.g. polyamides (Nylon), polyesters

$$n\,\mathrm{H_2N(CH_2)_6NH_2} + n\,\mathrm{HOOC(CH_2)_4COOH}$$

$$\longrightarrow n\,\mathrm{H_2N(CH_2)_6NHCO(CH_2)_4COOH} + n\,\mathrm{H_2O}$$

$$\vdots$$

$$\longrightarrow \mathrm{H}\left[\mathrm{NH(CH_2)_6NHCO(CH_2)_4CO}\right]_n\mathrm{OH}$$

$$\frac{d[\mathrm{polymer}]}{dt} = -\frac{d[\mathrm{NH_2}]}{dt} = -\frac{d[\mathrm{COOH}]}{dt} = k[\mathrm{COOH}][\mathrm{NH_2}] \qquad (1)$$

Assumption: The rate constant for the condensation is independent of the chain length.

For most polymerizations, the concentration of the two functional groups are very nearly stoichiometric:

$$[\mathrm{COOH}] = [\mathrm{NH_2}] = [\mathrm{A}]$$

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

$$[\mathrm{A}] = \frac{[\mathrm{A}]_0}{1 + kt[\mathrm{A}]_0} \qquad (3)$$

where $[\mathrm{A}]_0$ is the initial concentration of [A].

The extent of reaction *p*

$$p = \frac{[\mathrm{A}]_0 - [\mathrm{A}]}{[\mathrm{A}]_0} \qquad (4)$$

Combining eq. (3) and (4),

$$\frac{1}{1-p} = 1 + kt[\mathrm{A}]_0 \qquad (5)$$

where p is equal to the probability that a group $[\mathrm{COOH} \text{ or } \mathrm{NH_2}]$ has formed a link to another molecule: $t = 0,\ p = 0;\ t = \infty,\ p = 1.$

The probability that a polymer consists of n monomers (n-mer) is therefore equal to the probability that it has $\underbrace{n-1 \text{ reacted groups}}_{\text{probability} = p^{n-1}}$ and $\underbrace{\text{one unreacted A group.}}_{\text{probability} = (1-p)}$

total probability $\boldsymbol{p_n}$

$$\boldsymbol{p_n = p^{n\text{-}1}(1-p)}$$

Normalizing the probability function

$$\sum_{n=1}^{\infty} p_n = (1-p)\sum_{n=1}^{\infty} p^{n-1} = \frac{1-p}{p}\sum_{n=1}^{\infty} p^n$$

$$= \left(\frac{1-p}{p}\right)\left\{\left(\sum_{n=0}^{\infty} p^n\right) - 1\right\} = 1$$

$$\sum_{n=0}^{\infty} p^n = \frac{1}{1-p}$$

Calculate the average chain length $\langle n \rangle$

$$\langle n \rangle = \sum_{n=1}^{\infty} n\, p_n = (1-p)\sum_{n=1}^{\infty} n\, p^{n\text{-}1}$$

$$= (1-p)\frac{d}{dp}\sum_{n=0}^{\infty} p^n = (1-p)\frac{d}{dp}\left(\frac{1}{1-p}\right)$$

$$= \frac{1}{1-p}$$

From eq. (5),

$$\frac{1}{1-p} = 1 + kt[\mathrm{A}]_0$$

$$\boldsymbol{\langle n \rangle = 1 + kt[\mathrm{A}]_0}$$

$$\langle n \rangle = \frac{1}{1-p}$$

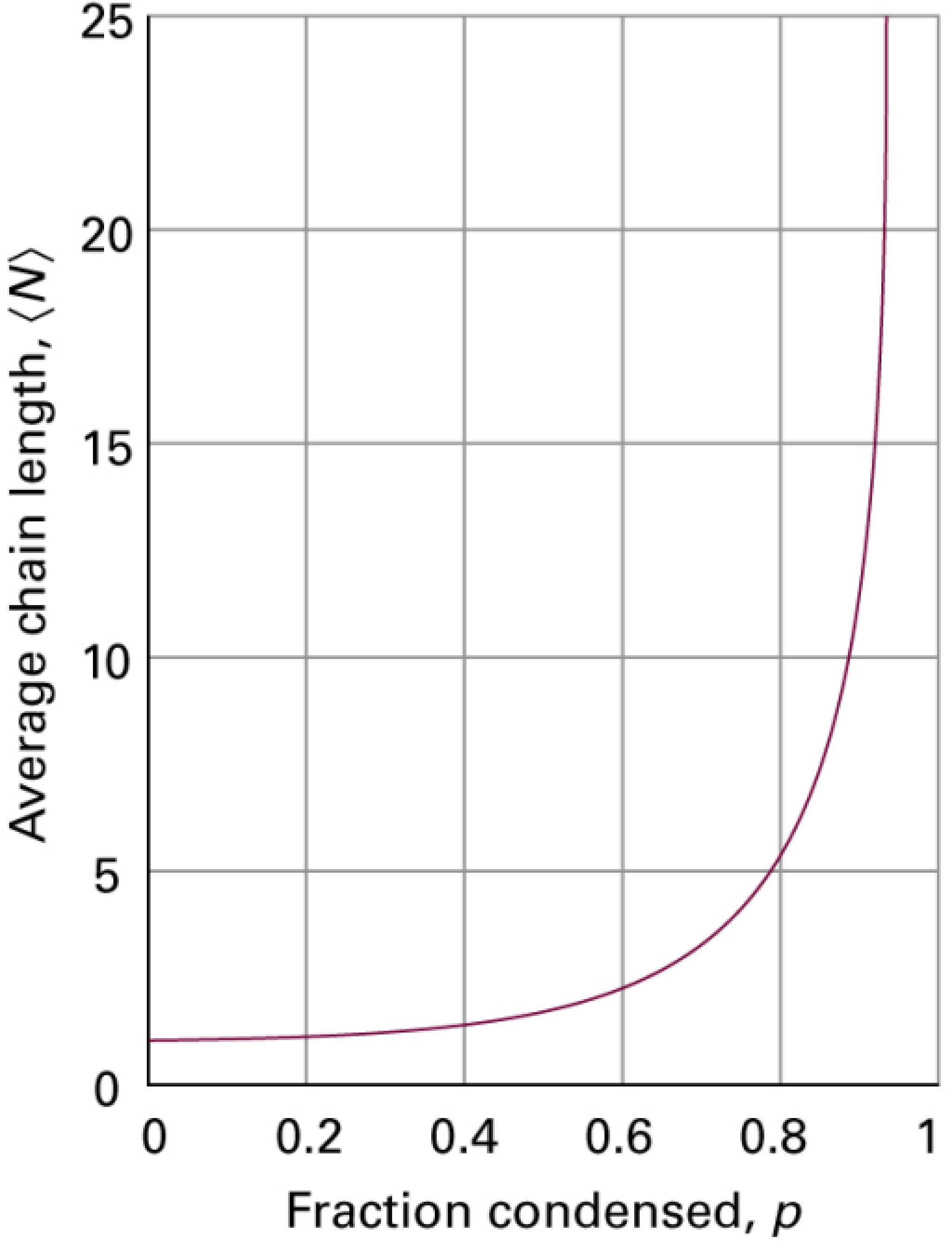


Figure 21.23
The average chain length of a polymer as a function of the fraction of reacted monomers, *p*.