Quiz4 (35)

(36) - 1

Review: Kinetics

Chapter 35, 36

Elementary Chemical Kinetics

Question: time scale, meachanism of a reaction

elementary reactions simple one-step reactions

$A \to B$

complex reactions reactions with a sequence of elementary reactions steps

for a correct mechanism: each step must be elementary

Thermodynamics yield only Gibbs ($p = const.$) or Helmholtz ($V = const.$) energies and equilibrium concentrations and thus equilibrium constant.

nothing about the speed of reactions

grafite ~~O~~ → diamond

Thermodynamics: grafite is stable,

diamond is not

but only kinetics tell that a grafite → ~~da~~diamond transition can need billions of years depending on P, and T

Fig. concentrations change with time

when an elementary reaction proceeds all reactant converts into product (no equilibrium in elementary reactions)

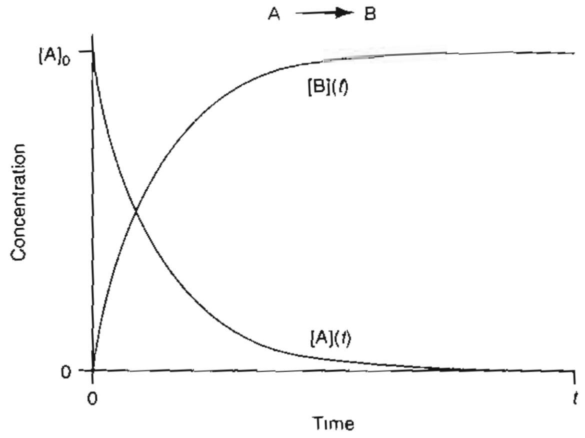


FIGURE 35.1
Concentration as a function of time for the conversion of reactant A into product B. The concentration of A at $t = 0$ is $[A]_0$, and the concentration of B is zero. As the reaction proceeds, the loss of A results in the production of B.

introduced in introductory chemistry: the conversion of reactant "A" into product "B." The figure illustrates that, as the reaction proceeds, a decrease in reactant concentration and a corresponding increase in product concentration are observed. One way to describe this process is to define the rate of concentration change with time, a quantity that is referred to as the reaction rate.

The central idea behind chemical kinetics is that by monitoring the rate at which chemical reactions occur and determining the dependence of this rate on system parameters such as temperature, concentration, and pressure, we can gain insight into the mechanism of the reaction. Experimental chemical kinetics includes the development of techniques that allow for the measurement and analysis of chemical reaction dynamics. In addition to experiments, theoretical work has been performed to understand reaction mechanisms and the underlying physics that govern the rates of chemical reactions. The synergy between experimental and theoretical chemical kinetics has provided for dramatic advances in this field.

35.2 Reaction Rates

Consider the following "generic" chemical reaction:

$$aA + bB + \ldots \rightarrow cC + dD + \ldots \tag{35.1}$$

In Equation (35.1), uppercase letters indicate a chemical species and lowercase letters represent the stoichiometric coefficient for the species in the balanced reaction. The number of moles of a species during any point of the reaction is given by

$$n_i = n_i^0 + \nu_i \xi \tag{35.2}$$

where n_i is the number of moles of species i at any given time during the reaction, n_i^0 is the number of moles of species i present before initiation of the reaction, ν_i is related to the stoichiometric coefficient of species i, and ξ the extent or advancement of the reaction equal to zero at the start of the reaction and one at completion. The advancement variable allows us to quantify the rate of the reaction with respect to all species, irrespective of stoichiometry (see the later discussion). For the reaction depicted in Equation (35.1), reactants will be consumed and products formed during the reaction. To ensure that this behavior is reflected in Equation (35.2), ν_i is set equal to -1 times the stoichiometric coefficient for reactants and is set equal to the stoichiometric coefficient for products.

The time evolution of the reactant and product concentrations is quantified by differentiating both sides of Equation (35.2) with respect to time:

$$\frac{dn_i}{dt} = \nu_i \frac{d\xi}{dt} \tag{35.3}$$

general reaction:

$$aA + bB + \cdots \rightarrow cC + dD + \cdots$$

lower case letter: stoichiometric coefficient of a chemical in a reaction

upper case letter: denote chemicals

left side: reactants

right side: products

$$n_i = n_i^0 + \nu_i \xi$$

n_i: number of moles of chemical i

n_i^0: initial value of n_i

ξ: extent of the reaction:

$\xi = 0$ at start of the reaction

$\xi = 1$ at end of reaction

reactants: $\nu_i = -1 \cdot$ stoich. coefficient of i

products: ν_i = stoich. coeff. of i

rectants are consumed

products are formed during reaction

differentiate n_i equation with respect to time t:

$$\frac{dn_i}{dt} = \nu_i \frac{d\xi}{dt}$$

reaction rate (Rate): Rate $= \dfrac{d\xi}{dt}$

$$\Rightarrow \quad \text{Rate} = \frac{1}{\nu_i} \frac{dn_i}{dt}$$

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

$$\text{Rate} = -\frac{1}{4}\frac{dn_{NO_2}}{dt} = -\frac{dn_{O_2}}{dt} = \frac{1}{2}\frac{dn_{N_2O_5}}{dt}$$

- sign at reactant make the rates positive for reactants $\frac{dn}{dt} < 0$, because n decreases with time

a given set of ν_i must be defined and kept that during all the reaction rate study

Rate defined with n, the number of moles is <u>extensive</u>, depends on size of the system

the rate is made ~~intensite~~ intensive (R) by division with the volume of the system:

$$R = \frac{\text{Rate}}{V} = \frac{1}{V}\left(\frac{1}{\nu_i}\frac{dn_i}{dt}\right) = \frac{1}{\nu_i}\frac{d[i]}{dt}$$

since $[i] = \frac{n_i}{V}$ $\underline{V = \text{const.}}$!

decomposition of acetaldehydei

$$CH_3CHO(g) \longrightarrow CH_4(g) + CO(g)$$

$$n_{CH_3CHO} = n^0_{CH_3CHO} - \xi$$

ideal gas law: $P_{CH_3CHO} = \frac{n_{CH_3CHO}}{V} RT$

$$= [CH_3CHO]RT$$

$$R = \frac{\text{Rate}}{V} = -\frac{1}{\nu_{CH_3CHO}}\frac{d[CH_3CHO]}{dt} = -\frac{1}{RT}\frac{dP_{CH_3CHO}}{dt}$$

homogeneous reaction happen all time c̄ of reaction in a single phase, liquid, solid, or gas (Chap. 35)

heterogeneous reâtions more than one phase

surface reactions for example (Chap. 36)

consider $A + B \to$ products

rate laws: empirical relation between the reactant concentration and the rate:

$$R = k[A]^{\alpha}[B]^{\beta}$$

k: rate constant

α, β orders of the reaction

α: order of the reaction with respect to A

$\alpha + \beta$: overall order of the reaction

k depends on p, T, but *not* on concentrations

orders can be integers or also fractions

orders have *nothing* to do with coefficients ν in the reaction equation and *must* be obtained by experiment (empirical)

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

experimentally found: $R = k[NO_2]^2[O_2]$

second order with respect to NO_2

first order with respect to O_2

third order overall

unit of R: always $\frac{M}{s}$

$\Rightarrow$ [k] different for different orders

$R = k$ 0 order, $[k] = Ms^{-1}$

$R = k[A]$ first order with respect to A

first overall order

$[R] = 1\ \frac{M}{s} = [k]\cdot M$

$\Rightarrow [k] = \frac{1}{s}$

$R = k[A]^2$ second order with respect to A

" " overall

$1\frac{M}{s} = [k]M^2 \Rightarrow [k] = \frac{1}{Ms}$

$R = k[A][B]$ first order with respect to A

" " " " " B

second overall order

$[k] = \frac{1}{Ms}$

$R = k[A][B][C]$ first order with respect to A

" " " " " B

" " " " " C

third order overall

$1\frac{M}{s} = [k]M^3 \Rightarrow [k] = \frac{1}{M^2 s}$

How to measure the rate of reaction ~~equations~~ ?

Example: $A \xrightarrow{k} B$

with $R = -\frac{d[A]}{dt} = k[A]$

for example $k = 40 \frac{1}{s}$

[A] is measured as f(t)

Fig. 35.2, p. 913

R = slope of tangent at [A](t) curve at a time t

R decreases wit increasing time :

$$R = k[A] = 40 \tfrac{1}{s} [A]$$

Figures $R_{t=0} = -\left.\frac{d[A]}{dt}\right|_{t=0} = 40 \frac{M}{s}$

$$R_{t=30ms} = -\left.\frac{d[A]}{dt}\right|_{t=30ms} = 12 \frac{M}{s}$$

thus rate R decreases with time

$$R_{t=0} = 40 s^{-1} [A]_{t=0} = 40 s^{-1} \cdot 1M = 40 \frac{M}{s}$$

t = 30 ms [A] has decreased to $[A]_{t=30ms} = 0.3 M$

$$R_{t=30ms} = 40 s^{-1} [A]_{t=30ms} = 40 s^{-1} \cdot 0.3 M = 12 \frac{M}{s}$$

1. method to define rate independent of time,
   initial rate method

   initial rate $R_{t=0}$ before much is changed in [A]

   normally: Rate = initial rate

   rate constant k : independent of time or conc.

TABLE 35.1 Relationship between Rate Law, Order, and the Rate Constant k*

Rate Law	Order	Units of k
$R = k$	Zero	$\mathrm{M\ s^{-1}}$
$R = k[\mathrm{A}]$	First order with respect to A First order overall	$\mathrm{s^{-1}}$
$R = k[\mathrm{A}]^2$	Second order with respect to A Second order overall	$\mathrm{M^{-1}\ s^{-1}}$
$R = k[\mathrm{A}][\mathrm{B}]$	First order with respect to A First order with respect to B Second order overall	$\mathrm{M^{-1}\ s^{-1}}$
$R = k[\mathrm{A}][\mathrm{B}][\mathrm{C}]$	First order with respect to A First order with respect to B First order with respect to C Third order overall	$\mathrm{M^{-2}\ s^{-1}}$

*In the units of k, M represents mol $\mathrm{L^{-1}}$ or moles per liter.

The rate of this reaction in terms of [A] is given by

$$R = -\frac{d[\mathrm{A}]}{dt} \tag{35.12}$$

Furthermore, suppose experiments demonstrate that at a certain temperature and pressure the reaction is first order in A, first order overall, and $k = 40\ \mathrm{s^{-1}}$ so that

$$R = k[\mathrm{A}] = (40\ \mathrm{s^{-1}})[\mathrm{A}]$$

Equation (35.12) states that the rate of the reaction is equal to the negative of the time derivative of [A]. Imagine that we perform an experiment in which [A] is measured as a function of time as shown in Figure 35.2. The derivative in Equation (35.12) is simply the slope of the tangent for the concentration curve at a specific time. Therefore, the reaction rate will depend on the time at which the rate is determined. Figure 35.2 presents a measurement of the rate at two time points, $t = 0$ ms(1 ms $= 10^{-3}$ s) and $t = 30$ ms. At $t = 0$ ms, the reaction rate is given by the negative of the slope of the line corresponding to the change in [A] with time, per Equation (35.12):

$$R_{t=0} = -\frac{d[\mathrm{A}]}{dt} = 40\ \mathrm{M\,s^{-1}}$$

However, when measured at 30 ms the rate is

$$R_{t=30\,\mathrm{ms}} = -\frac{d[\mathrm{A}]}{dt} = 12\ \mathrm{M\,s^{-1}}$$

Notice that the reaction rate is decreasing with time. This behavior is a direct consequence of the change of [A] as a function of time, as expected from the rate law of Equation (35.8). Specifically, at $t = 0$,

$$R_{t=0} = 40\ \mathrm{s^{-1}}[\mathrm{A}]_{t=0} = 40\ \mathrm{s^{-1}}(1\ \mathrm{M}) = 40\ \mathrm{M\,s^{-1}}$$

However, by $t = 30$ ms the concentration of A has decreased to 0.3 M so that the rate is

$$R_{t=30\,\mathrm{ms}} = 40\ \mathrm{s^{-1}}[\mathrm{A}]_{t=30\,\mathrm{ms}} = 40\ \mathrm{s^{-1}}(0.3\ \mathrm{M}) = 12\ \mathrm{M\,s^{-1}}$$

This difference in rates brings to the forefront an important issue in kinetics: how does one define a reaction rate if the rate changes with time? One convention is to define the rate before the reactant concentrations have undergone any substantial change from their initial values. The reaction rate obtained under such conditions is known as the **initial rate.** The initial rate in the previous example is that determined at $t = 0$. In the

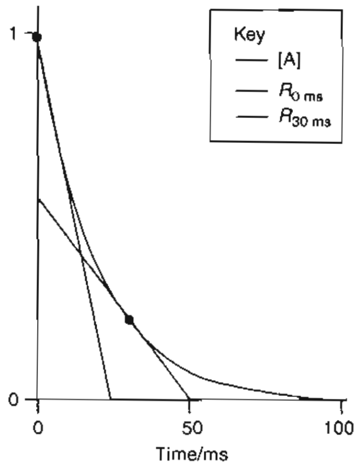


FIGURE 35.2
Measurement of the reaction rate. The concentration of reactant A as a function of time is presented. The rate R is equal to the slope of the tangent of this curve. This slope depends on the time at which the tangent is determined. The tangent determined 30 ms into the reaction is presented as the blue line, and the tangent at $t = 0$ is presented as the purple line.

2. Determination of orders of a reaction by the isolation method

$$A + B \xrightarrow{k} C$$

$$R = k\,[A]^{\alpha}\,[B]^{\beta}$$

measurement of R at 1 set of ([A], [B]) not enough → 1 equation for 2 unknowns α, β

What sets of conc. to use to obtain α, β?

for example : isolation method:

do the reaction with a very large concentration (excess) the other one with a very small conc.

only the small conc. reactant will change its concentration

for example $[A]_0 = 1.00\,M$, $[B]_0 = 0.01\,M$

when all $[B]_0$ is used up, reaction will stop ($R=0$)

but when 0.01 M of B is used, A will have changed only to 0.99 M, a negligible change

$\Rightarrow [\;]_{excess}$ = const. in relatively long time

then $R = k'[B]^{\beta}$ with $k' = k\,[A]^{\alpha}_{excess}$

$\Rightarrow$ R depends only on B in this case

so R at different [B] → order with respect to B

repeat with $[B]_{excess}$, $[A]_{small}$ → α

2) Method of initial rates

initial concentration of only 1 reactant is changed, others kept const., and initial rates measured

example rate R_1 is measured at $[A]_1$, $[B]_0$ and R_2 at $[A]_2$, $[B]_0$, $[B]$ = const. (k = const.)

$$\rightarrow \frac{R_1}{R_2} = \frac{k\,[A]_1^{\alpha}\,[B]_0^{\beta}}{k\,[A]_2^{\alpha}\,[B]_0^{\beta}} = \left(\frac{[A_0]_1}{[A]_2}\right)^{\alpha}$$

$$\ln\left(\frac{R_1}{R_2}\right) = \alpha \ln \frac{[A]_1}{[A]_2} \rightarrow \alpha$$

to get β: keep $[A]_0 = [A]_0$ = const.

	$[A]$ (M)	$[B]$ (M)	R_0 ($\frac{M}{s}$)
1	$2.30 \cdot 10^{-4}$	$3.10 \cdot 10^{-5}$	$5.25 \cdot 10^{-4}$
2	$4.60 \cdot 10^{-4}$	$6.20 \cdot 10^{-5}$	$4.20 \cdot 10^{-3}$
3	$9.20 \cdot 10^{-4}$	$6.20 \cdot 10^{-5}$	$1.68 \cdot 10^{-2}$

$$R = k\,[A]^{\alpha}\,[B]^{\beta}$$

find two equal concentrations, e.g. (2), (3)

$[B]_0 = 6.20 \cdot 10^{-5}$ M in both lines and thus cancels

$$\Rightarrow \ln \frac{R_2}{R_3} = \alpha \ln \frac{[A]_2}{[A]_3}$$

$$\ln \frac{4.20 \cdot 10^{-3}}{1.68 \cdot 10^{-2}} = \alpha \ln \frac{4.60 \cdot 10^{-4}}{9.20 \cdot 10^{-4}}$$

$$-1.386 = \alpha \cdot (-0.693)$$

$$\underline{\alpha = 2}$$

now α is known, so any two rates can be used for β, e.g. (1), (2)

$$\frac{R_1}{R_2} = \frac{k\,[A]_1^2\,[B]_1^{\beta}}{k\,[A]_2^2\,[B]_2^{\beta}} \qquad k = \text{const.}$$

$$\frac{R_1}{R_2} = \frac{5{,}25\cdot10^{-4}}{4{,}20\cdot10^{-3}} = \left(\frac{2{,}30\cdot10^{-4}}{4{,}60\cdot10^{-4}}\right)^2 \left(\frac{3{,}10\cdot10^{-5}}{6{,}20\cdot10^{-5}}\right)^{\beta}$$

$$\left(\frac{5{,}25\cdot10^{-4}}{4{,}20\cdot10^{-3}}\right)\cdot\left(\frac{4{,}60\cdot10^{-4}}{2{,}30\cdot10^{-4}}\right)^2 = \frac{1}{2}$$

$$0{,}500 = (0{,}500)^{\beta}$$

$$\Rightarrow \beta = 1$$

second order in A, first order in B

third order overall

now any line can be used for k

e.g. (1)

$$R_1 = k\,[A]_1^2\,[B]_1$$

$$5{,}25\cdot10^{-4}\,\frac{M}{s} = k\,(2{,}30\cdot10^{-4}\,M)^2\cdot 3{,}10\cdot10^{-5}\,M$$

$$\rightarrow k = 3{,}17\cdot10^{8}\,\frac{1}{M^2 s^2}, \quad R = 3{,}17\cdot10^{8}\,\frac{1}{M^2 s^2}\,[A]^2[B]$$

how to actually measure rates?

1. chemical methods

take samples out of the reaction mixture and stop the reaction in them, the do analysis

stopping of reaction e.g. by rapid cooking or be adding a chemical ~~with~~ which removes a reactant chemical methods can only be used for slow reactions

Physical Methods a property of the reaction mixture is measured at different times

example: P or V

$$PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$$

1 PCl_5 gas molecule produces 2 other gas molecules

⇒ system pressure will increase with time, when reaction done in closed container with const. volume

or also: spectroscopic methods:

electronic absorption of a molecule and Lambert-Beer law

infrared or Raman spectroscopy to measure vibrational transitions of ~~a~~ reactant or product

also NMR spectroscopy can be used

reaction times of about 1 ms (10^{-3} s):

stopped flow methods

Fig 35.3, p. 916

reactants A and B in different syringes

pressing the syringes: reactants are mixed in a mixing chamber

and is measured at a distance from the mixing chamber. different distant = different time for monitoring the progress of a reaction. For example, consider the thermal decomposition of PCl_5:

$$PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$$

As the reaction proceeds, for every gaseous PCl_5 molecule that decays, two gaseous product molecules are formed. Therefore, the total system pressure will increase as the reaction proceeds in a container with fixed volume. Measurement of this pressure increase as a function of time provides information on the reaction kinetics.

More complex physical methods involve techniques that are capable of monitoring the concentration of an individual species as a function of time. Many of the spectroscopic techniques described in this text are extremely useful for such measurements. For example, electronic absorption measurements can be performed in which the concentration of a species is monitored using the electronic absorption of a molecule and the Beer–Lambert law. Vibrational spectroscopic measurements using infrared absorption and Raman scattering can be employed to monitor vibrational transitions of reactants or products providing information on their consumption or production. Finally, NMR spectroscopy is a useful technique for following the reaction kinetics of complex systems.

The challenge in chemical kinetics is to perform measurements with sufficient time resolution to monitor the chemistry of interest. If the reaction is slow (seconds or longer), then the chemical methods just described can be used to monitor the kinetics. However, many chemical reactions occur on timescales as short as picoseconds (10^{-12} s) and femtoseconds (10^{-15} s). Reactions occurring on these short timescales are most easily studied using physical methods.

For reactions that occur on timescales as short as 1 ms (10^{-3} s), **stopped-flow techniques** provide a convenient method by which to measure solution phase reactions. These techniques are exceptionally popular for biochemical studies. A stopped-flow experiment is illustrated in Figure 35.3. Two reactants (A and B) are held in reservoirs connected to a syringe pump. The reaction is initiated by depressing the reactant syringes, and the reactants are mixed at the junction indicated in the figure. The reaction is monitored by observing the change in absorbance of the reaction mixture as a function of time. The temporal resolutions of stopped-flow techniques are generally limited by the time it takes for the reactants to mix.

Reactions that can be triggered by light are studied using **flash photolysis techniques.** In flash photolysis, the sample is exposed to a temporal pulse of light that initiates the reaction. Ultrafast light pulses as short as 10 femtoseconds (10 fs = 10^{-14} s) in the visible region of the electromagnetic spectrum are available such that reaction dynamics on this extremely short or ultrafast timescale can be studied. For reference, a 3000 cm^{-1} vibrational mode has a period of roughly 10 fs; therefore, using short optical pulses reactions can be initiated on the same timescale as vibrational molecular motion, and this capability has opened up many exciting fields in chemical kinetics, referred to as **femtochemistry.** This capability has been used to determine the ultrafast chemical kinetics associated with vision, photosynthesis, atmospheric processes, and charge-carrier dynamics in semiconductors. Very recently, femtochemical techniques have been extended to the X-ray region of the spectrum, allowing for the direct interrogation of photoinitiated structural changes using time-resolved scattering techniques. Recent references to some of this work are included in the "For Further Reading" section at the end of this chapter.

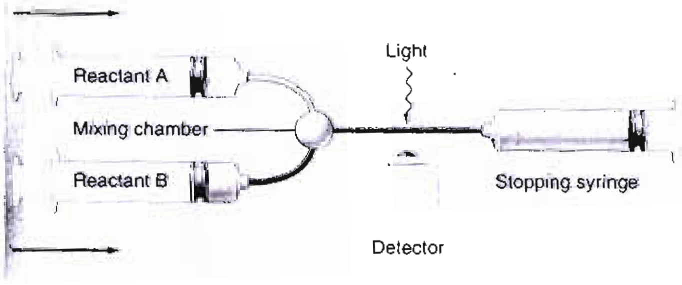


FIGURE 35.3
Schematic of a stopped-flow experiment. Two reactants are rapidly introduced into the mixing chamber by syringes. After mixing, the reaction kinetics are monitored by observing the change in sample concentration versus time, in this example by measuring the absorption of light as a function of time after mixing.

time-limit: mixing time!

reaction start by pulses of light possible
→ flash photolysis

nowadays light pulses about 10 fs (10^{-14} s)
long can be done
→ femto chemistry: reaction rates on fs scale

e.g. vision, photosynthesis, atmospheric reactions,
charge-carrier dynamis in semiconductors

nowadays also with X-ray pulses possible

NMR for µs (10^{-6} s) time scales

perturbation-relaxation methods avoids problems with mixing time

reaction mixture in equilibrium (no mixing)
then perturbation with fast jump of T,
fast P change, fast pH change

stoichiometric coefficients in overall reaction equation ≠ orders of reaction
because the overall equation is a combination of mechanism steps

mechanism = sequence of elementary one-step reactions leading from ~~pr~~ reactants (R) to products (P)

rate law and orders depend on mechanism

molecularity: no. of reactant molecules that
must collide to perform a
reaction step

only 1 reactant involved:
unimolecular reactions, e.g. $I_2 \xrightarrow{k} 2I$

interaction of 2 reactants in a step
→ ~~by~~ bimolecular reaction
e.g. $NO + O_3 \xrightarrow{k} NO_2 + O_2$ elementary
bimolecular if elementary!
for unimolecular dissociation of I_2:

$$R = -\frac{d[I_2]}{dt} = k[I_2]$$

bimolecular:

$$R = -\frac{d[NO]}{dt} = k[NO][O_3]$$

elementary reactions: order = stoichiometric coefficient
only true for elementary reactions

common problem: identify the correct mechanism among several possible ones

general rule in kinetics

One can proof with kinetics that a mechanism is wrong, but
it is never possible to prove the a menism is "the correct one"

a reaction A → P first order as written
but could also be
A → I (intermediate)
I → P, if so, I must be observed

if A→I is ~~a~~ slow, but I→P fast

then each I, slowly formed will react fast to P

⇒ [I] will be small so that I is difficult to detect

(see below) kinetics of formation of P is exactly *equal* for the one-step and for the two-step ~~mechanims~~ mechanism

⇒ one cannot prove one of the possibilities as the correct mechanism
usual assumption
most easy mechanism that gives correct rate laws and orders is correct unless otherwise proven wrong

Integrated Rate Laws

Sometime it is difficult to measure initial rates (instable reactants can react too fast to measure really at start of reaction)

Then ~~on can~~ one can solve the differential rate equations for a set of orders to get the corresponding time laws *or* integrated rate law expression and compare the results with experimentally determined time laws.

solution not always possible

⇒ numerical methods needed (below)

Firstorder reactions

$A \xrightarrow{k} P$ elementary

if firstorder: $R = -\frac{d[A]}{dt} = k[A]$

→ differential equation

1. homogeneous: all terms contain [A]
2. linear: $\frac{d[A]}{dt} = -k[A] \quad \Big| \times \frac{dt}{[A]}$

$$\frac{d[A]}{[A]} = -k\, dt$$

integration from 0 to t, thus $[A]_0$ to $[A]$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt \qquad \int \frac{dx}{x} = \ln x + C$$

$$\ln[A] - \ln[A]_0 = \ln\frac{[A]}{[A]_0} = -k(t-0) = -kt$$

$$\Rightarrow \frac{[A]}{[A]_0} = e^{-kt} \quad ; \quad [A] = [A]_0 e^{-kt}$$

at all times $[A]_0 = [A] + [P]$

since both [A] and [P] are parts of $[A]_0$

$$[P] = [A]_0 - [A]$$

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

taking ln ⇒ $\ln[A] = \ln[A]_0 - kt$

⇒ plot ln [A] vs t

if 1. order: straight line, slope ~~k~~ = −k

Fig. 35.4 p. 920

$\frac{[A]}{[A]_0}$ vs t → ~~ln~~ exp functions

and $\ln\frac{[A]}{[A]_0}$ vs t: straight lines, slope $= -k$

or $\ln[A]$ vs t: straight line, intercept $= \ln[A]_0$
slope $= -k$

must be done over long time to prove the 1. order behavior

<u>half-life</u> τ time for $[A]$ to decrease from $[A]_0$ to $\frac{1}{2}[A]_0$

take time law, but τ for t and $\frac{1}{2}[A]_0$ for $[A]$

$$-k\tau = -kt_{1/2} = -\ln\frac{[A]_0/2}{[A]_0} = -\ln 2$$

$$\Rightarrow t_{1/2} = \frac{\ln 2}{k}$$

only for 1. order: $t_{1/2}$ does not depend on $[A]_0$

troposphere: N_2O_5 decay, 1. order

$t_{1/2} = 2.05 \cdot 10^4\,s$

how long for $[N_2O_5]$ to decay to 60% $[N_2O_5]_0$

$$k = \frac{\ln 2}{t_{12}} = \frac{\ln 2}{2.05 \cdot 10^{+4}\,s} = 3.38 \cdot 10^{-5}\,s^{-1}$$

60% decay

$$\rightarrow [N_2O_5] = 0.6[N_2O_5]_0 = (N_2O_5)_0\, e^{-3.38 \cdot 10^{-5} s^{-1} t}$$

$$t_{60\%} = \frac{-\ln(0.6)}{3.38 \cdot 10^{-5}\,s^{-1}} = 1.51 \cdot 10^4\,s$$

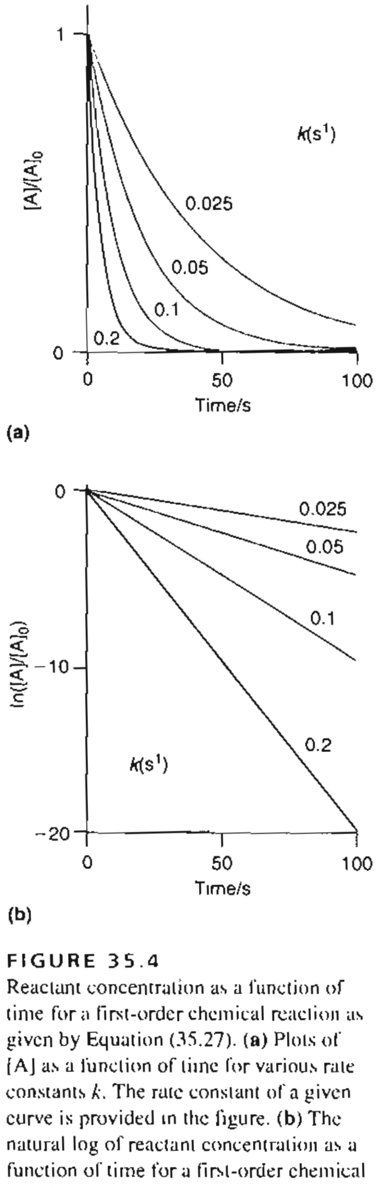


FIGURE 35.4
Reactant concentration as a function of time for a first-order chemical reaction as given by Equation (35.27). **(a)** Plots of [A] as a function of time for various rate constants k. The rate constant of a given curve is provided in the figure. **(b)** The natural log of reactant concentration as a function of time for a first-order chemical reaction as given by Equation (35.28).

Equation (35.29) predicts that for a first-order reaction, a plot of the natural log of the reactant concentration versus time will be a straight line of slope $-k$ and y intercept equal to the natural log of the initial concentration. Figure 35.4 provides a comparison of the concentration dependences predicted by Equations (35.27) and (35.29) for first-order reactions. It is important to note that the comparison of experimental data to an integrated rate law expression requires that the variation in concentration with time be accurately known over a wide range of reaction times to determine if the reaction indeed follows a certain order dependence.

35.5.2 Half-Life and First-Order Reactions

The time it takes for the reactant concentration to decrease to one-half of its initial value is called the **half-life** of the reaction and is denoted as $t_{1/2}$. For a first-order reaction, substitution of the definition for $t_{1/2}$ into Equation (35.29) results in the following:

$$-kt_{1/2} = \ln\left(\frac{[A]_0/2}{[A]_0}\right) = -\ln 2$$

$$t_{1/2} = \frac{\ln 2}{k} \tag{35.30}$$

Notice that the half-life for a first-order reaction is independent of the initial concentration, and only the rate constant of the reaction influences $t_{1/2}$.

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 (35.27):

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

$$0.6 = e^{-(3.38 \times 10^{-5}\ \text{s}^{-1})t}$$

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

Radioactive decay of unstable nuclear isotopes is an important example of a first-order process. The decay rate is usually stated as the half-life. Example Problem 35.4 demonstrates the use of radioactive decay in determining the age of a carbon-containing material.

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?

$^{14}_{12}C$: Carbon - 14 radioactive
with $t_{1/2} = 5760$ years $= 5760\,y$

as long as a plant e.g. is alive, decayed C-14 is taken up from CO_2 in air
and the C-14 level is constant

natural, constant C-14 level corresponds to
$15,3\ \frac{decays}{min}$

after death no more C-14 exchange with surroundings.

dead plant material (fossilized) shows
$2,4\ \frac{decays}{min}$ (counts on a Geiger counter) when did the ~~w~~ plant die?

$$\frac{[^{14}C]}{[^{14}C]_0} = \frac{2,40\ min^{-1}}{15.3\ min^{-1}} = 0,157$$

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{5760\ years}$$

$$t_{1/2} = 5760\ years \cdot \frac{365,25\ days}{year} \cdot 24\ \frac{hour}{day} \cdot 3600\ \frac{s}{day}$$

$$\uparrow$$

$$60\ \frac{min}{hour} \cdot 60\ \frac{\cancel{hour}\ min}{s}$$

$$= 1,82 \cdot 10^{11}\,s$$

$$k = \frac{\ln 2}{1,82 \cdot 10^{11}\,s} = 3,81 \cdot 10^{-12}\ \frac{1}{s}$$

1. order decays

$$\frac{[^{14}C]}{[^{14}C]_0} = e^{-kt}$$

$$\ln \frac{[^{14}C]}{[^{14}C]_0} = -kt$$

$$t = -\frac{1}{k} \ln \frac{[^{14}C]}{[^{14}C]_0} = \frac{\ln (0{,}157)}{3{,}81 \cdot 10^{-12}\,s}$$

$$= 4{,}86 \cdot 10^{11}\,s = 15400 \text{ years}$$

<u>2. order reactions (type I)</u>

type I: $2A \xrightarrow{k} P \quad \nu_A = -2$

$$R = \frac{1}{\nu_A} \frac{d[A]}{dt} = -\frac{1}{2} \frac{d[A]}{dt}$$

$$-\frac{d[A]}{dt} = 2k\,[A]^2 = k_{eff}\,[A]^2$$

$$k_{eff} = 2k$$

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

$$\int_{x_0}^{x} \frac{dx}{x^2} = -\frac{1}{x}\Big|_{x_0}^{x} = -\left(\frac{1}{x} - \frac{1}{x_0}\right)$$

$$\int x^n\,dt = \frac{x^{n+1}}{n+1} + C$$

$$-\int_{[A]_0}^{[A]} \int \frac{d[A]}{[A]^2} = -\left(-\frac{1}{[A]}\Big|_{[A]_0}^{[A]}\right)$$

$$= \frac{1}{[A]}\Big|_{[A]_0}^{[A]} = \frac{1}{[A]} - \frac{1}{[A]_0} = 2kt$$

$$\Rightarrow \quad \frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$$

half-life: $\dfrac{1}{\frac{1}{2}[A]_0} = \dfrac{1}{[A]_0} + 2k t_{1/2}$

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

$$\Rightarrow t_{1/2} = \frac{1}{2k[A]_0} = \frac{1}{k_{eff}[A]_0}$$

$\Rightarrow$ $t_{1/2}$ ~~decre~~ increases with time, since the starting $[A]_0$ decreases with time

2. order, type II

---

type II: $A + B \xrightarrow{k} P$

$$R \doteq -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B]$$

$$\Rightarrow \quad [A]_0 - [A] = [B]_0 - [B]$$

$$[B] = [B]_0 - [A]_0 + [A]$$

$$[B] = \Delta + [A] \qquad \Delta = [B]_0 - [A]_0$$

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

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A](\Delta + [A])} = -k\,dt$$

formula collection: $\displaystyle\int \frac{dx}{x(c+x)} = -\frac{1}{c}\ln\frac{c+x}{x}$

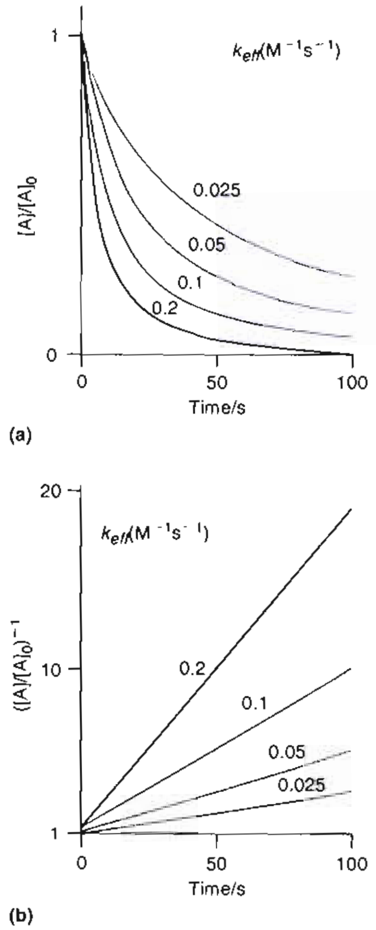


FIGURE 35.5
Reactant concentration as a function of time for a type I second-order chemical reaction. **(a)** Plots of [A] as a function of time for various rate constants. The rate constant of a given curve is provided in the figure. **(b)** The inverse of reactant concentration as a function of time as given by Equation (35.35).

Equation (35.35) demonstrates that for a second-order reaction, a plot of the inverse of reactant concentration versus time will result in a straight line having a slope of k_{eff} and y intercept of $1/[A]_0$. Figure 35.5 presents a comparison between [A] versus time for a second-order reaction and $1/[A]$ versus time. The linear behavior predicted by Equation (35.35) is evident.

Half-Life and Reactions of Second Order (Type I)

Recall that "half-life" refers to when the concentration of a reactant is half of its initial value. With this definition, the half-life for a type I second-order reaction is

$$t_{1/2} = \frac{1}{k_{eff}[A]_0} \tag{35.36}$$

In contrast to first-order reactions, the half-life for a second-order reaction is dependent on the initial concentration of reactant, with an increase in initial concentration resulting in a decrease in $t_{1/2}$. This behavior is consistent with a first-order reaction occurring through a unimolecular process, whereas the second-order reaction is a bimolecular process that involves the interaction of two species (for example, through collision). As such, the concentration dependence of the reaction rate is expected.

Second-Order Reaction (Type II)

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

$$A + B \xrightarrow{k} P \tag{35.37}$$

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

$$R = k[A][B] \tag{35.38}$$

In addition, the rate with respect to the time derivative of the reactant concentrations is

$$R = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} \tag{35.39}$$

The loss rate for the reactants is equal, so

$$\begin{aligned} [A]_0 - [A] &= [B]_0 - [B] \\ [B]_0 - [A]_0 + [A] &= [B] \\ \Delta + [A] &= [B] \end{aligned} \tag{35.40}$$

Equation (35.40) provides a definition for [B] in terms of [A] and the difference in initial concentration, $[B]_0 - [A]_0$, denoted as Δ. Beginning with the case where $\Delta \neq 0$ (that is, the initial concentrations of A and B are not the same) setting Equations (35.38) and (35.39) equal results in the following expression:

$$\frac{d[A]}{dt} = -k[A][B] = -k[A](\Delta + [A])$$

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

Next, the solution to an integral of the previous form is given by

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

Using this solution, the integrated rate law expression becomes

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

$$\Rightarrow -\frac{1}{\Delta}\ln\frac{\Delta+[A]}{[A]}\Big|_{[A]_0}^{[A]} = -kt$$

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

~~$\frac{1}{[B]_0-[A]_0}$ ln~~ $\Delta + [A] = B$

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

$\frac{1}{[B]_0-[A]_0}\ln\frac{[B][A]_0}{[A][B]_0} = kt$ if 2. order, $[A]_0 \neq [B]_0$

if $[A]_0 = [B]_0$, then $[A] = [B]$ at all times and it corresponds to case I!

no $t_{1/2}$ definition applies, only if $[A]_0 = [B]_0$ or $\frac{[A]_0}{2}$ and $\frac{[B]_0}{2}$ will not occur at the same time $t_{1/2}$

if integration not possible ⇒ numerical approaches to get $[A] = f(t)$ to compare with the order model to check

1. order examples $A \xrightarrow{k} P$

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

dt infinitesimally small = $dt \to 0$

if $dt = \Delta t$, small but not infinitesimally:

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

change of [A], $\Delta[A]$ in small Δt

$$\Delta[A] = -k\Delta t[A]$$

[A] is $[A]_t$ at a given time

$$\Rightarrow [A]_{t+\Delta t} = [A]_t + \Delta[A]$$
$$= [A]_t - k[A]_t \cdot \Delta t$$
$$= [A]_t(1 - k\Delta t)$$ Euler's method

Fig. 35.6, p 123 approximation

approximation gets better when Δt decreases

Fig. 35.7, p 124 ln [A] vs t

up-most straight line: exact solution for 1. order

points results of numerical approach for

Δt = 8 ms, 5 ms and 1 ms

if Δt must be too small, it can be that

$\Delta[A]$ too small to measure

then the better Runge-Kutta method

~~an~~ can be used which allows larger Δt

for the same accuracy in $[A] = f(t)$

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

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

$$\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]/[B]_0}{[A]/[A]_0}\right) = kt \qquad (35.41)$$

Equation (35.41) is applicable when $[B]_0 \neq [A]_0$. For the case where $[B]_0 = [A]_0$, the concentrations of [A] and [B] reduce to the expression for a second-order reaction of type I with $k_{eff} = k$. The time evolution in reactant concentrations depends on the amount of each reactant present. Finally, the concept of half-life does not apply to second-order reactions of type II. Unless the reactants are mixed in stoichiometric proportions (1:1 for the case discussed in this section), the concentrations of both species will not be 1/2 their initial concentrations at the identical time.

SUPPLEMENTAL

35.6 Numerical Approaches

For the simple reactions outlined in the preceding section, an integrated rate law expression can be readily determined. However, there is a wide variety of kinetic problems for which an integrated rate law expression cannot be obtained. How can one compare a kinetic model with experiment in the absence of an integrated rate law? In such cases, numerical methods provide another approach by which to determine the time evolution in concentrations predicted by a kinetic model. To illustrate this approach, consider the following first-order reaction:

$$A \xrightarrow{k} P \qquad (35.42)$$

The differential rate expression for this reaction is

$$\frac{d[A]}{dt} = -k[A] \qquad (35.43)$$

The time derivative corresponds to the change in [A] for a time duration that is infinitesimally small. Using this idea, we can state that for a finite time duration Δt, the change in [A] is given by

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

$$\Delta[A] = -\Delta t(k[A]) \qquad (35.44)$$

In Equation (35.44), [A] is the concentration of [A] at a specific time. Therefore, we can use this equation to determine the change in the concentration of A, or $\Delta[A]$, over a time period Δt and then use this concentration change to determine the concentration at the end of the time period. This new concentration can be used to determine the subsequent change in [A] over the next time period, and this process is continued until the reaction is complete. Mathematically,

$$\begin{aligned}[A]_{t+\Delta t} &= [A]_t + \Delta[A] \\ &= [A]_t - k\Delta t[A]_t \qquad (35.45)\end{aligned}$$

In Equation (35.45), $[A]_t$ is the concentration at the beginning of the time interval, and $[A]_{t+\Delta t}$ is the concentration at the end of the time interval. This process is illustrated in Figure 35.6. In the figure, the initial concentration is used to determine $\Delta[A]$ over the time interval Δt. The concentration at this next time point, $[A]_1$, is used to determine

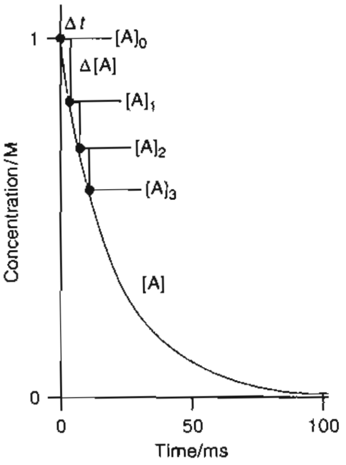


FIGURE 35.6
Schematic representation of the numerical evaluation of a rate law.

$\Delta[A]$ over the next time interval, resulting in concentration $[A]_2$. This process is continued until the entire concentration profile is evaluated.

The specific example discussed here is representative of the general approach to numerically integrating differential equations, known as **Euler's method.** Application of Euler's method requires some knowledge of the timescale of interest, and then selection of a time interval Δt that is sufficiently small to capture the evolution in concentration. Figure 35.7 presents a comparison of the reactant concentration determined using the integrated rate law expression for a first-order reaction to that determined numerically for three different choices for Δt. The figure illustrates that the accuracy of this method is highly dependent on an appropriate choice for Δt. In practice, convergence of the numerical model is demonstrated by reducing Δt and observing that the predicted evolution in concentrations does not change.

The numerical method can be applied to any kinetic process for which differential rate expressions can be prescribed. Euler's method provides the most straightforward way by which to predict how reactant and product concentrations will vary for a specific kinetic scheme. However, this method is "brute force" in that a sufficiently small time step must be chosen to accurately capture the slope of the concentration, and the time steps may be quite small, requiring a large number of iterations in order to reproduce the full time course of the reaction. As such, Euler's method can be computationally demanding. More elegant approaches, such as the Runge–Kutta method, exist that allow for larger time steps to be performed in numerical evaluations, and the interested reader is encouraged to investigate these approaches.

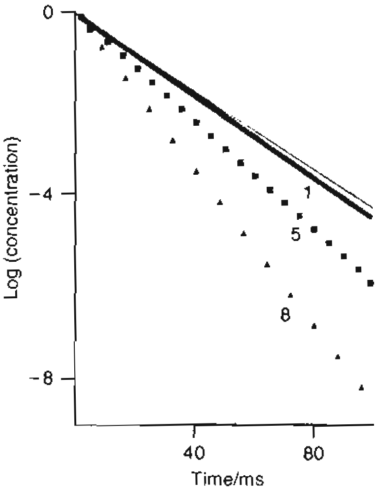


FIGURE 35.7
Comparison of the numerical approximation method to the integrated rate law expression for a first-order reaction. The rate constant for the reaction is $0.1\ \mathrm{M\ s^{-1}}$. The time evolution in reactant concentration determined by the integrated rate law expression of Equation (35.27) is shown as the solid red line. Comparison to three numerical approximations is given, and the size of the time step (in ms) employed for each approximation is indicated. Notice the improvement in the numerical approximation as the time step is decreased.

35.7 Sequential First-Order Reactions

Many chemical reactions occur in a series of steps in which reactants are transformed into products through multiple sequential elementary reaction steps. For example, consider the following **sequential reaction** scheme:

$$A \xrightarrow{k_A} I \xrightarrow{k_I} P \tag{35.46}$$

In this scheme, the reactant A decays to form intermediate I, and this intermediate undergoes subsequent decay resulting in the formation of product P. Species I is known as an **intermediate.** The sequential reaction scheme illustrated in Equation (35.46) involves a series of elementary first-order reactions. Recognizing this, the differential rate expressions for each species can be written as follows:

$$\frac{d[A]}{dt} = -k_A[A] \tag{35.47}$$

$$\frac{d[I]}{dt} = k_A[A] - k_I[I] \tag{35.48}$$

$$\frac{d[P]}{dt} = k_I[I] \tag{35.49}$$

These expressions follow naturally from the elementary reaction steps in which a given species participates. For example, the decay of A occurs in the first step of the reaction. The decay is a first-order process, consistent with the differential rate expression in Equation (35.47). The formation of product P is also a first-order process per Equation (35.49). The expression of Equation (35.48) for intermediate I reflects the fact that I is involved in both elementary reaction steps, the decay of A ($k_A[A]$), and the formation of P ($-k_I[I]$). Correspondingly, the differential rate expression for [I] is the sum of the rates associated with these two reaction steps. To determine the concentrations of each species as a function of time, we begin with Equation (35.47), which can be readily integrated given a set of initial concentrations. Let only the reactant A be present at $t = 0$ such that

$$[A]_0 \neq 0;\ [I]_0 = 0;\ [P]_0 = 0 \tag{35.50}$$

1. order reactions in sequence

(sequential)

I: intermediate

intermediates are no reactants and no products, but are formed in 1 or more reaction steps and consumed in 1 or more reaction steps

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

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

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

positive formation term of I

negative consumption term of I

$$\frac{d[P]}{dt} = k_I[I]$$

decay of A forms I, decay of I forms P

$t=0$: only A in the reaction mixture

$$[A]_0 \neq 0, \quad [I]_0 = [P]_0 = 0$$

$\Rightarrow$ time law for [A] same as before for 1. order reactions:

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

into equation for I:

$$\frac{d(I)}{dt} = k_A [A]_0 \, e^{-k_A t} - k_I (I)$$

in homogeneous differential equation (1 term does not contain [1])

solution:

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

at all $t > 0$: $[A]_0 = (A) + (I) + [P]$

$[A], [1], [P]$ all are out of $[A]_0$

$$[P] = (A)_0 - (A) - [I]$$

$$\Rightarrow \quad (P) = \left(\frac{k_A e^{-k_I t} - k_I e^{-k_A t}}{k_I - k_A} + 1 \right) (A)_0$$

Fig. 35.8, p. 925

8a: $k_A = 2 k_I$

A decays with $k_A \approx k_I$, forms I, which from a relatively large maximum $(I)_{max}$ decays to P, all on simalar time scales

8b $k_A = 8 k_I$, $k_A \gg k_I$

A decays and forms I relativelx quick to a large $[1]_{max}$ which decays slowly to P

8c. $k_A = 0.25 k_I$, $k_I \gg k_A$

A decays slowly to form a small $[I]_{max}$ which quickly decays to P $\Rightarrow$ small $[I]_{max}$ occuring late

With these initial conditions, the expression for [A] is exactly that derived previously:

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_A t} \tag{35.51}$$

The expression for [A] given by Equation (35.51) can be substituted into the differential rate expression for I resulting in

$$\begin{aligned}\frac{d[\mathrm{I}]}{dt} &= k_A[\mathrm{A}] - k_I[\mathrm{I}] \\ &= k_A[\mathrm{A}]_0 e^{-k_A t} - k_I[\mathrm{I}]\end{aligned} \tag{35.52}$$

Equation (35.52) is a differential equation that when solved yields the following expression for [I]:

$$[\mathrm{I}] = \frac{k_A}{k_I - k_A}\left(e^{-k_A t} - e^{-k_I t}\right)[\mathrm{A}]_0 \tag{35.53}$$

Finally, the expression for [P] is readily determined using the initial conditions of the reaction, with the initial concentration of A, $[\mathrm{A}]_0$, equal to the sum of all concentrations for $t > 0$:

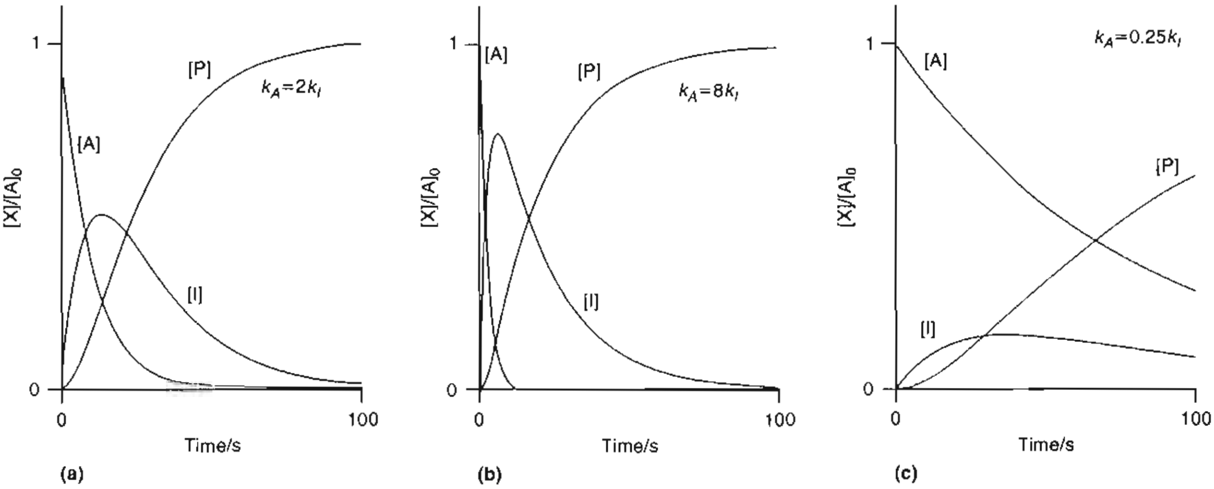
$$\begin{aligned}[\mathrm{A}]_0 &= [\mathrm{A}] + [\mathrm{I}] + [\mathrm{P}] \\ [\mathrm{P}] &= [\mathrm{A}]_0 - [\mathrm{A}] - [\mathrm{I}]\end{aligned} \tag{35.54}$$

Substituting Equations (35.51) and (35.53) into Equation (35.54) results in the following expression for [P]:

$$[\mathrm{P}] = \left(\frac{k_A e^{-k_I t} - k_I e^{-k_A t}}{k_I - k_A} + 1\right)[\mathrm{A}]_0 \tag{35.55}$$

Although the expressions for [I] and [P] look complicated, the temporal evolution in concentration predicted by these equations is intuitive as shown in Figure 35.8. Figure 35.8a presents the evolution in concentration when $k_A = 2k_I$. Notice that A undergoes exponential decay resulting in the production of I. The intermediate in turn undergoes subsequent decay to form the product. The temporal evolution of [I] is extremely dependent on the relative rate constants for the production k_A and decay k_I. Figure 35.8b presents the case where $k_A > k_I$. Here, the maximum intermediate concentration is greater than in the first case. The opposite limit is illustrated in Figure 35.8c, where $k_A < k_I$ and the maximum in intermediate concentration is significantly reduced. This behavior is consistent with intuition: if the intermediate undergoes decay at a faster rate than the rate at which it is being formed, then the intermediate concentration will be small. Of course, the opposite logic holds as evidenced by the $k_A > k_I$ example presented in the Figure 35.8b.

FIGURE 35.8
Concentration profiles for a sequential reaction in which the reactant (A, blue line) forms an intermediate (I, purple line) that undergoes subsequent decay to form the product (P, red line) where (**a**) $k_A = 2k_I = 0.1\ \mathrm{s}^{-1}$ and (**b**) $k_A = 8k_I = 0.4\ \mathrm{s}^{-1}$. Notice that both the maximal amount of I in addition to the time for the maximum is changed relative to the first panel. (**c**) $k_A = 0.025k_I = 0.0125\ \mathrm{s}^{-1}$. In this case, very little intermediate is formed, and the maximum in [I] is delayed relative to the first two examples.



$[I]_{max}$ occurs at maximum of $[I](t)$

$$\Rightarrow \left.\frac{d[I]}{dt}\right|_{t=t_{max}} = 0$$ extremum condition

$\Rightarrow$ with $[I](t)$ as discussed before

$$t_{max} = \frac{1}{k_A - k_I} \ln \frac{k_A}{k_I}$$

t_{max} for $k_A = 2k_I = 0{,}1\,\frac{1}{s}$

$k_A = 0{,}1\,\frac{1}{s}$, $k_I = 0{,}05\ s^{-1}$

$$t_{max} = \frac{1}{(0{,}1-0{,}05)\,s^{-1}} \ln\left(\frac{0{,}1}{0{,}05}\right) = 13{,}9\,s$$

if one step in a sequential reaction is much slower than all others, then the slow step will control the rate of product formation

$\Rightarrow$ slow step is the rate limiting (rl) step of the sequence

if $k_A \gg k_I \Rightarrow e^{-k_A t} \ll e^{-k_I t}$

$$\Rightarrow \lim_{k_A \gg k_I} [P] = \lim_{k_A \gg k_I} \left[\frac{\overset{\text{large}}{k_A e^{-k_I t}} - \overset{\text{small}}{k_I e^{-k_A t}}}{\underset{\text{small}}{k_I} - \underset{\text{large}}{k_A}} + 1 \right] [A]_0 = \left(1 - e^{-k_I t}\right)[A]_0$$

$[P](t)$ same as for 1. order I decay to P

$$k_I \gg k_A \Rightarrow e^{-k_I t} \gg e^{-k_A t}$$

$$\lim_{k_1 \gg k_A} (P) = \lim_{k_1 \gg k_A} \left[\frac{\overset{\cancel{\text{to}}\ \text{large}}{k_A e^{-k_1 t}} - \overset{\text{small}}{k_1 e^{-k_A t}}}{\underset{\text{large}}{k_1} - \underset{\text{small}}{k_A}} \right] [A]_0 = (1 - e^{-k_A t})[A]_0$$

[P](t) same as for A decay direct to P

Fig. 35.9a $k_A = 20\, k_I$ large I decays to P

b $k_A = 0.04\, k_I$, p 927 A direct → P

in both cases 1k by factor 20 larger than the the other one $[P]_{ss}$ (approx.) agrees very will to the exact [P] curve

Steady-State Approxima~~a~~tion (SSA)

$$A \xrightarrow{k_A} I_1 \xrightarrow{k_1} I_2 \xrightarrow{k_2} P$$

$$\frac{d(A)}{dt} = -k_A (A)$$

$$\frac{d(I_1)}{dt} = k_A(A) - k_1(I_1)$$

positive formation term of I_1

negative consumption term of I_1

$$\frac{d(I_2)}{dt} = k_1(I_1) - k_2(I_2)$$

positive formation term of I_2

negative consumption ~~terom~~ term of I

and

When is the rate-determining step approximation appropriate? For the two-step reaction under consideration, 20-fold differences between rate constants are sufficient to ensure that the smaller rate constant will be rate determining. Figure 35.9 presents a comparison for [P] determined using the exact result from Equation (35.55) and the rate-limited prediction of Equations (35.58) and (35.59) for the case where $k_A = 20k_I = 1\ \text{s}^{-1}$ and where $k_A = 0.04k_I = 0.02\ \text{s}^{-1}$. In Figure 35.9a, decay of the intermediate is the rate-limiting step in product formation. Notice the rapid reactant decay, resulting in an appreciable intermediate concentration, with the subsequent decay of the intermediate reflected by a corresponding increase in [P]. The similarity of the exact and rate-limiting curves for [P] demonstrates the validity of the rate-limiting approximation for this ratio of rate constants. The opposite limit is presented in Figure 35.9b. In this case, decay of the reactant is the rate-limiting step in product formation. When reactant decay is the rate-limiting step, very little intermediate is produced. In this case, the loss of [A] is mirrored by an increase in [P]. Again, the agreement between the exact and rate-limiting descriptions of [P] demonstrates the validity of the rate-limiting approximation when a substantial difference in rate constants for intermediate production and decay exists.

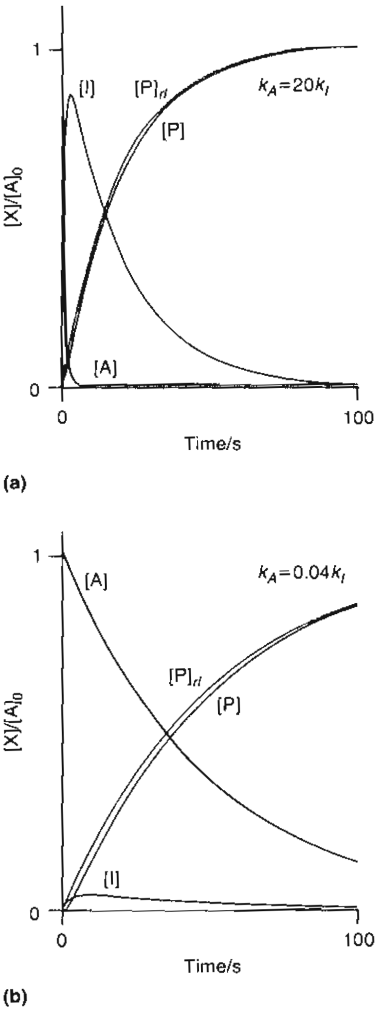


FIGURE 35.9
Rate-limiting step behavior in sequential reactions. **(a)** $k_A = 20k_I = 1\ \text{s}^{-1}$ such that the rate-limiting step is the decay of intermediate I. In this case, the reduction in [I] is reflected by the appearance of [P]. The time evolution of [P] predicted by the sequential mechanism is given by the purple 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.

35.7.3 The Steady-State Approximation

Consider the following sequential reaction scheme:

$$\text{A} \xrightarrow{k_A} \text{I}_1 \xrightarrow{k_1} \text{I}_2 \xrightarrow{k_2} \text{P} \tag{35.60}$$

In this reaction, product formation results from the formation and decay of two intermediate species, I_1 and I_2. The differential rate expressions for this scheme are as follows:

$$\frac{d[\text{A}]}{dt} = -k_A[\text{A}] \tag{35.61}$$

$$\frac{d[\text{I}_1]}{dt} = k_A[\text{A}] - k_1[\text{I}_1] \tag{35.62}$$

$$\frac{d[\text{I}_2]}{dt} = k_1[\text{I}_1] - k_2[\text{I}_2] \tag{35.63}$$

$$\frac{d[\text{P}]}{dt} = k_2[\text{I}_2] \tag{35.64}$$

A determination of the time-dependent concentrations for the species involved in this reaction by integration of the differential rate expressions is not trivial; therefore, how can the concentrations be determined? One approach is to use Euler's method (Section 35.6) and numerically determine the concentrations as a function of time. The result of this approach for $k_A = 0.02\ \text{s}^{-1}$ and $k_1 = k_2 = 0.2\ \text{s}^{-1}$ is presented in Figure 35.10. Notice that the relative magnitude of the rate constants results in only modest intermediate concentrations.

Inspection of Figure 35.10 illustrates that $[\text{I}_1]$ and $[\text{I}_2]$ undergo little change with time. As such, the time derivative of these concentrations is approximately equal to zero:

$$\frac{d[\text{I}]}{dt} \approx 0 \tag{35.65}$$

Equation (35.65) is known as the **steady-state approximation.** This approximation is used to evaluate the differential rate expressions by simply setting the time derivative of all intermediates to zero. This approximation is particularly good when the decay rate of the intermediate is greater than the rate of production so that the intermediates are present at very small concentrations during the reaction (as in the case illustrated in Figure 35.10). Applying the steady-state approximation to I_1 in our example reaction results in the following expression for $[\text{I}_1]$:

$$\frac{d[\text{I}_1]_{ss}}{dt} = 0 = k_A[\text{A}] - k_1[\text{I}_1]_{ss}$$

$$[\text{I}_1]_{ss} = \frac{k_A}{k_1}[\text{A}] = \frac{k_A}{k_1}[\text{A}]_0 e^{-k_A t} \tag{35.66}$$

$\frac{d[P]}{dt} = k_2 [I_2]$ rate of formation of P

integration not easy!

solution with Euler's numerical methode:

Fig. 35,10, p 928

only small intermediate concentrations
when $k_A = 0{,}02 \frac{1}{s}$, $k_1 = k_2 = 0{,}2 \frac{1}{s}$, so ~~slow~~ fast
intermediates decay to P, slow I_1 formation by A decay

$[I_1]$, $[I_2]$ ~~slow~~ show not much change

$$\Rightarrow \text{SSA} \quad \frac{d[I_1]}{dt} = \frac{d[I_2]}{dt} = 0$$

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

$$\Rightarrow [I_1]_{SSA} = \frac{k_A}{k_1} [A] = \frac{k_A}{k_I} [A]_0 \underset{\downarrow}{e^{-k_A t}}$$

integrated time law
for 1. order A decay
with $[A]_0 \neq 0$

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

$$[I_2]_{SSA} = \frac{k_1}{k_2} [I_1]_{SSA} = \frac{k_A}{k_2} [A]_0 e^{-k_A t}$$

⇒ integration of $\frac{d[P]}{dt} = k_2 [I_2]_{SSA}$

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

P is formed directly from A decay

$$\frac{d[I_1]_{SSA}}{dt} = \frac{d}{dt}\left[\frac{k_A}{k_1} [A]_0 e^{-k_A t}\right]$$

$$= -\frac{k_A^2}{k_1} [A]_0 e^{-k_A t}$$

SSA is ok, when $\frac{d[I_1]_{SSA}}{dt} = 0$, so SSA is ok when $k_1 \gg k_A^2 [A]_0$ and for $\frac{d[I_2]_{SSA}}{dt} = 0$ follows that $k_2 \gg k_A^2 [A]_0$

Fig. 35.11, p 928

as above: when $k_A = 0.02\ s^{-1}$

and $k_1 = k_2 = \cancel{0.025}\ 0.2\ s^{-1}$

so large k_1, k_2, small k_A

even then $[P]_{SSA}$ rather different from $[P]$ from Euler's method

⇒ SSA for many reactions not working very good

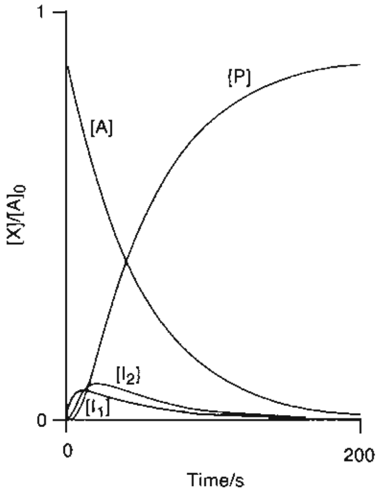


FIGURE 35.10
Concentrations determined by numerical evaluation of the sequential reaction scheme presented in Equation (35.60) where $k_A = 0.02\ \text{s}^{-1}$ and $k_1 = k_2 = 0.2\ \text{s}^{-1}$.

where the subscript *ss* indicates that the concentration is that predicted using the steady-state approximation. The final equality in Equation (35.66) results from integration of the differential rate expression for [A] with the initial conditions that $[A]_0 \neq 0$ and all other initial concentrations are zero. The corresponding expression for $[I_2]$ under the steady-state approximation is

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

$$[I_2]_{ss} = \frac{k_1}{k_2}[I_1]_{ss} = \frac{k_A}{k_2}[A]_0 e^{-k_A t} \tag{35.67}$$

Finally, the differential expression for *P* is

$$\frac{d[P]_{ss}}{dt} = k_2[I_2] = k_A[A]_0 e^{-k_A t} \tag{35.68}$$

Integration of Equation (35.68) results in the now familiar expression for [P]:

$$[P]_{ss} = [A]_0(1 - e^{-k_A t}) \tag{35.69}$$

Equation (35.69) demonstrates that within the steady-state approximation, [P] is predicted to demonstrate appearance kinetics consistent with the first-order decay of A.

When is the steady-state approximation valid? The approximation requires that the concentration of intermediate be constant as a function of time. Consider the concentration of the first intermediate under the steady-state approximation. The time derivative of $[I_1]_{ss}$ is

$$\frac{d[I_1]_{ss}}{dt} = \frac{d}{dt}\left(\frac{k_A}{k_1}[A]_0 e^{-k_A t}\right) = -\frac{k_A^2}{k_1}[A]_0 e^{-k_A t} \tag{35.70}$$

The steady-state approximation is valid when Equation (35.70) is equal to zero, which is true when $k_1 \gg k_A^2[A]_0$. In other words, k_1 must be sufficiently large such that $[I_1]$ is small at all times. Similar logic applies to I_2 for which the steady-state approximation is valid when $k_2 \gg k_A^2[A]_0$.

Figure 35.11 presents a comparison between the numerically determined concentrations and those predicted using the steady-state approximation for the two-intermediate sequential reaction where $k_A = 0.02\ \text{s}^{-1}$ and $k_1 = k_2 = 0.2\ \text{s}^{-1}$. Notice that even for these conditions where the steady-state approximation is expected to be valid, the discrepancy between [P] determined by numerical evaluation versus the steady-state approximation value, $[P]_{ss}$, is evident. For the examples presented here, the steady-state approximation is relatively easy to implement; however, for many reactions the approximation of constant intermediate concentration with time is not appropriate. In addition, the steady-state approximation is difficult to implement if the intermediate concentrations are not isolated to one or two of the differential rate expressions derived from the mechanism of interest.

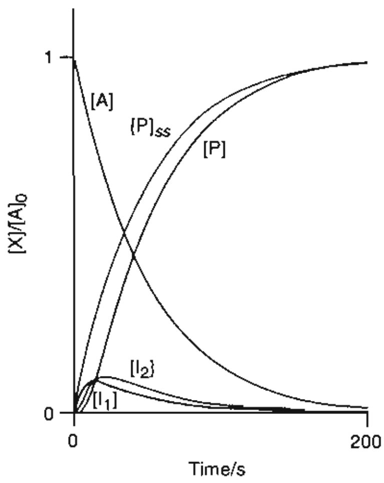


FIGURE 35.11
Comparison of the numerical and steady-state concentration profiles for the sequential reaction scheme presented in Equation (35.44) where $k_A = 0.02\ \text{s}^{-1}$ and $k_1 = k_2 = 0.2\ \text{s}^{-1}$. Curves corresponding to the steady-state approximation are indicated by the subscript *ss*.

EXAMPLE PROBLEM 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 Equations (35.47), (35.48), and (35.49):

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

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

$$\frac{d[P]}{dt} = k_I[I]$$

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

$$[A]_0 \neq 0 \,, \quad [I]_0 = [P]_0 = 0$$

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

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

$$\frac{d[P]}{dt} = k_I [I]$$

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

$$\Rightarrow [I]_{ssA} = \frac{k_A}{k_1} [A] = \frac{k_A}{k_1} [A]_0 e^{-k_A t}$$

$$\frac{d[P]}{dt} = k_1 [I]_{ssA} = \frac{k_A}{k_1} \left(k_1 [A]_0 e^{-k_A t} \right)$$

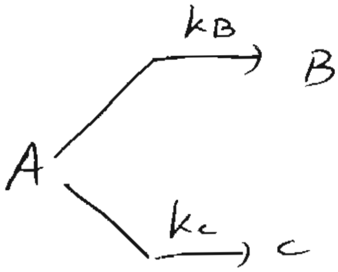
$$\int_{[P]_0=0}^{[P]} d[P] = k_A [A]_0 \int_0^t e^{-k_A t} dt$$

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

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

same as derived with rate limiting approximation

Parallel Reactions



$$\frac{d(A)}{dt} = -k_B(A) - k_c(A) = -(k_B + k_c)(A)$$

$$\frac{d[B)}{dt} = k_B[A)$$

$$\frac{d[C)}{dt} = k_c(A)$$

$$[A]_0 \neq 0 \;,\; [B)_0 = (C)_0 = 0$$

$$[A] = [A]_0 \, e^{-(k_B + k_c)t}$$

Into [B) and [C) and integration yields $\frac{1}{k_B + k_c}$

$$(B) = \frac{k_B}{k_B + k_c} (A]_0 \left(1 - e^{-(k_B + k_c)t}\right)$$

$$(C) = \frac{k_c}{k_B + k_c} [A)_0 \left(1 - e^{-(k_B + k_c)t}\right)$$

Fig. 35.12 case $k_B = 2k_c = 0.1\,s^{-1}$ p. 930

k_{eff} for A decay is $k_B + k_c$ = sum of rate constants for each reaction branch

ratio $\frac{(B]}{(C)}$ is time independent!

$$\frac{[B]}{[C]} = \frac{k_B}{k_c}$$

yield ϕ of product i:

$$\phi_i = \frac{k_i}{\sum_{n} k_n} = \frac{k_i}{\sum_{n} k_n}$$

$$\Rightarrow \sum_i \phi_i = 1$$

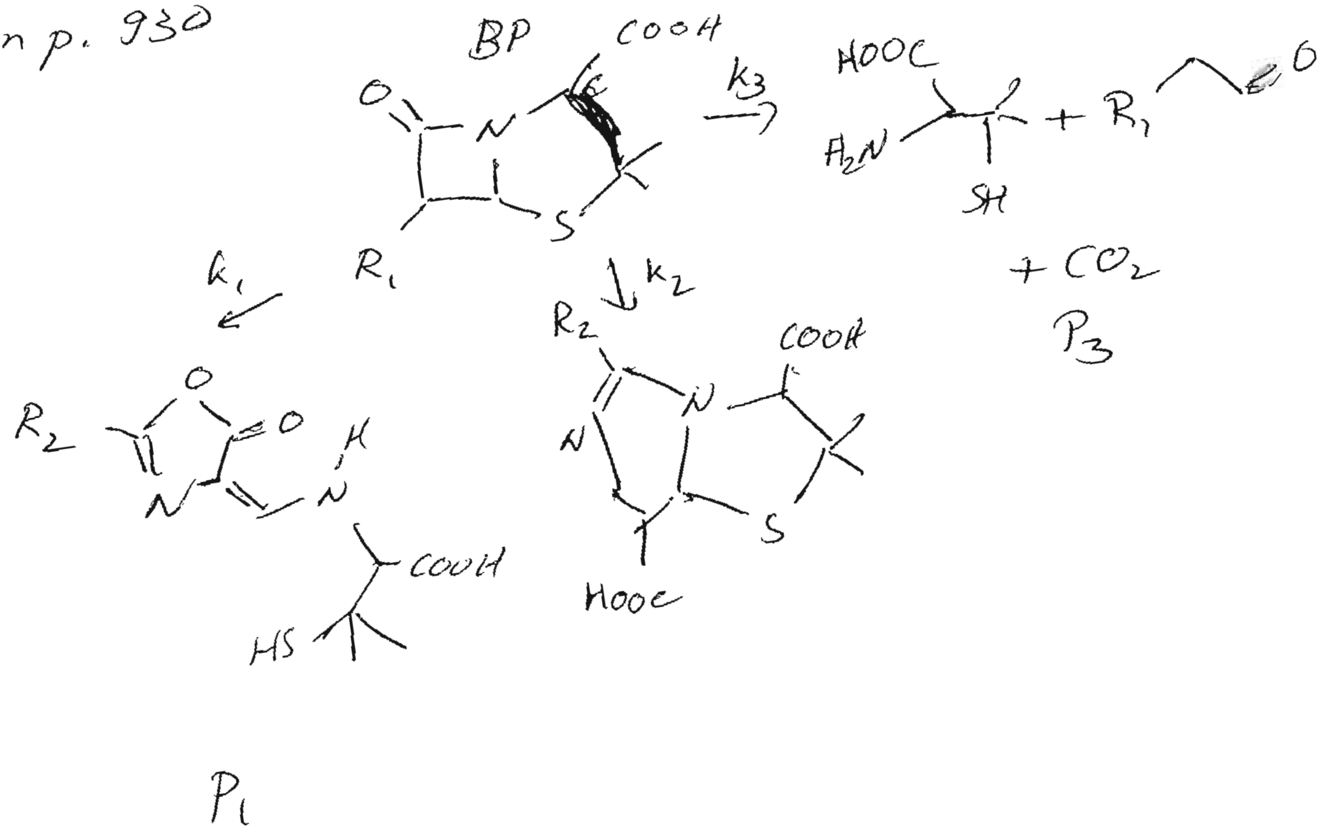
in Fig 35,12: $k_B = 2k_C$

$$\rightarrow \phi_C = \frac{k_C}{k_B + k_C} = \frac{k_C}{2k_C + k_C} = \frac{1}{3}$$

only 2 branches $\Rightarrow \phi_B = 1 - \phi_C = \frac{2}{3}$

in Fig 35,12, $[B] = 2[C]$

benzyl penicillin (BP) in acidic medium undergoes the parallel reactions shown on p. 930



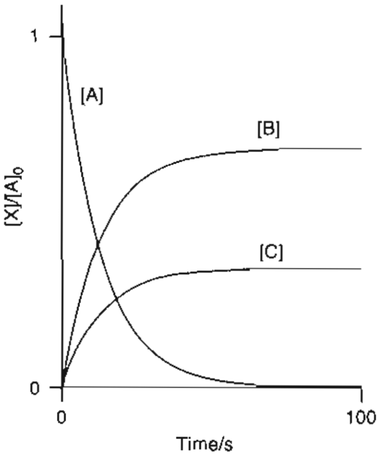


FIGURE 35.12
Concentrations for a parallel reaction where $k_B = 2k_C = 0.1\ s^{-1}$.

Figure 35.12 provides an illustration of the reactant and product concentrations for this branching reaction where $k_B = 2k_C = 0.1\ s^{-1}$. A few general trends demonstrated by branching reactions are evident in the figure. First, notice that the decay of A occurs with an apparent rate constant equal to $k_B + k_C$, the sum of rate constants for each reaction branch. Second, the ratio of product concentrations is independent of time. That is, at any time point the ratio $[B]/[C]$ is identical. This behavior is consistent with Equations (35.76) and (35.77) where this ratio of product concentrations is predicted to be

$$\frac{[B]}{[C]} = \frac{k_B}{k_C} \tag{35.78}$$

Equation (35.78) is a very interesting result. The equation states that as the rate constant for one of the reaction branches increases relative to the other, the final concentration of the corresponding product increases as well. Furthermore, notice that the ratio of the product concentrations in Equation (35.78) contains no time dependence; therefore, the product ratio will be the same throughout the course of the reaction.

Equation (35.78) demonstrates that the extent of product formation in a parallel reaction is dependent on the rate constants. Another way to view this behavior is with respect to probability; the larger the rate constant for a given process, the more likely that product will be formed. The **yield** Φ is defined as the probability that a given product will be formed by decay of the reactant:

$$\Phi_i = \frac{k_i}{\sum_n k_n} \tag{35.79}$$

In Equation (35.79), k_i is the rate constant for the reaction leading to formation of the product of interest indicated by the subscript i. The denominator is the sum over all rate constants for the reaction branches. The total yield is the sum of the yields for forming each product, and it is normalized such that

$$\sum_i \Phi_i = 1 \tag{35.80}$$

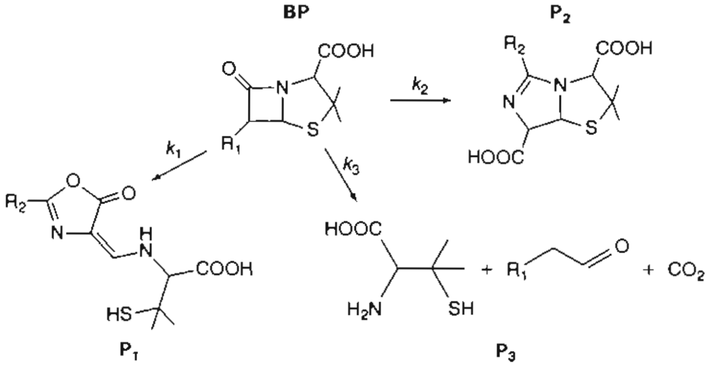
In the example reaction depicted in Figure 35.12 where $k_B = 2k_C$, the yield for the formation of product C is

$$\Phi_C = \frac{k_C}{k_B + k_C} = \frac{k_C}{(2k_C) + k_C} = \frac{1}{3} \tag{35.81}$$

Because there are only two branches in this reaction, $\Phi_B = 2/3$. Inspection of Figure 35.12 reveals that $[B] = 2[C]$, which is consistent with the calculated yields.

EXAMPLE PROBLEM 35.7

In acidic conditions, benzyl penicillin (BP) undergoes the following parallel reaction:



R_1, R_2 = alkyl rests

in stomach pH ≈ 3, then $k_1 = 7{,}0 \cdot 10^{-4}\, s^{-1}$, $k_2 = 4{,}1 \cdot 10^{-3}\, s^{-1}$, $k_3 = 5{,}7 \cdot 10^{-3}$ at 22°C

what is the yield ϕ_{P_1} for product P_1?

$$\phi_{P_1} = \frac{k_1}{k_1+k_2+k_3} = \frac{7{,}0 \cdot 10^{-4} s^{-1}}{(7{,}0 \cdot 10^{-4} + 4{,}1 \cdot 10^{-3} + 5{,}7 \cdot 10^{-3})\, s^{-1}}$$

$$= 0{,}067$$

⇒ there will be 6,7% of product P_1

experiments for many reactions a plot of $\ln k$ vs $\frac{1}{T}$ is linear

Arrhenius equation (empirical):

$$k = A e^{-E_a/RT}$$

A = pre-exponential factor in Arrhenius theory A is independent of T

E_a: activation energy

units $[A] = [k]$

$[E_a] = 1 \frac{kJ}{mol}$

$$\rightarrow \ln k = \ln A - \frac{E_a}{RT}$$

⇒ $\ln k$ vs $\frac{1}{T}$ should be linear

(36) - 37

acid calalyzed hydrolysis of penicillin:

$T(^\circ C)$	$k\,(s^{-1})$
22,2	$7{,}0 \cdot 10^{-4}$
27,2	$9{,}8 \cdot 10^{-4}$
33,7	$1{,}6 \cdot 10^{-3}$
38,0	$2{,}0 \cdot 10^{-3}$

linear plot of $\ln k$ vs $\frac{1}{T}\,(K^{-1})$ is on p. 932

$$\ln k = (-6300\,K)\frac{1}{T} + 14{,}1$$

$$\text{slope} = -6300\,K = -\frac{E_a}{R}$$

$$E_a = 52\,400\,\frac{J}{mol} = 52{,}4\,\frac{kJ}{mol}$$

$$\ln A = 14{,}1$$

$$A = e^{14{,}1}\,s^{-1} = 1{,}33 \cdot 10^{6}\,s^{-1}$$

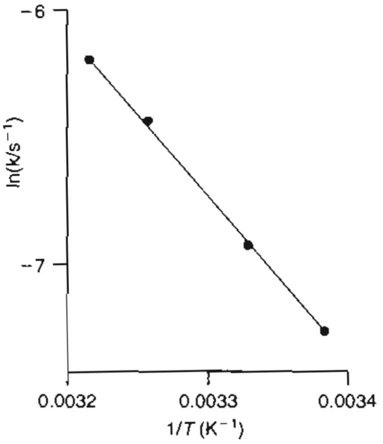
Fig. 35,13, p 932

fraction of molecules with ~~an~~ a translational energy > E_a ~~at~~ increases with increasing T
↓
from Boltzmann distribution

when at T = const. E_a increases, no. of molecules with ~~t~~ enough E_{trans} to react decreases ⇒ k will decrease

Solution

A plot of $\ln(k_1)$ versus T^{-1} is shown here:



The data are indicated by the points, and the solid line corresponds to the linear least-squares fit to the data. The equation for the line is

$$\ln(k) = (-6300\ \text{K})\frac{1}{T} + 14.1$$

As shown in Equation (35.83), the slope of the line is equal to $-E_a/R$ such that

$$6300\ \text{K} = \frac{E_a}{R} \Rightarrow E_a = 52{,}400\ \text{J mol}^{-1} = 52.4\ \text{kJ mol}^{-1}$$

The y intercept is equal to $\ln(A)$ such that

$$A = e^{14.1} = 1.33 \times 10^{6}\ \text{s}^{-1}$$

The origin of the energy term in the Arrhenius expression can be understood as follows. The activation energy corresponds to the energy needed for the chemical reaction to occur. Conceptually, we envision a chemical reaction as occurring along an energy profile as illustrated in Figure 35.13. If the energy content of the reactants is greater than the activation energy, the reaction can proceed. In Figure 35.13 Boltzmann distributions

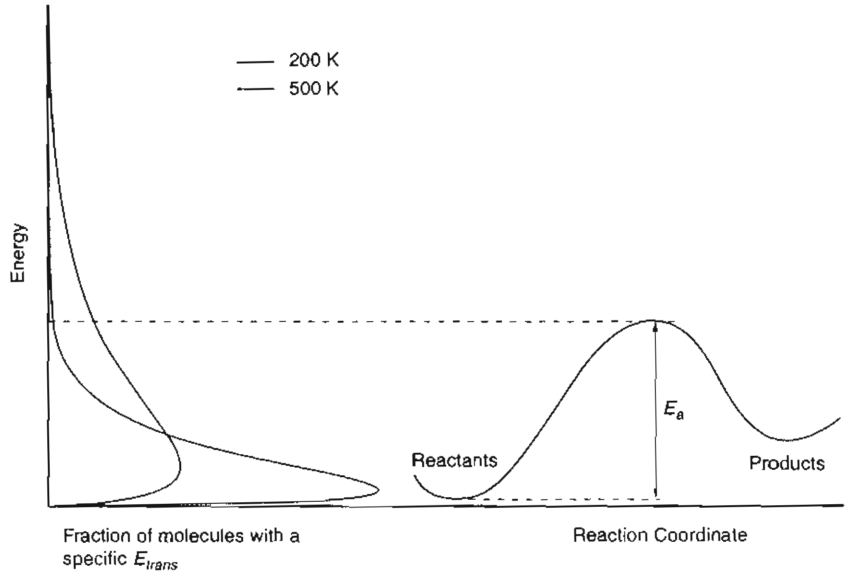


FIGURE 35.13
A schematic drawing of the energy profile for a chemical reaction. Reactants must acquire sufficient energy to overcome the activation energy E_a for the reaction to occur. The reaction coordinate represents the bonding and geometry changes that occur in the transformation of reactants into products. Shown here are Boltzmann distributions of molecular translational energy (E_{trans}) at 200 and 500 K. Notice that the fraction of molecules with translational energy greater than E_a increase with temperature.

in many reactions A, E_a are not constant $\Rightarrow$ $\ln k$ vs $\frac{1}{T}$ <u>not</u> straight line

better:

$$k = a T^m e^{-E'/RT}$$

m can be 1, $1/2$, $-1/2$ depending on theory used

Fig. 35.14 ~~P~~ Potential curve

If reactants have enough energy to overcome the activation energy E_a, they react and form ~~prd~~ products

But for the way back the same holds:

If products have enough energy to overcome E_a' the react back to form the reactants again.

$\Rightarrow$ reversible reaction

$$A \underset{k_B}{\overset{k_A}{\rightleftharpoons}} B$$

$$\rightarrow \quad \frac{d(A)}{dt} = \underbrace{-k_A(A)}_{\text{consumption of } A} + \overbrace{k_B(B)}^{\text{formation of } A}$$

$$\frac{d(B)}{dt} = k_A(A) - k_B(B)$$

$(A)_0 \neq 0$, $(B)_0 = 0$

$\Rightarrow$ $(A)_0 = (A) + (B)$ in all time of translational energy at 200 K and 500 K are presented. Notice that the number of molecules with translational energy greater than E_a increases with temperature. This behavior is captured in the exponential dependence on the activation energy, given by $\exp(-E_a/RT)$. At fixed temperature, as the activation energy for a reaction increases the fraction of molecules with sufficient energy to react will decrease, and this will be reflected as a decrease in the reaction rate.

Not all chemical reactions demonstrate Arrhenius behavior. Specifically, the inherent assumption in Equation (35.83) is that both E_a and A are temperature-independent quantities. There are many reactions for which a plot of $\ln(k)$ versus T^{-1} does not yield a straight line, consistent with the temperature dependence of one or both of the Arrhenius parameters. Modern theories of reaction rates predict that the rate constant will demonstrate the following behavior:

$$k = aT^{m}e^{-E'/RT}$$

where a and E' are temperature-independent quantities, and m can assume values such as 1, 1/2, and −1/2 depending on the details of the theory used to predict the rate constant. For example, in the upcoming section on activated complex theory (Section 35.14), a value of $m = 1$ is predicted. With this value for m, a plot of $\ln(k/T)$ versus T^{-1} should yield a straight line with slope equal to $-E'/R$ and the y intercept equal to $\ln(a)$. Although the limitations of the Arrhenius expression are well known, this relationship still provides an adequate description of the temperature dependence of reaction rate constants for a wide variety of reactions.

35.10 Reversible Reactions and Equilibrium

In the kinetic models discussed in earlier sections, it was assumed that once reactants form products, the opposite or "back" reaction does not occur. However, the **reaction coordinate** presented in Figure 35.14 suggests that, depending on the energetics of the reaction, such reactions can indeed occur. Specifically, the figure illustrates that reactants form products if they have sufficient energy to overcome the activation energy for the reaction. But what if the reaction coordinate is viewed from the product's perspective? Can the coordinate be followed in reverse, with products returning to reactants by overcoming the activation energy barrier from the product side E_a' of the coordinate? Such **reversible reactions** are discussed in this section.

Consider the following reaction in which the forward reaction is first order in A, and the back reaction is first order in B:

$$A \underset{k_B}{\overset{k_A}{\rightleftharpoons}} B \tag{35.84}$$

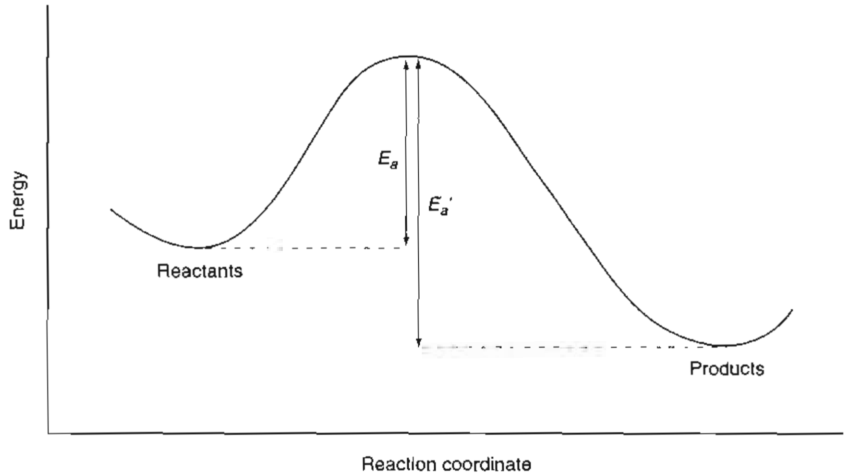


FIGURE 35.14
Reaction coordinate demonstrating the activation energy for reactants to form products E_a and the back reaction in which products form reactants E_a'.

$$\frac{d[A]}{dt} = -k_A[A] + k_B[B]$$

$$= -k_A[A] + k_B([A]_0 - [A])$$

$$= -[A](k_A+k_B) + k_B[A]_0$$

$$= -\left[[A](k_A+k_B) - k_B[A]_0\right]$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A](k_A+k_B) - k_B[A]_0} = -\int_0^t dt$$

formula collection: $\int \frac{dx}{a+bx} = \frac{1}{b}\ln(a+bx) + C$

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

$$\ln\frac{[A](k_A+k_B) - k_B[A]_0}{[A]_0(k_A+k_B) - k_B[A]_0} = -(k_A+k_B)t$$

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

$$[A](k_A+k_B) - k_B[A]_0 = k_A[A]_0 e^{-(k_A+k_B)t}$$

$$[A](k_A+k_B) = k_A[A]_0 e^{-(k_A+k_B)t} + k_B[A]_0$$

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

$$[B] = [A]_0 - [A]$$

$$\Rightarrow [B] = [A]_0 \left(1 - \frac{k_B + k_A e^{-(k_A+k_B)t}}{k_A + k_B} \right) \quad ⓷⓺$$

Fig, 35,15 special case plot

[A] decays exponentially with $k_{eff} = k_A + k_B$

and [B] appears the opposite way.

<u>but</u> because of back reaction [A] does <u>not</u> go exponentially to 0 but to an equilibrium value.

same way [B] increasin exponentiall to an equilibrium value

Those equibibrium values are

$$[A]_{eq} = \lim_{t\to\infty} [A] = [A]_0 \frac{k_B}{k_A + k_B}$$

exponential $\to 0$

$$[B]_{eq} = \lim_{t\to\infty} [B] = [A]_0 \left(1 - \frac{k_B}{k_A + k_B} \right)$$

no need to go to $t\to\infty$ for $[A]_{eq}$, $[B]_{eq}$

after t_{eq} [A] and [B] do not change any more and system has reached equilibrium

after t_{eq} $\frac{d[A]_{eq}}{dt} = \frac{d[B]_{eq}}{dt} = 0$

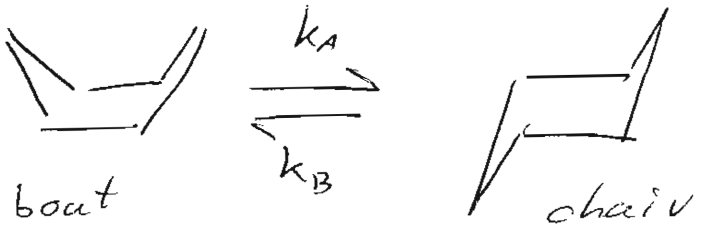
at equilibrium forward and backward reactions <u>still</u> happen but at equal rates, so that [ ] do not change in time

$$\frac{d[A]_{eq}}{dt} = \frac{d[B]_{eq}}{dt} = 0 = -k_A [A]_{eq} + k_B [B]_{eq}$$

$$\Rightarrow \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_A}{k_B} = K_c$$

$\Rightarrow$ equilibrium constant $K_c = \frac{k_A}{k_B}$

$\Rightarrow$ Fig. 35.16



cyclohexane

$K_c = 10^4$

chair → boat : $E_a = 42 \frac{kJ}{mol}$ all at 298K

Arrhenius pre-exponential factor $A = 10^{12} \frac{1}{s}$

$$k_B = Ae^{-E_a/RT} = 10^{12} \frac{1}{s} \exp\left[\frac{-42000 \frac{J}{mol}}{8{,}314 \frac{J}{K\,mol} \cdot 298\,K}\right]$$

$$= 4{,}34 \cdot 10^4 \frac{1}{s}$$

$$K_c = 10^4 = \frac{k_A}{k_B}$$

$$\Rightarrow k_A = 10^4 k_B = 10^4 (4{,}34 \cdot 10^4 \frac{1}{s})$$

$$= 4{,}34 \cdot 10^8 \frac{1}{s}$$

product concentrations are sufficiently close to equilibrium, and the change in these concentrations with time is so modest that approximating the system as having reached equilibrium is reasonable. This time is indicated by t_{eq} in Figure 35.15, where inspection of the figure demonstrates that the concentrations are at their equilibrium values for times $> t_{eq}$. After equilibrium has been established, the reactant and product concentrations are time independent such that

$$\frac{d[\mathrm{A}]_{eq}}{dt} = \frac{d[\mathrm{B}]_{eq}}{dt} = 0 \tag{35.93}$$

The subscripts in Equation (35.93) indicate that equality applies only after equilibrium has been established. A common misconception is that Equation (35.93) states that at equilibrium the forward and back reaction rates are zero. Instead, at equilibrium the forward and back reaction rates are equal, but not zero, such that the macroscopic concentration of reactant or product does not evolve with time. That is, the forward and back reactions still occur, but they occur with equal rates at equilibrium. Using Equation (35.93) in combination with the differential rate expressions for the reactant [Equation (35.85)], we arrive at what is hopefully a familiar relationship:

$$\frac{d[\mathrm{A}]_{eq}}{dt} = \frac{d[\mathrm{B}]_{eq}}{dt} = 0 = -k_A[\mathrm{A}]_{eq} + k_B[\mathrm{B}]_{eq}$$

$$\frac{k_A}{k_B} = \frac{[\mathrm{B}]_{eq}}{[\mathrm{A}]_{eq}} = K_c \tag{35.94}$$

In this equation, K_c is the equilibrium constant defined in terms of concentrations. This quantity is identical to that first encountered in thermodynamics (Chapter 6) and statistical mechanics (Chapter 32). We now have a definition of equilibrium from the kinetic perspective; therefore, Equation (35.94) is a remarkable result in which the concept of equilibrium as described by these three different perspectives is connected into one deceptively simple equation. From the kinetic standpoint, K_c is related to the ratio of forward and backward rate constants for the reaction. The greater the forward rate constant relative to that for the back reaction, the more equilibrium will favor products over reactants.

Figure 35.16 illustrates the methodology by which forward and backward rate constants can be determined. Specifically, measurement of the reactant decay kinetics (or equivalently the product formation kinetics) provides a measure of the apparent rate constant, $k_A + k_B$. The measurement of K_c, or the reactant and product concentrations at equilibrium, provides a measure of the ratio of the forward and backward rate constants.

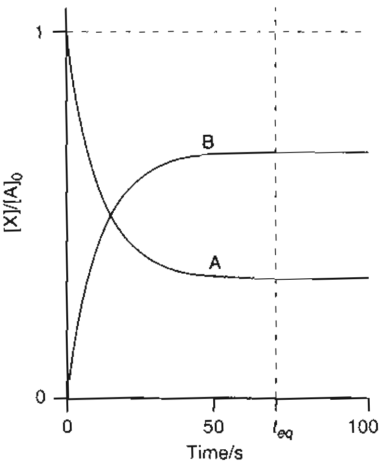


FIGURE 35.15
Time-dependent concentrations in which both forward and back reactions exist between reactant A and product B. In this example, $k_A = 2k_B = 0.06\ \mathrm{s}^{-1}$. Note that the concentrations reach a constant value at longer times ($t \geq t_{eq}$) at which point the reaction reaches equilibrium.

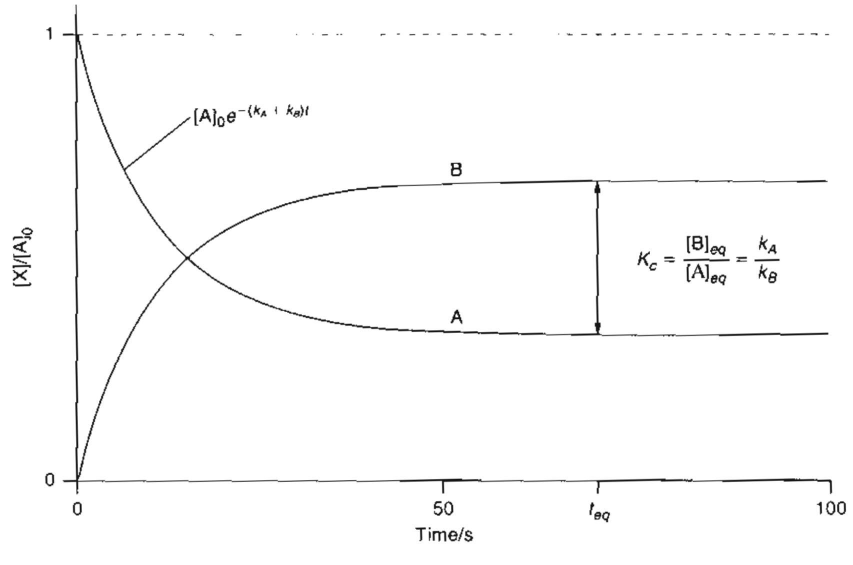
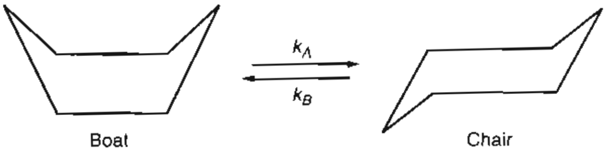


FIGURE 35.16
Methodology for determining forward and backward rate constants. The apparent rate constant for reactant decay is equal to the sum of forward k_A and backward k_B rate constants. The equilibrium constant is equal to k_A/k_B. These two measurements provide a system of two equations and two unknowns that can be readily evaluated to produce k_A and k_B.

Together, these measurements represent a system of two equations and two unknowns that can be readily solved to determine k_A and k_B.

EXAMPLE PROBLEM 35.9

Consider the interconversion of the "boat" and "chair" conformations of cyclohexane:



The reaction is first order in each direction, with an equilibrium constant of 10^4. The activation energy for the conversion of the chair conformer to the boat conformer is 42 kJ/mol. Assuming an Arrhenius preexponential factor of 10^{12} s^{-1}, what is the expected observed reaction rate constant at 298 K if one were to initiate this reaction starting with only the boat conformer?

Solution

Using the Arrhenius expression of Equation (35.82), k_B is given by

$$k_B = Ae^{-E_a/RT} = 10^{12}\,\text{s}^{-1}\exp\left[\frac{-42{,}000\ \text{J mol}^{-1}}{(8.314\ \text{J mol}^{-1}\,\text{K}^{-1})(298\ \text{K})}\right]$$

$$= 4.34 \times 10^4\ \text{s}^{-1}$$

Using the equilibrium constant, k_A can be determined as follows:

$$K_c = 10^4 = \frac{k_A}{k_B}$$

$$k_A = 10^4\,k_B = 10^4(4.34 \times 10^4\ \text{s}^{-1}) = 4.34 \times 10^8\ \text{s}^{-1}$$

Finally, the apparent rate constant is simply the sum of k_A and k_B:

$$k_{app} = k_A + k_B = 4.34 \times 10^8\ \text{s}^{-1}$$

SUPPLEMENTAL

35.11 Perturbation-Relaxation Methods

The previous section demonstrated that for reactions with appreciable forward and backward rate constants, concentrations approaching those at equilibrium will be established at some later time after initiation of the reaction. The forward and backward rate constants for such reactions can be determined by monitoring the evolution in reactant or product concentrations as equilibrium is approached and by measuring the concentrations at equilibrium. But what if the initial conditions for the reaction cannot be controlled? For example, what if it is impossible to sequester the reactants such that initiation of the reaction at a specified time is impossible? In such situations, application of the methodology described in the preceding section to determine forward and backward rate constants is not possible. However, if one can perturb the system by changing temperature, pressure, or concentration, the system will no longer be at equilibrium and will evolve until a new equilibrium is established. If the perturbation occurs on a

$$k_{eff} = k_A + k_B = 4{,}34 \cdot 10^8 \ \frac{1}{s}$$

System prepared and allowed to establish equilibrium, Then ~~by~~ after a change in T, p or concentrations the system is no longer in equilibrium and will relax to the new equilibrium at the new T. When the T-jump is fast compared to the relaxation of the system to the new equilibrium, then the relaxation kinetics can be determined.

Consider $A \underset{k_B}{\overset{k_A}{\rightleftarrows}} B$ for- and backward reactions are of 1. order

Then a fast T-jump occurs and the rate constants change to their values $\overset{+}{k}_A, \overset{+}{k}_B$ after the T-jump, according to ~~A~~ the Arrhenius equation at the new T. The new equilibrium is

$$A \underset{\overset{+}{k}_B}{\overset{\overset{+}{k}_A}{\rightleftarrows}} B$$

At the new equilibrium $\frac{d[A]_{eq}}{dt} = 0 = -\overset{+}{k}_A [A]_{eq} + \overset{+}{k}_B [B]_{eq}$

$$\Rightarrow \overset{+}{k}_A [A]_{eq} = \overset{+}{k}_B [B]_{eq}$$

eq stands for the new equilibrium

x (= ξ) is the extent by which the pre jump concentration is shifted away from the new equilibrium after the T jump

$$[A] - x = [A]_{eq}$$

when x must be subtracted to get $[A]_{eq}$, then it must be added to $[B]$:

$$[B] + x = [B]_{eq}$$

what is missing in $[B]$ to get $[B]_{eq}$ is too much in $[A]$ to get $[A]_{eq}$; also negative x is possible!
the evolution of x during ~~scale~~ relaxation is given by the new rate constants:

$$\frac{dx}{dt} = -\overset{+}{k}_A [A] + \overset{+}{k}_B [B]$$

$$\Rightarrow \frac{dx}{dt} = -\overset{+}{k}_A \underbrace{(x + [A]_{eq})}_{=[A]} + \overset{+}{k}_B \underbrace{(-x + [B]_{eq})}_{=[B]}$$

$$= \underbrace{-\overset{+}{k}_A [A]_{eq} + \overset{+}{k}_B [B]_{eq}}_{=0} - x(\overset{+}{k}_A + \overset{+}{k}_B)$$

(see above)

$$\frac{dx}{dt} = -x(\overset{+}{k}_A + \overset{+}{k}_B)$$

$$\Rightarrow \text{relaxation } \tau: \quad \tau = \frac{1}{\overset{+}{k}_A + \overset{+}{k}_B}$$

$$\Rightarrow \frac{dx}{dt} = -\frac{x}{\tau}$$

$$\int_0^x \frac{dx}{x} = -\frac{1}{\tau}\int_0^t dt$$

$$x = x_0 e^{-t/\tau}$$

⇒ exponential change of concentration

and the initial deviation x will decrease to $\frac{x_0}{e}$ after τ

measure τ ⇒ $\overset{+}{k}_A + \overset{+}{k}_B$

then using the new equilibrium constant (from equilibrium concentrations) one can obtain the rate constants ~~l~~ alone.

$$K^+ = \frac{\overset{+}{k}_A}{\overset{+}{k}_B} \quad , \quad \frac{1}{\tau} = \overset{+}{k}_A + \overset{+}{k}_B = \overset{+}{k}_A + \frac{\overset{+}{k}_A}{K^+}$$

$$= \overset{+}{k}_A \left(1 + \frac{1}{K^+}\right)$$

$$\overset{+}{k}_A = \frac{1/\tau}{1 + \frac{1}{K^+}}$$

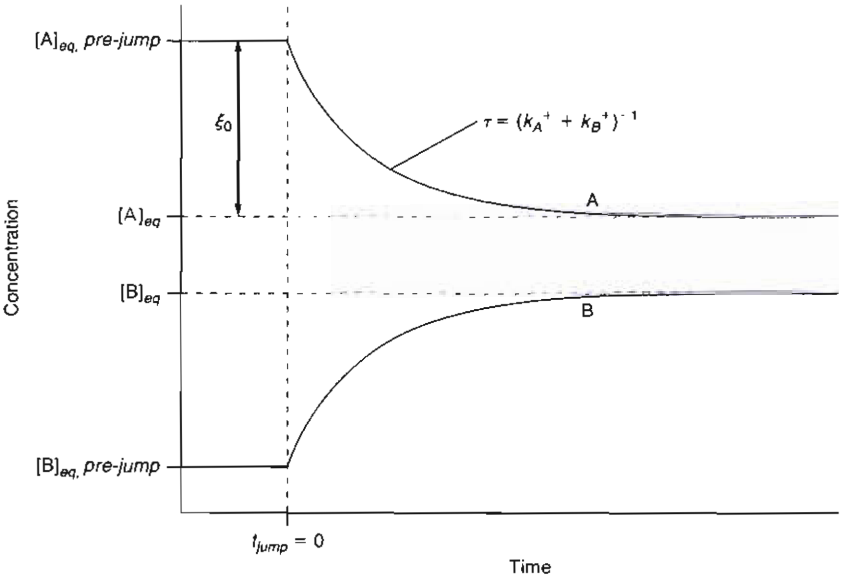
$$\overset{+}{k}_B = \frac{\overset{+}{k}_A}{K^+} = \frac{1/\tau}{K^+\left(1 + \frac{1}{K^+}\right)}$$

K^+: ~~equil~~ new equilibrium constant after jump

Fig. 35.17 concentration evolution after a T-jump

$$K^+ = \frac{[B]_{eq}}{[A]_{eq}} = \cancel{\frac{[B]+x}{[A]-x}} \quad \cancel{[B]+x)} \quad \cancel{\frac{[B]+x}{[A]-x}}$$

FIGURE 35.17
Example of a temperature-jump experiment for a reaction in which the forward and backward rate processes are first order. The orange and light green portions of the graph indicate times before and after the temperature jump, respectively. After the temperature jump, [A] decreases with a time constant related to the sum of the forward and backward rate constants. The change between the pre-jump and post-jump equilibrium concentrations is given by ξ_0.



Employing the relaxation time, Equation (35.100) is readily evaluated:

$$\frac{d\xi}{dt} = -\frac{\xi}{\tau}$$

$$\int_{\xi_0}^{\xi} \frac{d\xi'}{\xi'} = -\frac{1}{\tau}\int_0^t dt'$$

$$\xi = \xi_0 e^{-t/\tau} \tag{35.102}$$

Equation (35.102) demonstrates that for this reaction the concentrations will change exponentially, and the relaxation time is the time it takes for the coefficient of reaction advancement to decay to e^{-1} of its initial value. The timescale for relaxation after the temperature jump is related to the sum of the forward and backward rate constants. This information in combination with the equilibrium constant (given by measurement of $[A]_{eq}$ and $[B]_{eq}$) can be used to determine the individual values for the rate constants. Figure 35.17 presents a schematic of this process.

SUPPLEMENTAL

35.12 The Autoionization of Water: A Temperature-Jump Example

In the autoionization of water, the equilibrium of interest is the following:

$$H_2O(aq) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H^+(aq) + OH^-(aq) \tag{35.103}$$

The reaction is first order in the forward direction and second order in the reverse direction. The differential rate expressions that describe the temporal evolution of H_2O and H^+ concentrations are as follows:

$$\frac{d[H_2O]}{dt} = -k_f[H_2O] + k_r[H^+][OH^-] \tag{35.104}$$

$$\frac{d[H^+]}{dt} = k_f[H_2O] - k_r[H^+][OH^-] \tag{35.105}$$

Following a temperature jump to 298 K, the measured relaxation time constant was 37 μs. In addition, the pH of the solution is 7. Given this information, the forward and back rate

Auto ionization of water ㊱-39

$$H_2O(aq) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H^+(aq) + OH^-(aq)$$

forward: 1. order

backward: 2. order

$$\frac{d[H_2O]}{dt} = -k_f[H_2O] + k_r[H^+][OH^-]$$

$$\frac{d(H^+)}{dt} = k_f[H_2O) - k_r[H^+)(OH^-)$$

T jump from lower T to 298K

→ $\tau = 37\,\mu s$, pH = 7

$$K^+ = \frac{k_f^+}{k_r^+} = \frac{[H^+]_{eq}[OH]_{eq}}{[H_2O]_{eq}}$$

time-evolution of x follows the time evolution according to the kinetics

$$\frac{dx}{dt} = -k_f^+[H_2O] + k_r^+[H^+][OH^-)$$

$$= -k_f^+\underbrace{(x+[H_2O]_{eq})}_{[H_2O)} + k_r^+\underbrace{(x-[H^+]_{eq})}_{[H^+]}\underbrace{(x-[OH^-]_{eq})}_{[OH^-)}$$

$$[H_2O]_{eq} = \frac{[H^+]_{eq}[OH^-]_{eq}}{K^+} = \frac{k_r^+}{k_f^+}[H^+]_{eq}[OH^-]_{eq}$$

$$\Rightarrow \frac{dx}{dt} = -k_f^+\left(x + \frac{k_r^+}{k_f^+}[H^+]_{eq}[OH^-]_{eq}\right) + k_r^+(x - [H^+]_{eq})(x - [OH^-]_{eq})$$

$$= -k_f^+ x - k_r^+ x([H^+]_{eq} + [OH^-]_{eq}) + O(x^2)$$

$-k_f^+ \frac{k_r^+}{k_f^+}[H^+]_{eq}[OH^-]_{eq}$ cancels with $k_r^+[H^+]_{eq}[OH^-]_{eq}$ from the second part

$O(x^2)$ contains all terms containing x^2, e.g. $k_r^+ x^2$

When x is small (has to be since only small T jumps can be done fast enough)

$\Rightarrow O(x^2)$ can be neglected

x small $\Rightarrow x^2$ much smaller

$$\Rightarrow \frac{dx}{dt} = -x\left[k_f^+ + k_r^+([H^+]_{eq} + [OH^-]_{eq})\right]$$

$\Rightarrow$ relaxation times

$$\frac{1}{\tau} = k_f^+ + k_r^+([H^+]_{eq} + [OH^-]_{eq})$$

$$\Rightarrow \frac{dx}{dt} = -\frac{x}{\tau}$$ as before!

$\tau = 37\,\mu s$ (see before)

measured!

㊱ − 41

$$\Rightarrow \frac{1}{3.7 \cdot 10^{-5}\,s} = \left[\left(k_f^+ + k_r^+\left([H^+]_{eq} + [OH^-]_{eq}\right)\right)\right]$$

$$pH = 7 \Rightarrow [H^+] = [OH^-] = 1.0 \cdot 10^{-7}\,M$$

$[H_2O] = 55.5\,M$ at 298 K

$$\Rightarrow \frac{k_f^+}{k_r^+} = \frac{[H^+]_{eq}[OH^-]_{eq}}{[H_2O]_{eq}}$$

$$= \frac{(1.0 \cdot 10^{-7}\,M)^2}{55.5\,M} = 1.8 \cdot 10^{-16}\,M$$

$$\Rightarrow \frac{1}{3.7 \cdot 10^{-5}\,s} = 1.8 \cdot 10^{-16}\,M\,k_r^+ + (2.0 \cdot 10^{-7}\,M)\,k_r^+$$

small ⇒ neglect
compared to 10^{-7}

$$\Rightarrow k_r^+ = \frac{1}{3.7 \cdot 10^{-5}\,s \cdot 2.0 \cdot 10^{-7}\,M}$$

$$= 1.4 \cdot 10^{11}\,\frac{1}{M\,s}$$

k_f^+ (from $\frac{k_f^+}{k_i^+}$)

$$k_f^+ = 1.8 \cdot 10^{-16}\,M \cdot k_r^+ = 1.8 \cdot 10^{-16}\,M \cdot 1.4 \cdot 10^{11}\,\frac{1}{M\,s}$$

$$= 2.5 \cdot 10^{-5}\,\frac{1}{s}$$

$k_f^+ \ll k_r^+$ because not much auto ionization in water

Arrhenius equation ⇒ energetis in a reaction determine partially rates

→ potential energy surfaces: plot of E_{pot} as function of geometry

usually many dimensions, not only

E_{pot}-functions: $E_{pot} = f(r)$ potential energy function

for illustration:

$$AB + C \to A + BC$$

diatomics AB, BC are assumed to be stable

further triatomic ABC and AC are not formed in the reaction

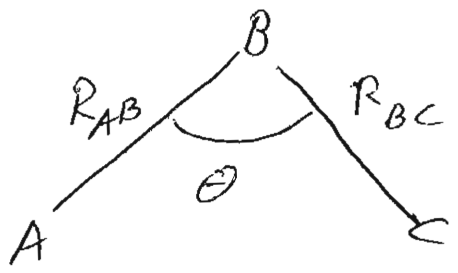
reactions interaction of 3 atoms

⇒ E_{pot} can be calculated from the relative positions of A, B, C in space.

⇒ 3 geometric variables:

$$E_{pot} = f(R_{AB}, R_{BC}, \sphericalangle AB, BC)$$

$\sphericalangle AB, BC$: angle between AB and BC, Θ:



Notice the substantial difference between the forward and backward rate constants, consistent with the modest amount of autoionized species in water. In addition, the forward and reverse rate constants are temperature dependent, and the autoionization constant also demonstrates temperature dependence.

35.13 Potential Energy Surfaces

In the discussion of the Arrhenius equation, the energetics of the reaction were identified as an important factor determining the rate of a reaction. This connection between reaction kinetics and energetics is central to the concept of the potential energy surface. To illustrate this concept, consider the following bimolecular reaction:

$$AB + C \rightarrow A + BC \tag{35.112}$$

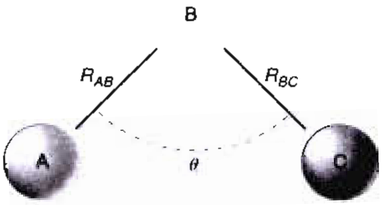


FIGURE 35.18
Definition of geometric coordinates for the AB + C → A + BC reaction.

The diatomic species AB and BC are stable, but we will assume that the triatomic species ABC and the diatomic species AC are not formed during the course of the reaction. This reaction can be viewed as the interaction of three atoms, and the potential energy of this collection of atoms can be defined with respect to the relative positions in space. The geometric relationship between these species is generally defined with respect to the distance between two of the three atoms (R_{AB} and R_{BC}) and the angle formed between these two distances, as illustrated in Figure 35.18.

The potential energy of the system can be expressed as a function of these coordinates. The variation of the potential energy with a change along these coordinates can then be presented as a graph or surface referred to as a **potential energy surface.** Formally, for our example reaction this surface would be four-dimensional (the three geometric coordinates and energy). The dimensionality of the problem can be reduced by considering the energetics of the reaction at a fixed value for one of the geometric coordinates. In our example reaction, the centers of A, B, and C must be aligned during the reaction such that $\theta = 180°$. With this constraint, the potential energy is reduced to a three-dimensional problem as shown in Figure 35.19. The graphs represent the variation in energy with displacement along R_{AB} and R_{BC} with the arrows indicating the direction of increased separation.

Figures 35.19a and 35.19b illustrate the three-dimensional potential energy surface, and the two minima in this surface corresponding to the stable diatomic molecules AB and BC. A more convenient way to view the potential energy surface is to use a two-dimensional **contour plot,** as illustrated in Figure 35.19c. One can think of this plot as a view straight down onto the three-dimensional surface presented in Figure 35.19. The lines on the contour plot connect regions of equal potential energy. On the lower left-hand region of the surface is a broad energetic plateau that corresponds to the energy when the three atoms are separated or the dissociated state A + B + C. The pathway corresponding to the reaction of B + C to form BC is indicated by the dashed line between points a and a'. The cross section of the potential energy surface along this line is presented in Figure 35.19d, and this contour is simply the potential energy diagram for the diatomic molecule BC. The depth of the potential is equal to the dissociation energy of the diatomic, $D_e(BC)$, and the minimum along R_{BC} corresponds to the equilibrium bond length of the diatomic. Figure 35.19e presents the corresponding diagram for the diatomic molecule AB, as indicated by the dashed line between points b and b' in Figure 35.19c.

The dashed line between points c and d in Figure 35.19c represents the system energy as C approaches AB and reacts to form BC and A under the constraint that $\theta = 180°$. This pathway represents the AB + C → A + BC reaction. The maximum in energy along this pathway is referred to as the **transition state** and is indicated by the double dagger symbol, ‡. The variation in energy as one proceeds from reactants to products along this reactive pathway can be plotted to construct a reaction coordinate diagram as presented in Figure 35.20. Note that the transition state corresponds to a maximum along the reaction coordinate; therefore, the activated complex is not a stable species (i.e., an intermediate) along the reaction coordinate.

⇒ plot of $E_{pot}(R_{AB}, R_{BC}, \Theta)$

would have 4 dimensions

→ simple plot not possible

but if one coordinate is fixed the dimensions can be reduced: assume E_{pot} be studied at fixed values of the angle Θ

examples $\Theta = 180°$

= linear arrangement A—B—C

⇒ E_{pot} is 3 dimensional:

Fig. 35.19, p. 941

AB → BC → define ~~the~~ a plane and the height above the plane is E_{pot} at ~~two~~ a values of R_{AB} and R_{BC}

AB → or BC → indicate directions of increasing distance

The reaction path way is the valley of minimal E_{pot} with minimal E_{pot} alonge the reaction pathway

the two minima on the reaction path way correspond to the molecules AB and BC,

molecule AB at R_{AB} = bond distance and R_{BC} large

molecule BC at R_{BC} = bond distance and ~~A~~ R_{AB} large

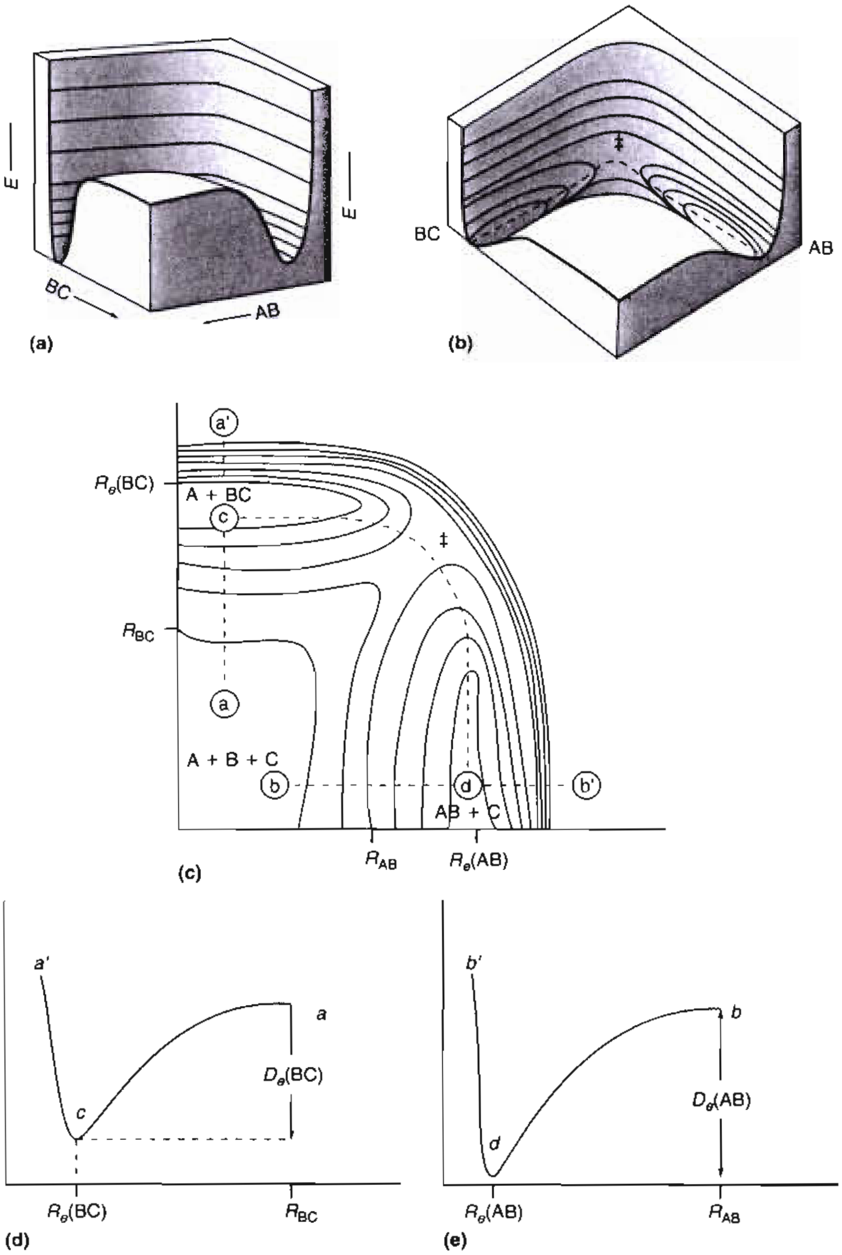


FIGURE 35.19
Illustration of a potential energy surface for the AB + C reaction at a colinear geometry ($\theta = 180°$ in Figure 35.18).
(a, b) Three-dimensional views of the surface. **(c)** Contour plot of the surface with contours of equipotential energy.
The curved dashed line represents one possible path of a reactive event, corresponding to its reaction coordinate.
The transition state for this coordinate is indicated by the symbol ‡. **(d, e)** Cross sections of the potential energy surface along the lines $a'-a$ and $b'-b$, respectively. These two graphs correspond to the potential for two-body interactions of B with C, and A with B. [Adapted from J. H. Noggle, *Physical Chemistry*, 3rd Edition, © 1996. Reprinted and electronically reproduced by permission of Pearson Education, Inc., Upper Saddle River, New Jersey.]

The discussion of potential energy surfaces just presented suggests that the kinetics and product yields will depend on the energy content of the reactants and the relative orientation of reactants. This sensitivity can be explored using techniques of crossed-molecular beams. In this approach, reactants with well-defined energies are seeded into a molecular beam that intersects another beam of reactants at well-defined beam geometries. The products formed in the reaction can be analyzed in terms of their energetics, spatial distribution of the products, and beam geometry. This experimental information is then used to construct a potential energy surface (following a substantial amount of analysis). Crossed-molecular beam techniques have provided much insight into the nature of reactive pathways, and detailed, introductory references to this important area of research are provided at the end of this chapter.

better is a two-dimensional contour plot (Fig. 35.19c)

in such a plot ~~x~~ the x axis is R_{AB}, the y axis is R_{BC}

and along each line in the plot the potential energy is constant

= straight downward view on the 3 dimensional plots a and B

lower left corner: R_{AB} and R_{BC} are large.

in this corner the three atoms ~~AB~~ A, B, and C are so ~~fare~~ far away from each other that a distance change does not change E_{pot}.

Plateau where E_{pot} does not change and atoms A, B, and C are free and separated

dashed line from a → c to a':

R_{BC} decreases: first E_{pot} comes down from the high plateau value to the stable ~~AB~~ BC molecule distance where E_{pot} is smallest

then E_{pot} increases again when R_{BC} becomes larger until a constant value of E_{pot} is reached

⇒ along a → c → a' R_{AB} is large and constant
and ~~R_{BC} is~~ $E_{pot}(R_{BC})$ is the potential energy curve for ~~molecl~~ molecule BC
where the energy distance from the ~~or~~ constant E_{pot} at large R_{BC} to E_{pot} at the minimum is $D_e(BC)$, the dissociation energy of molecule BC: Fig. 35.19d

the dashed ~~linen~~ line b → d → d'
describes the same for AB:
here R_{BC} is large and constant
when ~~from th~~ ~~R_{BC}~~ R_{AB} increases from the high plateau value of E_{pot} at b, E_{pot} decreases to the minimum energy of molecule AB, $R_e(AB)$ at d.
then when R_{AB} increases further, E_{pot} increases until E_{pot} gets constant at large distance R_{AB}
the energy between the constant value of E_{pot} at large R_{AB} and the minimum ~~enger~~ energy is $D_e(AB)$, the dissociation energy of molecule AB:
potential curve of A: Fig. 35.19e

The reaction pathway is the curved dashed line ~~form~~ from d ($R_e(AB)$) to c ($R_e(BC)$): reaction pathway;

lowest energy path between d and c corresponds ~~to~~ to $AB + C \rightarrow BC + A$

the path begins at the E_{pot} minimum for molecule AB, then it follow rising E_{pot} to a maximum of E_{pot} along the path, the transition state (given as ‡) and then E_{pot} falls again to the minimum of the BC molecule

E_{pot} along the reaction path can be plotted as E vs reaction coordinate (points on the path): Fig. 35.20, p. 942

The digram shows left the mimum for AB + C and right the minimum for BC + A

between reactants and products, the energy goes through a maximum at $(ABC)^{‡}$, the transition state, also called activated complex

⇒ the activated complex is not stable (it is not a stable intermediate, but in stable)

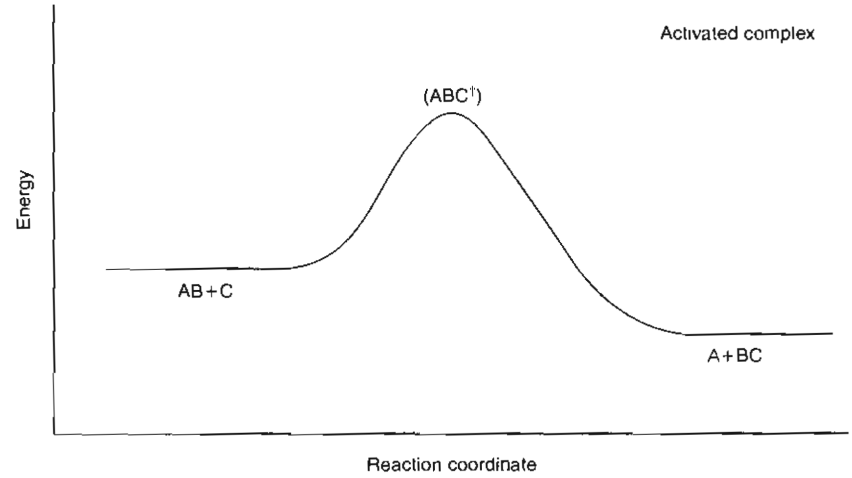


FIGURE 35.20
Reaction coordinate diagram involving an activated complex and a reactive intermediate. The graph corresponds to the reaction-coordinate derived from the dashed line between points *c* and *d* on the contour plot of Figure 35.19c. The maximum in energy along this coordinate corresponds to the transition state, and the species at this maximum is referred to as an activated complex.

35.14 Activated Complex Theory

The concept of equilibrium is central to a theoretical description of reaction rates developed principally by Henry Eyring in the 1930s. This theory, known as **activated complex theory** or **transition state theory,** provides a theoretical description of reaction rates. To illustrate the conceptual ideas behind activated complex theory, consider the following bimolecular reaction:

$$\mathrm{A} + \mathrm{B} \xrightarrow{k} \mathrm{P} \tag{35.113}$$

Figure 35.21 illustrates the reaction coordinate for this process, where A and B react to form an activated complex that undergoes decay, resulting in product formation. The **activated complex** represents the system at the transition state. This complex is not stable and has a lifetime on the order of one to a few vibrational periods ($\sim 10^{-14}$ s). When this theory was first proposed, experiments were incapable of following reaction dynamics on such short timescales such that evidence for an activated complex corresponding to the transition state was not available. However, recent developments in experimental kinetics have allowed for the investigation of these transient species, and a few references to this work are provided at the end of this chapter.

Activated complex theory involves a few major assumptions. The primary assumption is that an equilibrium exists between the reactants and the activated complex. It is also assumed that the reaction coordinate describing decomposition of the activated complex can be mapped onto a single energetic degree of freedom of the activated complex. For example, if product formation involves the breaking of a bond, then the vibrational degree of freedom corresponding to bond stretching is taken to be the reactive coordinate.

With these approximations in mind, we can take the kinetic methods derived earlier in this chapter and develop an expression for the rate of product formation. For the example of the bimolecular reaction from Equation (35.113), the kinetic mechanism corresponding to the activated complex model described earlier is

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AB}^\ddagger \tag{35.114}$$

$$\mathrm{AB}^\ddagger \xrightarrow{k_2} \mathrm{P} \tag{35.115}$$

Equation (35.114) represents the equilibrium between reactants and the activated complex, and Equation (35.115) represents the decay of the activated complex to form product. With the assumption of an equilibrium between the reactants and the activated complex, the

E_{pot} surfaces can be measured with crossed molecular beams:

In one beam all ~~molecules~~ reactant molecules have the same ~~geom~~ relative geometry, in the other beam, they have all the same energy.

After crossing the products are measured in terms of their energies and their distribution in space.

Henry Eyring (1930s): activated complex theory
transition state theory

look at $A + B \xrightarrow{k} P$

Fig. 35.21, p. 943

Epot as f(rc) rc: reaction coordinate

energy maximum: activated complex
= transition state

A reacts with B and forms the activated complex $AB^{\neq}$

lifetime of $AB^{\neq}$: $\approx 10^{-14}$ s $\hat{=}$ some vibrational periods

In the 1930 it was not possible to show that $AB^{\neq}$ exists because of its short lifetime

now - possible

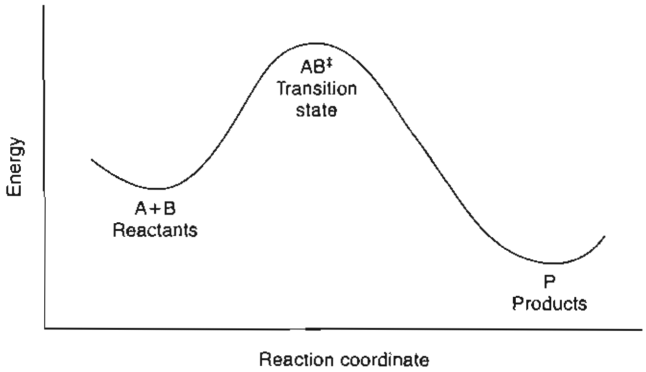


FIGURE 35.21
Illustration of transition state theory. Similar to reaction coordinates depicted previously, the reactants (A and B) and products (P) are separated by an energy barrier. The transition state is an activated reactant complex envisioned to exist at the free-energy maximum along the reaction coordinate.

differential rate expression for one of the reactants (A in this case) is set equal to zero consistent with equilibrium, and an expression for $[\mathrm{AB}^{\ddagger}]$ is obtained as follows:

$$\frac{d[\mathrm{A}]}{dt} = 0 = -k_1[\mathrm{A}][\mathrm{B}] + k_{-1}[\mathrm{AB}^{\ddagger}]$$

$$[\mathrm{AB}^{\ddagger}] = \frac{k_1}{k_{-1}}[\mathrm{A}][\mathrm{B}] = \frac{K_c^{\ddagger}}{c^\circ}[\mathrm{A}][\mathrm{B}] \quad \textbf{(35.116)}$$

In Equation (35.116), $K_c^{\ddagger}$ is the equilibrium constant involving the reactants and the activated complex, and it can be expressed in terms of the molecular partition functions of these species as described in Chapter 31. In addition, c° is the standard state concentration (typically 1 M), which appears in the following definition for $K_c^{\ddagger}$:

$$K_c^{\ddagger} = \frac{[\mathrm{AB}^{\ddagger}]/c^\circ}{([\mathrm{A}]/c^\circ)([\mathrm{B}]/c^\circ)} = \frac{[\mathrm{AB}^{\ddagger}]c^\circ}{[\mathrm{A}][\mathrm{B}]}$$

The rate of the reaction is equal to the rate of product formation, which by Equation (35.115) is equal to

$$R = \frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{AB}^{\ddagger}] \quad \textbf{(35.117)}$$

Substitution into Equation (35.117) of the expression for $[\mathrm{AB}^{\ddagger}]$ provided in Equation (35.116) yields the following expression for the reaction rate:

$$R = \frac{d[\mathrm{P}]}{dt} = \frac{k_2 K_c^{\ddagger}}{c^\circ}[\mathrm{A}][\mathrm{B}] \quad \textbf{(35.118)}$$

Further evaluation of the reaction rate expression requires that k_2 be defined. This rate constant is associated with the rate of activated complex decay. Imagine that product formation requires the dissociation of a weak bond in the activated complex (since this bond eventually breaks, resulting in product formation). The activated complex is not stable, and the complex dissociates with motion along the corresponding bond-stretching coordinate. Therefore, k_2 is related to the vibrational frequency associated with bond stretching, ν. The rate constant is exactly equal to ν only if every time an activated complex is formed, it dissociates, resulting in product formation. However, it is possible that the activated complex will instead revert back to reactants in which case only a fraction of the activated complexes formed will result in product formation. To account for this possibility, a term referred to as the transmission coefficient κ is included in the definition of k_2:

$$k_2 = \kappa\nu \quad \textbf{(35.119)}$$

With this definition of k_2, the reaction rate becomes

$$R = \frac{\kappa\nu K_c^{\ddagger}}{c^\circ}[\mathrm{A}][\mathrm{B}] \quad \textbf{(35.120)}$$

One can express $K_c^{\ddagger}$ in terms of the partition function of reactants and the activated complex using the techniques outlined in Chapter 32. In addition, the partition function for the asscemption: equilibrium between reactants and $AB^\ddagger$

further: rc can be described by 1 degree of freedam, corresponding to the bond stretching vibration of the bond that must be broken to form the products

that vibrational coordinate = rc

mechani~~m~~sm :

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB^\ddagger$$ equilibrium between $AB^\ddagger$ and reactants

$$AB^\ddagger \xrightarrow{k} P$$ decay of $AB^\ddagger$

$$\frac{d(A)}{dt} = 0$$ because of equilibrium

$$\frac{d[A]}{dt} = 0 = -k_1 [A][B] + k_{-1} [AB^\ddagger]$$

$$\Rightarrow [\cancel{B}AB^\ddagger] = \frac{k_1}{k_{-1}} [A][B] = \frac{K_c^\ddagger}{c^0} [A][B]$$

$K_c^\ddagger$ equilibrium constant of $AB^\ddagger$ formation

$c^0 = 1M$ standard concentration

$$K_c^\ddagger = \frac{[AB^\ddagger]/c^0}{[[A]/c^0]([B]/c^0)} = \frac{[AB^\ddagger]}{[A][B]} c^0$$

rate of product formation:

$$R = \frac{d[P]}{dt} = k_2 [AB^\ddagger]$$

k_2: $AB^\ddagger$ decay rate constant

k_2 related to vibration frequency ν of the breaking bond

$AB^{\ddagger}$ can break the bond and forms product or it can also go back to the reatants

$\Rightarrow$ transmission ~~f~~ coefficient κ

$$\kappa = \frac{\text{number of } AB^{\ddagger} \text{ forming products}}{\text{total number of } AB^{\ddagger} \text{ formed}}$$

$$\Rightarrow k_2 = \kappa \nu$$

$$\Rightarrow R = \frac{\kappa \nu K_c^{\ddagger}}{c^{\circ}} [A][B]$$

Ignore "partition function" which is discussed in 312

$$K_c^{\ddagger} = \frac{k_B T}{h\nu} \overline{K_c}^{\ddagger}$$

part of $K_c^{\ddagger}$ which describes bond breaking

equilibrium constant without the term for bond breaking

$\frac{k_B T}{h\nu}$ "partition function" of the breaking bond

$$\Rightarrow R = \frac{\kappa \nu K_c^{\ddagger}}{c^{\circ}} (A)(B) = \frac{\kappa\nu}{c^{\circ}} \frac{k_B T}{h\nu} \overline{K_c}^{\ddagger} [A][B]$$

$$= \kappa \frac{k_B T}{h c^{\circ}} \overline{K_c}^{\ddagger} [A][B]$$

$$\Rightarrow k = \kappa \frac{k_B T}{h c^{\circ}} \overline{K_c}^{\ddagger}$$

$$\Delta G^\ddagger = -RT \ln \overline{K_c^\ddagger}$$

$$k = \frac{k_B T}{h c^\circ} e^{-\Delta G^\ddagger / RT}$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger$$

$$\Rightarrow k = \frac{k_B T}{h c^\circ} e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT}$$ Eyring equation

in Arrhenius equation for k, pre-exponential factor is assumed to be indepen~~t~~detnt of T

Arrhenius equation: empirical

in experiments it is easy to overlook a ~~linier~~ linear dependence on T vs an exponential T dependence

However, parameters in Eyring equation ($\Delta H^\ddagger$, $\Delta S^\ddagger$) should be related to Arrhenius parameters (A, E_a)

Arrhenius: $k = A e^{-E_a/RT}$

$$\rightarrow \ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T}$$

$$\Rightarrow \frac{d \ln k}{dT} = \frac{d \ln A}{dT} + \frac{E_a}{R} \cdot \frac{1}{T^2}$$

$\frac{d \ln A}{dT} = 0$ in Arrhenius theory

$$\frac{E_a}{RT^2} = \frac{d \ln k}{dt}$$

$$E_a = RT^2 \frac{d \ln k}{RT}$$

$$\Rightarrow \quad E_a = RT^2\left[\frac{d}{dT}\ln\left(\frac{k_BT}{hc^o}\overline{K}_c^{\ddagger}\right)\right]$$

$$= RT^2\left\{\frac{d}{dT}\ln\frac{k_BT}{hc^o} + \frac{d\ln\overline{K}^{\ddagger}}{dT}\right\}$$

$$\frac{d}{dT}\ln\frac{k_BT}{hc^o} \ast \frac{d}{dx}\ln \text{const.}\cdot x$$

$$= \frac{1}{\text{const.}\cdot x}\cdot\text{const.}$$

$$E_a = RT^2\left\{\frac{hc^o}{k_BT}\,\frac{k_B}{hc^o} + \frac{d\ln\overline{K}^{\ddagger}}{dT}\right\}$$

$$= RT^2\left\{\frac{1}{T} + \frac{d\ln\overline{K}^{\ddagger}}{dT}\right\}$$

$$= RT + RT^2\,\frac{d\ln\overline{K}^{\ddagger}}{dT}$$

Thermodynamics: ~~ln~~ $\frac{d\ln K_c}{dT} = \frac{\Delta U}{RT^2}$ ← in~~ner~~ternal energy

$$\Rightarrow \quad E_a = RT + \Delta U^{\ddagger}$$

further $H = U + PV$

$$\rightarrow \quad \Delta U^{\ddagger} = \Delta H^{\ddagger} - \Delta(PV^{\ddagger})$$

$\Delta(PV^{\ddagger})$ = PV (activated complex) − PV (reactants) reaction in solution:

$P =$ const. , change in V can be neglected

$$\Rightarrow \Delta U^\ddagger \approx \Delta H^\ddagger$$

$\rightarrow$ solution: $E_a = \Delta H^\ddagger + RT$

~~Arrhenius $k = Ae$~~

~~Arrhenius: $k = Ae^{-E_a/RT}$~~

~~$k = A e e^{-\Delta H^\ddagger/RT}$~~

$\uparrow$

~~$e^{-RT/RT}$~~

$$e^{-\Delta H^\ddagger/RT} = e^{-\frac{E_a - RT}{RT}} = e\, e^{-E_a/RT}$$

Eyring in solutions: $k = \frac{e k_B T}{h c^\circ} e^{\Delta S^\ddagger/RT} e^{-E_a/RT}$

Arrhenius : $k = Ae^{-E_a/RT}$

$\Rightarrow A = \frac{e k_B T}{h c^\circ} e^{\Delta S^\ddagger/RT}$ bimolecular reaction in solutions

unimolecular reactions in solution: c° is lost

$$A = \frac{e k_B T}{h} e^{\Delta S^\ddagger/RT}$$

~~*~~ gas phase reactions

$$\Delta(PV^\ddagger) = \Delta n_g$$

change in number of gas moles when going from $AB^\ddagger$ to reactants:

$$n_g(AB^\ddagger) - n_g(\text{reactants})$$

unimolecular gas phase reactions

$$A(g) \rightarrow A^{\ddagger}(g) \Rightarrow \Delta n_g = 0$$

$$\Rightarrow E_a = \Delta H^{\ddagger} + RT \; , \quad A = \frac{e k_B T}{h} e^{\Delta S^{\ddagger}/R}$$

bimolecular gas phase reactions

$$A(g) + B(g) \rightarrow AB^{\ddagger}(g) \quad \Delta n_g = \overset{1-2}{\cancel{2-1}} = \cancel{0} -1$$

$$E_a = \Delta H^{\ddagger} + 2RT \; , \quad A = \frac{e^2 k_B T}{h c^{\circ}} e^{\Delta S^{\ddagger}/RT}$$

trimolecular:

$$A = \frac{e^3 k_B T}{h} e^{\Delta S^{\ddagger}/RT}$$

if $\Delta H^{\ddagger} \gg RT$: the E_a not much T dependent

also if $\Delta H(AB^{\ddagger}) < \Delta H(\text{reactants})$

$\Rightarrow$ rate <u>may</u> become faster when T is lowered

if $E_a \approx 0$ rate might be controlled by entropy

decomposition of nitrosyl halides important in atmospheric chemistry:

$$2\,NOCl(g) \rightarrow 2\,NO(g) + Cl_2(g)$$

$$A = 1{,}00 \cdot 10^{13} \frac{1}{Ms} \; , \quad E_a = 104{,}0 \; kJ/mol$$

at 300 K what is $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$?

(36) -54

bimolecular (2 NOCl), gas phase

$$\Rightarrow \quad \Delta H^{\ddagger} = E_a - 2RT = 104\,\frac{kJ}{mol} - 2\cdot\left(8{,}314\,\frac{J}{K\,mol}\cdot 300K\right)$$

$$= 104\,\frac{kJ}{mol} - 4{,}99\cdot 10^{3}\,\frac{J}{mol}$$

$$= 104\,\frac{kJ}{mol} - 4{,}99\,\frac{kJ}{mol} = 99{,}0\,\frac{kJ}{mol}$$

$$\Delta S^{\ddagger} = R \ln \frac{A h c^{0}}{e^{2} k_B T}$$

$$= 8{,}314\,\frac{J}{K\,mol} \ln\left[\frac{1{,}00\cdot 10^{13}\,\frac{1}{Ms}\cdot 6{,}626\cdot 10^{-34}\,Js\cdot 1M}{e^{2}\cdot 1{,}38\cdot 10^{-23}\,\frac{J}{K}\cdot 300\,K}\right]$$

$$= -12{,}7\,\frac{J}{K\,mol}$$

negative $\Delta S^{\ddagger}$ $\Rightarrow$ $AB^{\ddagger}$ is more ordered than the ~~reta~~ reactants

$\rightarrow$ $2\,NOCl \rightarrow (NOCl)_2$

$AB^{\ddagger}$

2 bound NOCl more ordered than 2 free NOCl

Fig. 35.22, p. 946

in gas-phase direct collision between reactants is possible

⇒ rate is determined by average distance an speed of molecules

speed from average kinetic energy $\frac{3}{2}RT$

in solution also $\frac{3}{2}RT$ for av. kinetic energy.

But before a reactant can hit the other, there will be many solute-solvent collisions

⇒ rate of diffusion can control reaction rate

rate constant of diffusion k_d

" " of product formation k_p

$$\Rightarrow \quad A + B \xrightarrow{k_d} AB$$

$$AB \xrightarrow{k_r} A + B \quad \text{backward reaction}$$

$$AB \xrightarrow{k_p} P$$

AB stable <u>intermediate</u> $\quad R = k_p [AB]$

AB intermediate ⇒ SSA:

$$\frac{d[AB]}{dt} \overset{(SSA)}{=} 0 = k_d [A][B] - k_r [AB] - k_p [AB]$$

$$\rightarrow [AB] = \frac{k_d [A][B]}{k_r + k_p}$$

$$\Rightarrow \quad R = \frac{k_p k_d}{k_r + k_p} [A][B]$$

EXAMPLE PROBLEM 35.10

The thermal decomposition reaction of nitrosyl halides is important in tropospheric chemistry. For example, consider the decomposition of NOCl:

$$2\,\mathrm{NOCl}(g) \rightarrow 2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g)$$

The Arrhenius parameters for this reaction are $A = 1.00 \times 10^{13}\ \mathrm{M^{-1}\,s^{-1}}$ and $E_a = 104.0\ \mathrm{kJ\ mol^{-1}}$. Calculate $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for this reaction with $T = 300.\ \mathrm{K}$.

Solution

This is a bimolecular reaction such that

$$\begin{aligned}\Delta H^{\ddagger} &= E_a - 2RT = 104\ \mathrm{kJ\ mol^{-1}} - 2(8.314\ \mathrm{J\ mol^{-1}\,K^{-1}})(300.\ \mathrm{K})\\ &= 104.0\ \mathrm{kJ\ mol^{-1}} - (4.99 \times 10^{3}\ \mathrm{J\ mol^{-1}})\left(\frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}}\right) = 99.0\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta S^{\ddagger} &= R\ln\left(\frac{Ahc^{\circ}}{e^{2}kT}\right)\\ &= (8.314\ \mathrm{J\,mol^{-1}\,K^{-1}})\ln\left(\frac{(1.00 \times 10^{13}\mathrm{M^{-1}s^{-1}})(6.626 \times 10^{-34}\mathrm{J\,s})(1\ \mathrm{M})}{e^{2}(1.38 \times 10^{-23}\mathrm{J\,K^{-1}})(300.\ \mathrm{K})}\right)\\ &= -12.7\ \mathrm{J\,mol^{-1}\,K^{-1}}\end{aligned}$$

One of the utilities of this calculation is that the sign and magnitude of $\Delta S^{\ddagger}$ provide information on the structure of the activated complex at the transition state relative to the reactants. The negative value in this example illustrates that the activated complex has a lower entropy (or is more ordered) than the reactants. This observation is consistent with a mechanism in which the two NOCl reactants form a complex that eventually decays to produce NO and Cl.

35.15 Diffusion Controlled Reactions

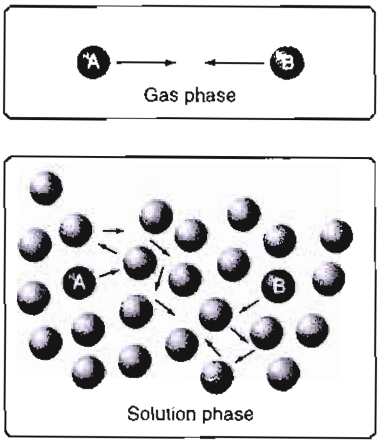


FIGURE 35.22
Top: Reactants A and B approach each other and collide in the gas phase. Bottom: In solution, the reactants undergo a series of collisions with the solvent. In this case, the approach of the reactants is dependent on the rate of reactant diffusion in solution.

For bimolecular chemical reactions in solution, the presence of solvent molecules can result in reaction dynamics that differ significantly from those in the gas phase. For example, the activation energy and relative orientation of reacting species were identified as being key factors in defining the rate constant for the reaction in the previous section. Imagine a reaction occurring in solution as illustrated in Figure 35.22. Since the average kinetic energy of the reactants is 3/2 RT, the average translational velocity is the same as in the gas phase. However, in solution the presence of the solvent molecules results in a number of solvent–solute collisions before the reactants collide. Subsequently, the uninterrupted approach of the reactants characteristic of a gas-phase reaction is replaced by the reactants undergoing diffusion in solution until they encounter each other. In this case, the rate of diffusion can determine the rate of reaction.

The role of diffusion in solution-phase chemistry can be described using the following kinetic scheme:

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_d} \mathrm{AB} \tag{35.134}$$

$$\mathrm{AB} \xrightarrow{k_r} \mathrm{A} + \mathrm{B} \tag{35.135}$$

$$\mathrm{AB} \xrightarrow{k_p} \mathrm{P} \tag{35.136}$$

In this scheme, reactants A and B diffuse with rate constant k_d until they make contact and form the intermediate complex AB. Once this complex is formed, dissociation can

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diffusion control: $k_\beta \gg k_r$

$\rightarrow$ $R = k_d [A][B]$ since k_d: diffusion control

~~A~~ D_{AB}: diffusion coefficient of reactants:

$$D_{AB} = D_A + D_B$$

$$k_d = 4\pi N_A (r_A + r_B) D_{AB}$$

r_A, r_B reactant radii

for spherical particles (radius r) in solution:

Stokes-Einstein equation (see Chapter 34):

$$D = \frac{k_B T}{6\pi \eta r}$$

η: solvent viscosity

$\Rightarrow$ k_d should decrease when solvent viscosity increases

protonation of Ac^-, Acetate in water

$D_{Ac^-} = 1.1 \cdot 10^{-5}\ \frac{cm^2}{s}$ $\quad D_{H^+} = 9{,}3 \cdot 10^{-5}\ \frac{cm^2}{s}$

$r_{Ac^-} + r_{H^+} \approx 5$ Å $\quad k_d = 3{,}9 \cdot 10^{10}\ \frac{1}{M s}$

acid/base rate constants much large because of Coulomb attractions between ions opposite limit: activation control:

$$k_r \gg k_p$$

$$R = \frac{k_p k_d}{k_r}[A][B]$$

in water, 25°C, pH = 7.4

$D(\text{hemoglobin}) = 7.6 \cdot 10^{-7}\,\frac{cm^2}{s}$

$r(\text{hemoglobin}) = 35\,Å$

$D(O_2) = 2.2 \cdot 10^{-5}\,\frac{cm^2}{s}$

$r(O_2) = 2.0\,Å$

experiment: effective rate constant for binding of O_2 to hemoglobin is $4 \cdot 10^{7}\,\frac{1}{Ms}$

diffusion control?

$$k_d = 4\pi N_A (r_A + r_B) D_{AB}$$

$$= 4\pi N_A (35 + 2.0) \cdot 10^{-8}\,cm\,(7.6 \cdot 10^{-7} + 2.2 \cdot 10^{-5})\,\frac{cm^2}{s}$$

$$= 6.4 \cdot 10^{10}\,\frac{1}{Ms}$$

$k_d \gg k_{exp} \Rightarrow$ <u>no</u> diffusion control!

Chapter 36

Reaction mechanism: sequence of elementary reaction steps leading from reactants to products

valid mechanism (useful): rate expression predicted by mechanism must be equal to experiment

example: decomposition of N_2O_5:

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

possible: simple 1 step mechanism where $2N_2O_5$ reacts directly to products

then reaction would be 2. order in N_2O_5

experiment: 1. order in N_2O_5

$\Rightarrow$ It cannot be a 1 step reaction

proposed mechanism:

$$\underset{\uparrow}{2}\cdot\left\{N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3\right\}$$

stoichiometric number: indicates that the reaction must occur 2 times in the mechanism

$$NO_2 + NO_3 \xrightarrow{k_2} NO_2 + O_2 + NO$$

$$NO + NO_3 \xrightarrow{k_3} 2NO_2$$

equilibrium must occur 2 times ~~bef~~ because the 2 later steps need NO_3 each!

complex reaction : 2 or more elementary steps

2 chemicals in the mechanism which are not in the overall reaction equation (NO, NO_3) : reaction intermediates

intermediates are <u>no</u> reactants and <u>no</u> products

They are formed by 1 or more steps in the mechanism and consumed again by 1 or more other steps in the mechanism.

valid mechanism: rate law from mechanism must be equal to experimental rate law

$$R = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{2}\left(k_1[N_2O_5] - k_{-1}[NO_2][NO_3]\right)$$

NO_2, NO_3 are reaction intermediates

$\Rightarrow$ SSA

rule: never have intermediat
in final rate expression!

$$\frac{d[NO]}{dt} \overset{SSA}{=} 0 = k_2[NO_2][NO_3] - k_3[NO][NO_3]$$

$$[NO] = \frac{k_2}{k_3}[NO_2]$$

[NO] into here

$$\frac{d[NO_3]}{dt} \overset{SSA}{=} 0 = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO_2][NO$$

$$- k_3[NO][NO_3]$$

$$\Rightarrow \; 0 = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO_2][NO_3]$$

$$- k_3\left(\frac{k_2}{k_3}[NO_2]\right)[NO_3]$$

$$0 = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - 2k_2[NO_2][NO_3]$$

$$\Rightarrow [NO_2][NO_3] = \frac{k_1}{k_{-1}+2k_2}[N_2O_5]$$

into R:

$$R = \frac{1}{2}\left(k_1[N_2O_5] - k_{-1}[NO_2][NO_3]\right)$$

$$= \frac{1}{2}\left(k_1[N_2O_5] - k_{-1}\frac{k_1}{k_{-1}+2k_2}[N_2O_5]\right)$$

$$= \frac{1}{2}\,\frac{k_1(k_{-1}+2k_2) - k_{-1}k_1}{k_{-1}+2k_2}[N_2O_5]$$

$$= \frac{1}{2}\,\frac{\overset{\checkmark}{k_1k_{-1}} + 2k_1k_2 - \overset{\checkmark}{k_{-1}k_1}}{\cancel{+}k_{-1} + 2k_2}[N_2O_5]$$

$$= \frac{k_1k_2}{k_{-1}+2k_2}[N_2O_5] = k_{eff}[N_2O_5] \,,\quad k_{eff} = \frac{k_1k_2}{k_{-1}+2k_2}$$

⇒ equal to experimental 1. order in N_2O_5

This is no proof the mechanism is the true one, it only" proof ~~tat~~ that the mechanism can be true = valid mechanism

important never have intermediates in a rate law !

Pre-equilibrium Approximation

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} I$$

$$I \xrightarrow{k_p} P$$

k_f forward rate constant

k_r reverse or backward rate constant

A, B form intermediate I, then I decays to product P

if $k_f, k_r \gg k_p$ then there are 2 distinct steps:

1. equilibrium between reactants and intermediate is maintained in ~~reaction~~ all reaction time (if there are enough reactants for this)
2. The intermediate decays to product P

$$\frac{d[P]}{dt} = k_p[I]$$

pre-equilibrium approximation:

$$\frac{[I]}{[A][B]} = \frac{k_f}{k_r} = K_c$$

$\Rightarrow [I] = K_c[A][B]$ to remove [I] from rate laws

$$\Rightarrow \frac{d[P]}{dt} = k_p[I] = k_p K_c [A][B] = k_{eff} [A][B]$$

$$k_{eff} = k_p K_c$$

examples:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

possible simple trimolecular reaction between 2NO and 1 O_2 if it is consistent with experiment showing 2. ~~and~~ order in NO and 1. order in O_2

if correct: increasing T will increase the number of ~~collissi~~ collision

→ increase of T ~~shoul~~ should increase the rate if the mechanism is correct

but experimental: decrease of rate when ~~#~~ T increases

→ simple 1 step mechanism not correct

proposed other mechanism:

$$2NO \underset{k_r}{\overset{k_f}{\rightleftharpoons}} N_2O_2 \qquad k_f, k_r \gg k_p$$

$$N_2O_2 + O_2 \xrightarrow{k_p} 2NO_2$$

pre-equilibrium approx: $[N_2O_2] = \frac{k_f}{k_r}[NO]^2$

$$= K_c [NO]^2$$

$$R = \frac{1}{2}\frac{d[NO_2]}{dt} = k_p [N_2O_2][O_2]$$

$\Rightarrow \quad R = k_p [N_2O_2][O_2] = k_p K_c [NO_2]^2 [O_2] = k_{eff} [NO]^2 [O_2]$

2. order for NO, 1. order for O_2, consistent with experiment

Further formation of N_2O_2 is exothermic

$\Rightarrow$ T increase shifts equilibrium to reactants

$\Rightarrow$ T increase yields less N_2O_2 to react

→ Rate will decrease when T increases

Lindemann Mechanism for unimolecular ~~de~~ dissociation reactions:

$A \rightarrow$ fragments (parts of A)

A decays when the energy in a vibration is large enough to break a bond this energy can come ~~thro~~ from ~~e~~ collisions with other A but that would yield ~~to~~ 2. order kinetics while experiment shows 1. order kinetics at large reactant concentration

Lindemann: $A + A \xrightarrow{k_1} A^* + A$

A^*: activated reactant with enough energy for decomposition for A^* there are now ~~t~~ 2 possible further steps:

$$A^* + A \xrightarrow{k_{-1}} A + A \quad \text{backward reaction}$$

or $$A^* \xrightarrow{k_2} P$$

$$\Rightarrow R = \frac{d[P]}{dt} = k_2[A^*]$$

A^*: intermediate → SSA

$$\frac{d[A^*]}{dt} \overset{SSA}{=} 0 = k_1[A]^2 - k_{-1}[A][A^*] - k_2[A^*]$$

$$\Rightarrow [A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2}$$

$$\Rightarrow \frac{d[P]}{dt} = \frac{k_1 k_2 [A]^2}{k_{-1}[A] + k_2}$$

<u>Large [A]</u>: $k_{-1}[A] \gg k_2$

$$\Rightarrow \frac{d[P]}{dt} = \frac{k_1 k_2}{k_{-1}}[A]$$

→ rate of product formation will be 1. order when [A] or P_A are large

$$\frac{P_A}{RT} = \frac{n_A}{V} = [A]$$

at high P A^* will be produced faster than the decomposition happens

⇒ rate of ~~product formation~~ decomposition limits the rate of product formation

Low [A]: $k_2 \gg k_{-1}[A]$

$$\rightarrow \frac{d[P]}{dt} = k_1 [A]^2$$

at low P formation of A^* is rate limiting

generalized form: in the reaction mixture a collision partner M is present which does not react (added buffer gas)

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M$$

$$A^* \xrightarrow{k_2} P$$

$\Rightarrow$ (as before)

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_2} = k_{uni} [A]$$

$$k_{uni} = \frac{k_1 k_2 [M]}{k_{-1}[M] + k_2}$$

high [M]: $k_{-1}[M] \gg k_2$

$$\rightarrow k_{uni} = \frac{k_1 k_2}{k_{-1}}$$

decrease of [M]: k_{uni} will be constant until

$k_2 \gg k_{-1}[M]$, then $k_{uni} = k_1 [M]$

k_{uni} vs P: straight line for low P, getting const at high P

Fig 36.1 and 36.2, p 960

straight line from inversions

$$k_{uni} = \frac{k_1 k_2 (M)}{k_{-1}(M) + k_2}$$

$$\frac{1}{k_{uni}} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1} \frac{1}{(M)}$$

k_{uni}^{-1} vs $[M]^{-1}$ or p^{-1}

→ straight line

slope $= \frac{1}{k_1}$, intercept $= \frac{k_{-1}}{k_1 k_2}$

catalysis

a catalyst takes part in a reaction and speeds it up, but it is not changed or consumed.

a catalyst opens a second reaction pathway with lower activation energy

without the catalyst the reaction rate is r_0

with catalyst it is $r_0 + r_1$, r_1 being the catalyzed path

The reaction goes in both pathways, but the catalyzed one with rate r_1 is simply faster.

Fig 36.3 shows a analogy an electric circuit

a catalyst combines with 1 or more reactant or an intermediate, and after the reaction gets free again unchanged.

Substituting Equation (36.27) into Equation (36.26) results in the final differential rate expression for [P]:

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_1 k_2 [\mathrm{A}]^2}{k_{-1}[\mathrm{A}] + k_2} \tag{36.28}$$

Equation (36.28) is the central result of the Lindemann mechanism. It states that the observed order dependence on [A] depends on the relative magnitude of $k_{-1}[\mathrm{A}]$ versus k_2. At high reactant concentrations, $k_{-1}[\mathrm{A}] > k_2$ and Equation (36.28) reduces to

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_1 k_2}{k_{-1}}[\mathrm{A}] \tag{36.29}$$

Equation (36.29) demonstrates that at high reactant concentrations or pressures (recall that $P_A/RT = n_A/V = [A]$) the rate of product formation will be first order in [A], consistent with experiment. Mechanistically, at high pressures activated molecules will be produced faster than decomposition occurs such that the rate of decomposition is the rate-limiting step in product formation. At low reactant concentrations $k_2 > k_{-1}[\mathrm{A}]$ and Equation (36.28) becomes

$$\frac{d[\mathrm{P}]}{dt} = k_1[\mathrm{A}]^2 \tag{36.30}$$

Equation (36.30) demonstrates that at low pressures the formation of activated complex becomes the rate-limiting step in the reaction and the rate of product formation is second order in [A].

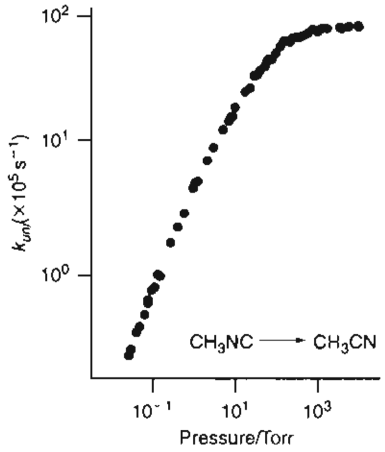


FIGURE 36.1
Pressure dependence of the observed rate constant for the unimolecular isomerization of methyl isocyanide.
[Data from Schneider and Rabinovitch, "Thermal Unimolecular Isomerization of Methyl Isocyanide - Fall-Off Behavior," *J. American Chemical Society* 84 (1962): 4225.]

The Lindemann mechanism can be generalized to describe a variety of unimolecular reactions through the following generic scheme:

$$\mathrm{A} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + M \tag{36.31}$$

$$\mathrm{A}^* \xrightarrow{k_2} \mathrm{P} \tag{36.32}$$

In this mechanism, M is a collisional partner that can be the reactant itself (A) or some other species such as a nonreactive buffer gas added to the reaction. The rate of product formation can be written as follows:

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_1 k_2 [\mathrm{A}][\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2} = k_{uni}[\mathrm{A}] \tag{36.33}$$

In Equation (36.33), k_{uni} is the apparent rate constant for the reaction defined as

$$k_{uni} = \frac{k_1 k_2 [\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2} \tag{36.34}$$

In the limit of high M concentrations, $k_{-1}[\mathrm{M}] \gg k_2$ and $k_{uni} = k_1 k_2 / k_{-1}$, resulting in an apparent rate constant that is independent of [M]. As [M] decreases, k_{uni} will decrease until $k_2 > k_{-1}[\mathrm{M}]$, at which point $k_{uni} = k_1[\mathrm{M}]$ and the apparent rate demonstrates first-order dependence on M. Figure 36.1 presents a plot of the observed rate constant for the isomerization of methyl isocyanide versus pressure measured at 230.4°C by Schneider and Rabinovitch. The figure demonstrates that the predicted linear relationship between k_{uni} and pressure at low pressure, which is consistent with the corresponding limiting behavior of Equation (36.34), is observed for this reaction. In addition, at high pressure k_{uni} reaches a constant value, which is also consistent with the limiting behavior of Equation (36.34).

The Lindemann mechanism provides a detailed prediction of how the rate constant for a unimolecular reaction will vary with pressure or concentration. Inverting Equation (36.34), the relationship between k_{uni} and reactant concentration becomes

$$\frac{1}{k_{uni}} = \frac{k_{-1}}{k_1 k_2} + \left(\frac{1}{k_1}\right)\frac{1}{[\mathrm{M}]} \tag{36.35}$$

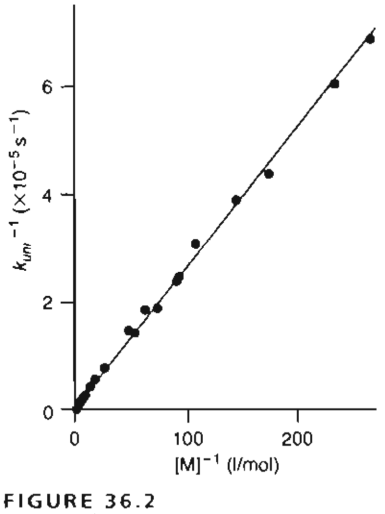


FIGURE 36.2
Plot of k_{uni}^{-1} versus $[\mathrm{M}]^{-1}$ for the unimolecular isomerization of methyl isocyanide at 230.4°C. The solid line is the best fit to the data.

a catalyst is not consumed, so that a small amount of it is enough to speed up many reactions

mechanism (S = substrate, reactant, C = catalyst
SC substrate-catalyst complex):

$$S + C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SC$$

$$SC \xrightarrow{k_2} P \qquad P = \text{product}$$

rate of product formation $\frac{d[P]}{dt} = k_2[SC]$

The intermediate SC must be eliminated: SSA

$$\frac{d[SC]}{dt} \overset{SSA}{=} 0 = k_1[S][C] - k_{-1}[SC] - k_2[SC]$$

$$\Rightarrow \cancel{[S]}\ [SC] = \frac{k_1[S][C]}{k_{-1} + k_2} = \cancel{K_m}\ \frac{1}{K_m}[S][C]$$

$\Rightarrow$ composite constant $K_m = \frac{k_{-1} + k_2}{k_1}$

$$\frac{d[P]}{dt} = \frac{k_2}{K_m}[S][C]$$

[S], [C] are the chemicals ~~S~~ S and C which are not in the complex and can be difficult to measure

easier to measure $[S]_0$ and $[C]_0$ at the beginning of the reaction

Equation (36.35) predicts that a plot of k_{uni}^{-1} versus $[\mathrm{M}]^{-1}$ should yield a straight line with slope $1/k_1$ and y intercept of k_{-1}/k_1k_2. A plot of the data presented in Figure 36.1 employing Equation (36.35) is presented in Figure 36.2. The figure demonstrates that the expected linear relationship between k_{uni}^{-1} and $[\mathrm{M}]^{-1}$ that is observed for this reaction is consistent with the Lindemann mechanism. The solid line in the figure is the best fit to the data by a straight line. The slope of this line provides a value for k_1 of $4.16 \times 10^6\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, and the y intercept in combination with the value for k_1 dictates that $k_{-1}/k_2 = 1.76 \times 10^5\ \mathrm{M}^{-1}$.

36.4 Catalysis

A **catalyst** is a substance that participates in chemical reactions by increasing the reaction rate, yet the catalyst itself remains intact after the reaction is complete. The general function of a catalyst is to provide an additional mechanism by which reactants are converted to products. The presence of a new reaction mechanism involving the catalyst results in a second reaction coordinate that connects reactants and products. The activation energy along this second reaction coordinate will be lower in comparison to the uncatalyzed reaction; therefore, the overall reaction rate will increase. For example, consider Figure 36.3 in which a reaction involving the conversion of reactant A to product B with and without a catalyst is depicted. In the absence of a catalyst, the rate of product formation is given by rate $= r_0$. In the presence of the catalyst, a second pathway is created, and the reaction rate is now the sum of the original rate plus the rate for the catalyzed reaction, or $r_0 + r_c$.

An analogy for a catalyzed reaction is found in the electrical circuits depicted in Figure 36.3. In the "catalyzed" electrical circuit, a second, parallel pathway for current flow has been added, allowing for increased total current when compared to the "uncatalyzed" circuit. By analogy, the addition of the second, parallel pathway is equivalent to the alternative reaction mechanism involving the catalyst.

To be effective, a catalyst must combine with one or more of the reactants or with an intermediate species involved in the reaction. After the reaction has taken place, the catalyst is freed and can combine with another reactant or intermediate in a subsequent reaction. The catalyst is not consumed during the reaction, so a small amount of catalyst can participate in numerous reactions. The simplest mechanism describing a catalytic process is as follows:

$$\mathrm{S} + \mathrm{C} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{SC} \tag{36.36}$$

$$\mathrm{SC} \xrightarrow{k_2} \mathrm{P} + \mathrm{C} \tag{36.37}$$

where S represents the reactant or substrate, C is the catalyst, and P is the product. The **substrate–catalyst complex** is represented by SC and is an intermediate species in this mechanism. The differential rate expression for product formation is

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{SC}] \tag{36.38}$$

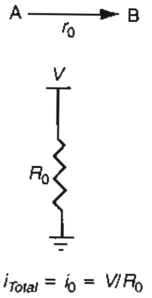
Given that SC is an intermediate, we write the differential rate expression for this species and apply the steady-state approximation:

$$\frac{d[\mathrm{SC}]}{dt} = k_1[\mathrm{S}][\mathrm{C}] - k_{-1}[\mathrm{SC}] - k_2[\mathrm{SC}] = 0$$

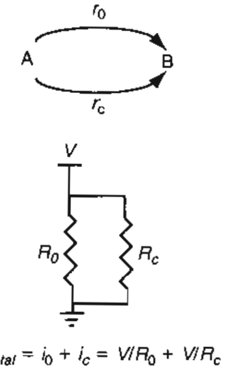
$$[\mathrm{SC}] = \frac{k_1[\mathrm{S}][\mathrm{C}]}{k_{-1} + k_2} = \frac{[\mathrm{S}][\mathrm{C}]}{K_m} \tag{36.39}$$

In Equation (36.39), K_m is referred to as the **composite constant** and is defined as

$$K_m = \frac{k_{-1} + k_2}{k_1} \tag{36.40}$$



Uncatalyzed



Catalyzed

FIGURE 36.3
Illustration of catalysis. In the uncatalyzed reaction, the rate of reaction is given by r_0. In the catalyzed case, a new pathway is created by the presence of the catalyst with corresponding rate r_c. The total rate of reaction for the catalyzed case is $r_0 + r_c$. The analogous electrical circuits are also presented for comparison.

$$\underset{0}{[S]} = [S]_{\cancel{0}} - [SC] - [P]$$

both [SC] and [P] must be formed from $[S]_0$

$$[C]_0 = [C] + [SC]$$

$$\Rightarrow [S] = [S]_0 - [SC] - [P]$$

$$[C] = [C]_0 - [SC]$$

$$\Rightarrow K_m [SC] = [S][C] \left(\text{because } [SC] = \frac{[S][C]}{K_m}\right)$$

$$K_m [SC] = ((\cancel{[S]=}\ [S]_0 - [SC] - [P])([C_0] - [SC]))$$

$$0 = \left[[C]_0 ([S]_0 - [P]) \right] - [SC]([S]_0 + [C]_0 - [P] + K_m) + [SC]^2$$

quadratic equation for [SC]

to make it easier:

1) control of $[S]_0$, $[C]_0$ such that [SC] is small

2) initial states of the reaction, where [P] is small

so neglect $[SC]^2$ and all terms with [P]:

$$0 = [C]_0 [S]_0 - [SC]([S]_0 + [C_0] + K_m)$$

$$\Rightarrow \boxed{S}C] = \frac{[C]_0 [S]_0}{[S]_0 + [C]_0 + K_m}$$

$\Rightarrow$ <u>initial</u> rates

$$R_0 = \frac{d[P]_0}{dt} = k_2 [SC] = \frac{k_2 [C]_0 [S]_0}{[S]_0 + [C]_0 + K_m}$$

o indicates initial = beginning of reaction

Limiting Case 1 : $[C]_0 \ll [S]_0$

most common case

negleet $[C]_0$ in denominator

$$\rightarrow R_0 = \frac{k_2 [S]_0 [C]_0}{[S]_0 + K_m}$$

inversion :

$$\frac{1}{R_0} = \frac{K_m}{k_2 [S]_0 [C]_0} + \frac{1}{k_2 [C]_0}$$

$$\frac{1}{R_0} = \frac{K_m}{k_2 [C]_0} \cdot \frac{1}{[S]_0} + \frac{1}{k_2 [C]_0}$$

plot of $\frac{1}{R_0}$ vs $\frac{1}{[S]_0}$: straight line

slope = $\frac{K_m}{k_2 [C]_0}$

intercept = $\frac{1}{k_2 [C]_0}$

Fig. 36.4, page 863

when $[S]_0 \gg K_m$ then $[S]_0 + K_m \approx [S]_0$

$\Rightarrow R_0 = k_2 [C]_0 = R_{max}$ limiting, maximum rate

Limiting Case 2 : $[C]_0 \gg [S]_0$

not used many times, since all data needed can be obtained from Case 1

and also large $[C]_0$ can be very expensive!

here $R_0 = \frac{k_2 [S]_0 [C]_0}{[C]_0 + K_m}$

For substrate concentrations where $[S]_0 < K_m$, the reaction rate should increase linearly with substrate concentration, with a slope equal to $k_2[C]_0/K_m$. Parameters such as k_2 and K_m can be obtained by comparing experimental reaction rates to Equation (36.49). An alternative approach to determining these parameters is to invert Equation (36.49) to obtain the following relationship between the reaction rate and initial substrate concentration:

$$\frac{1}{R_0} = \left(\frac{K_m}{k_2[C]_0}\right)\frac{1}{[S]_0} + \frac{1}{k_2[C]_0} \tag{36.50}$$

Equation (36.50) demonstrates that a plot of the inverse of the initial reaction rate versus $[S]_0^{-1}$, referred to as a **reciprocal plot,** should yield a straight line. The *y* intercept and slope of this line provide a measure of K_m and k_2, assuming $[C]_0$ is known.

At elevated concentrations of substrate where $[S]_0 \gg K_m$, the denominator in Equation (36.49) can be approximated as $[S]_0$, resulting in the following expression for the reaction rate:

$$R_0 = k_2[C]_0 = R_{max} \tag{36.51}$$

In other words, the rate of reaction will reach a limiting value where the rate becomes zero order in substrate concentration. In this limit, the reaction rate can only be enhanced by increasing the amount of catalyst. An illustration of the variation in the reaction rate with initial substrate concentration predicted by Equations (36.49) and (36.50) is provided in Figure 36.4.

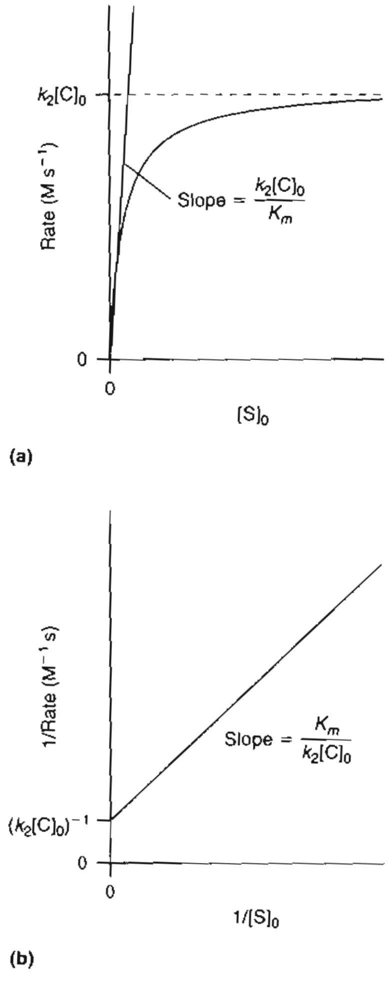


FIGURE 36.4
Illustration of the variation in the reaction rate with substrate concentration under Case 1 conditions as described in the text. **(a)** Plot of the initial reaction rate with respect to substrate concentration [Equation (36.49)]. At low substrate concentrations, the reaction rate increases linearly with substrate concentration. At high substrate concentrations, a maximum reaction rate of $k_2[C]_0$ is reached. **(b)** Reciprocal plot where the inverse of the reaction rate is plotted with respect to the inverse of substrate concentration [Equation (36.50)]. The *y* intercept of this line is equal to the inverse of the maximum reaction rate, or $(k_2[C]_0)^{-1}$. The slope of the line is equal to $K_m(k_2[C]_0)^{-1}$; therefore, with the slope and *y* intercept, K_m can be determined.

36.4.2 Case 2: $[C]_0 \gg [S]_0$

In this limit Equation (36.48) becomes

$$R_0 = \frac{k_2[S]_0[C]_0}{[C]_0 + K_m} \tag{36.52}$$

In this concentration limit, the reaction rate is first order in $[S]_0$ but can be first or zero order in $[C]_0$ depending on the magnitude of $[C]_0$ relative to K_m. In catalysis studies, this limit is generally avoided because the insight to be gained regarding the rate constants for the various reaction steps are more easily evaluated for the previously discussed Case 1. In addition, good catalysts can be expensive; therefore, employing excess catalyst in a reaction is not cost effective.

36.4.3 Michaelis–Menten Enzyme Kinetics

Enzymes are protein molecules that serve as catalysts in a wide variety of chemical reactions. Enzymes are noted for their reaction specificity, with nature having developed specific catalysts to facilitate the vast majority of biological reactions required for organism survival. An illustration enzyme with associated substrate is presented in Figure 36.5. The figure presents a space-filling model derived from a crystal structure of phospholipase A_2 (white) containing a bound substrate analogue (red). This enzyme catalyzes the hydrolysis of esters in phospholipids. The substrate analogue contains a stable phosphonate group in place of the enzyme-susceptible ester. The substrate analogue is resistant to enzymatic hydrolysis so that it does not suffer chemical breakdown during the structure determination process. With reactive substrate, ester hydrolysis occurs and the products of the reaction are released from the enzyme, resulting in regeneration of the free enzyme.

The kinetic mechanism of phospholipase A_2 catalysis can be described using the **Michaelis–Menten mechanism** of enzyme activity illustrated in Figure 36.6. The figure depicts the "lock-and-key" model for enzyme reactivity in which the substrate is bound to the active site of the enzyme where the reaction is catalyzed. The enzyme and substrate form the enzyme–substrate complex, which dissociates into product and uncomplexed enzyme. The interactions involved in creation of the enzyme–substrate

Michaelis - Menten Enzyme Kinetics

Enzymes: protein which can serve as catalysts for most reactions in a living cell

Fig. 36.5 p. 964

Crystal structure of phospholipase (A_2) which catalyzes ester hydrolysis with a bound substrate analogue

the analogue is not an organic ester, which would react before an x-ray can be done but a stable phosphonate group:

phosphoric acid ester which is not attacked by the enzyme

Michaelis - Menten mechanism.

lock - key model

Fig. 36.6 p. 964

substrate (the key) is bound to the enzymatic active site of the protein (the lock)

→ ES (enzyme - substrate complex)

yields enzyme back and the product

mechanism:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{k_2} E + P$$

Same as general catalysis mechanism

only C is now the enzyme E

important: Case I $[S]_0 \gg [E]_0$

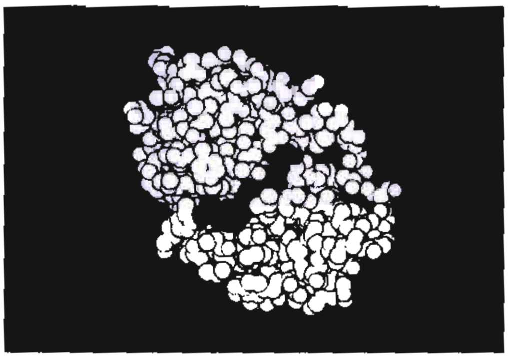


FIGURE 36.5
Space-filling model of the enzyme phospholipase A_2 (white) containing a bound substrate analogue (red). The substrate analogue contains a stable phosphonate group in place of the enzyme-susceptible ester; therefore, the substrate analogue is resistant to enzymatic hydrolysis and the enzyme–substrate complex remains stable in the complex during the X-ray diffraction structure determination process. [Structural data from Scott, White, Browning, Rosa, Gelb, and Sigler. "Structures of Free Inhibited Human Secretory Phospholipase A_2 from Inflammatory Exudate." *Science* 5034 (1991): 1007.]

complex are enzyme specific. For example, the active site may bind the substrate in more than one location, thereby creating geometric strain that promotes product formation. The enzyme may orient the substrate so that the reaction geometry is optimized. In summary, the details of enzyme-mediated chemistry are highly dependent on the reaction of interest. Rather than an exhaustive presentation of enzyme kinetics, our motivation here is to describe enzyme kinetics within the general framework of catalyzed reactions.

A schematic description of the mechanism illustrated in Figure 36.6 is as follows:

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES} \xrightarrow{k_2} \mathrm{E} + \mathrm{P} \tag{36.53}$$

In this mechanism, E is enzyme, S is substrate, ES is the complex, and P is product. Comparison of the mechanism of Equation (36.53) to the general catalytic mechanism described earlier in Equations (36.36) and (36.37) demonstrates that this mechanism is identical to the general catalysis mechanism except that the catalyst C is now the enzyme E. In the limit where the initial substrate concentration is substantially greater than that of the enzyme ($[\mathrm{S}]_0 \gg [\mathrm{E}]_0$ or Case 1 conditions as described previously), the rate of product formation is given by

$$R_0 = \frac{k_2[\mathrm{S}]_0[\mathrm{E}]_0}{[\mathrm{S}]_0 + K_m} \tag{36.54}$$

In enzyme kinetics the composite constant K_m in Equation (36.54) is referred to as the **Michaelis constant** in enzyme kinetics, and Equation (36.54) is referred to as the **Michaelis–Menten rate law.** When $[\mathrm{S}]_0 \gg K_m$, the Michaelis constant can be neglected, resulting in the following expression for the rate:

$$R_0 = k_2[\mathrm{E}]_0 = R_{max} \tag{36.55}$$

Equation (36.55) demonstrates that the rate of product formation will plateau at some maximum value equal to the product of initial enzyme concentration and k_2, the rate constant for product formation, consistent with the behavior depicted in Figure 36.4. A reciprocal plot of the reaction rate can also be constructed by inverting Equation (36.54), which results in the **Lineweaver–Burk equation:**

$$\frac{1}{R_0} = \frac{1}{R_{max}} + \frac{K_m}{R_{max}}\frac{1}{[\mathrm{S}]_0} \tag{36.56}$$

For the Michaelis–Menten mechanism to be consistent with experiment, a plot of the inverse of the initial rate with respect to $[\mathrm{S}]_0^{-1}$ should yield a straight line from which the y intercept and slope can be used to determine the maximum reaction rate and the Michaelis constant. This reciprocal plot is referred to as the **Lineweaver–Burk plot.** In addition, because $[\mathrm{E}]_0$ is readily determined experimentally, the maximum rate can be used to determine k_2, referred to as the **turnover number** of the enzyme [Equation (36.55)]. The turnover number can be thought of as the maximum number of

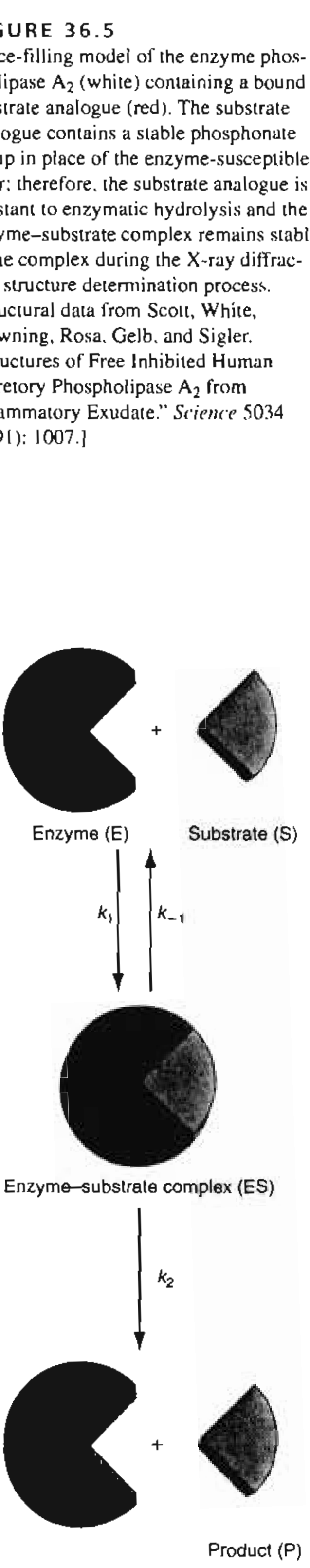


FIGURE 36.6
Schematic of enzyme catalysis.

→ (as before)

$$R_0 = \frac{k_2 [S]_0 [E]_0}{[S]_i + K_m}$$

here: K_m is called Michaelis constant

when $[S]_0 \gg K_m$ $\quad R_0 = k_2 [E]_0 = R_{max}$ limiting rate

inversion:

$$\frac{1}{R_0} = \frac{1}{k_2 [E]_0} + \frac{K_m}{k_2 [E]_0 [S]_0}$$

$$\frac{1}{R_0} = \frac{1}{R_{max}} + \frac{K_m}{R_{max}} \cdot \frac{1}{[S]_0}$$

Lineweaver-Burk plot:

$\frac{1}{R_0}$ vs $\frac{1}{[S]_0}$: straight line wit

~~slope~~ intercept $= \frac{1}{R_{max}}$, ~~intercept~~ slope $= \frac{K_m}{R_{max}}$

R_{max} together with $[E]_0$ yields k_2

k_2: turnover number = maximum number of substrate molecules that can be converted to product per unit time

k_2 mostly between 1 and $10^5 \, s^{-1}$ for enzymes

if $R_0 = \frac{1}{2} R_{max}$, then:

$$R_0 = \frac{R_{max} [S]_0}{[S]_0 + K_m} \Rightarrow \frac{1}{2} R_{max} = \frac{R_{max} [S]_0}{[S]_0 + K_m}$$

$$\Rightarrow [S]_0 + K_m = 2 [S]_0$$

and $\quad K_m = [S]_0$ if $R_0 = \frac{1}{2} R_{max}$

example

CO_2 hydration catalyzed by carbonic anhydrase (E)

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

HCO_3^- goes through the blood stream and converted back to CO_2 in the lungs by the same enzyme with $[E]_0 = 2,3\ nM$ at 0,5°C:

R_0 (M/s)	$[CO_2]_0$ (mM)
$2,78 \cdot 10^{-5}$	1,25
$5,00 \cdot 10^{-5}$	2,5
$8,33 \cdot 10^{-5}$	5,0
$1,67 \cdot 10^{-4}$	20,0

$\frac{1}{R_0}$ vs $\frac{1}{[CO_2]_0}$ see page ~~9675~~ 965

intercept = 4000 s/M

$\rightarrow R_{max} = 2,5 \cdot 10^{-4}\ M/s$, ~~R_{max}~~ $[E]_0 = 2,3\ nM$

$$\Rightarrow k_2 = \frac{R_{max}}{[E]_0} = \frac{2,5 \cdot 10^{-4}\ M/s}{2,3 \cdot 10^{-9}\ M} = 1,1 \cdot 10^5\ \frac{1}{s}$$

slope = 40 s

$$K_m = \text{slope} \cdot R_{max}$$

$$= 40\,s \cdot 2,5 \cdot 10^{-4}\ \frac{M}{s}$$

$$= 10\ mM$$

substrate molecules per unit time that can be converted into product. Most enzymes demonstrate turnover numbers between 1 and $10^5\ s^{-1}$ under physiological conditions.

EXAMPLE PROBLEM 36.1

DeVoe and Kistiakowsky [*J. American Chemical Society* 83 (1961): 274] studied the kinetics of CO_2 hydration catalyzed by the enzyme carbonic anhydrase:

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

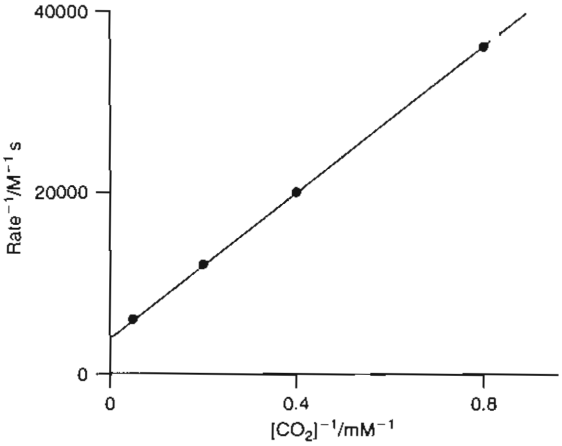
In this reaction, CO_2 is converted to bicarbonate ion. Bicarbonate is transported in the bloodstream and converted back to CO_2 in the lungs, a reaction that is also catalyzed by carbonic anhydrase. The following initial reaction rates for the hydration reaction were obtained for an initial enzyme concentration of 2.3 nM and temperature of 0.5°C:

Rate ($M\ s^{-1}$)	**[CO_2] (mM)**
2.78×10^{-5}	1.25
5.00×10^{-5}	2.5
8.33×10^{-5}	5.0
1.67×10^{-4}	20.0

Determine K_m and k_2 for the enzyme at this temperature.

Solution

The Lineweaver–Burk plot of the rate^{-1} versus $[CO_2]^{-1}$ is shown here:



The y intercept for the best fit line to the data is $4000\ M^{-1}\ s$ corresponding to $R_{max} = 2.5 \times 10^{-4}\ M\ s^{-1}$. Using this value and $[E]_0 = 2.3$ nM, k_2 is

$$k_2 = \frac{R_{max}}{[E]_0} = \frac{2.5 \times 10^{-4}\ M\ s^{-1}}{2.3 \times 10^{-9}\ M} = 1.1 \times 10^5\ s^{-1}$$

Notice that the units of k_2, the turnover number, are consistent with a first-order process, in agreement with the Michaelis–Menten mechanism. The slope of the best fit line is 40 s such that, per Equation (36.56), K_m is given by

$$K_m = slope \times R_{max} = (40\ s)(2.5 \times 10^{-4}\ M\ s^{-1})$$
$$= 10\ mM$$

Fig. 36.7 p. 966

R_0 vs $[CO_2]_0$

note difficult to make sure that the real R_{max} is found!

Competitive Inhibition

Happens, when a chemical is in the reation mixture which has a structure similar to that of the substrate, the inhibitor I

It can be bound at the catalytic active site of an enzyme, but does not react and is not released

So I blocks the enzyme from catalytic activity

mechanism:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{k_2} E + P$$

$$E + I \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} EI \text{ (no further reaction)}$$

$$[E]_0 = [E] + [EI] + [ES]$$

if $k_1, k_{-1}, k_3, k_{-3} \gg k_2$: pre-equilibrium approx.:

$$\frac{1}{K_1} = K_s = \frac{[E][S]}{[ES]} \approx K_m \quad \left(K_m = \frac{k_{-1} + k_2}{k_1} = \frac{k_{-1}}{k_1}\right.$$

when $k_{-1} \gg k_2$

$$\frac{1}{K_3} = K_I = \frac{[E][I]}{[EI]}$$

In addition to the Lineweaver–Burk plot, K_m can be estimated if the maximum rate is known. Specifically, if the initial rate is equal to one-half the maximum rate, Equation (36.54) reduces to

$$R_0 = \frac{k_2[S]_0[E]_0}{[S]_0 + K_m} = \frac{R_{max}[S]_0}{[S]_0 + K_m}$$

$$\frac{R_{max}}{2} = \frac{R_{max}[S]_0}{[S]_0 + K_m}$$

$$[S]_0 + K_m = 2[S]_0$$

$$K_m = [S]_0 \qquad (36.57)$$

Equation (36.57) demonstrates that when the initial rate is half the maximum rate, K_m is equal to the initial substrate concentration. Therefore, K_m can be determined by viewing a substrate saturation curve, as illustrated in Figure 36.7 for the carbonic-anhydrase catalyzed hydration of CO_2 discussed in Example Problem 36.1. The figure demonstrates that the initial rate is equal to half the maximum rate when $[S]_0 = 10$ mM. Therefore, the value of K_m determined in this relatively simple approach is in excellent agreement with that determined from the Lineweaver–Burk plot. Notice in Figure 36.7 that the maximum rate depicted was that employed using the Lineweaver–Burk analysis as shown in the example problem. When employing this method to determine K_m, the high-substrate-concentration limit must be carefully explored to ensure that the reaction rate is indeed at a maximum.

36.4.4 Competitive Inhibition in Enzyme Catalysis

The activity of an enzyme can be affected by the introduction of species that structurally resemble the substrate and that can occupy the enzyme active site; however, once bound to the active site the molecules are nonreactive. Such molecules are referred to as **competitive inhibitors.** The phosphonated substrate bound to phospholipase A_2 in Figure 36.5 is an example of a competitive inhibitor. Competitive inhibition can be described using the following mechanism:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \qquad (36.58)$$

$$ES \xrightarrow{k_2} E + P \qquad (36.59)$$

$$E + I \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} EI \qquad (36.60)$$

In this mechanism, I is the inhibitor, EI is the enzyme–inhibitor complex, and the other species are identical to those employed in the standard enzyme kinetic scheme of Equation (36.53). How does the rate of reaction differ from the noninhibited case discussed earlier? To answer this question, we first define the initial enzyme concentration:

$$[E]_0 = [E] + [EI] + [ES] \qquad (36.61)$$

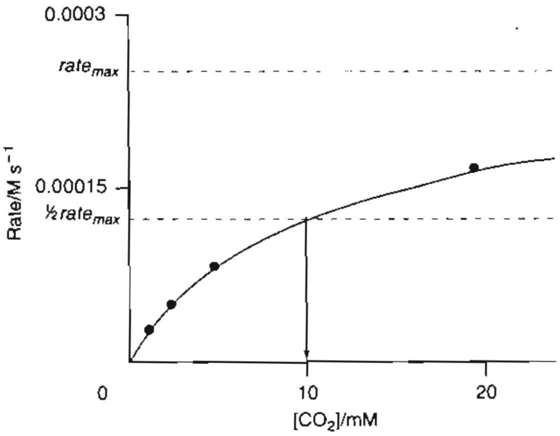


FIGURE 36.7
Determination of K_m for the carbonic-anhydrase catalyzed hydration of CO_2. The substrate concentration at which the rate of reaction is equal to half that of the maximum rate is equal to K_m.

$$\Rightarrow [E] = \frac{K_m [ES]}{[S]}$$

$$[EI] = \frac{[E][I]}{K_I}$$

$$\frac{K_m [ES]}{[S]}$$

$$\Rightarrow [E]_0 = \frac{K_m [ES]}{[S]} + \frac{[E][I]}{K_I} + [ES]$$

$$= \frac{K_m}{[S]}[ES] + \left(\frac{K_m [ES]}{[S]}\right)\frac{[I]}{K_I} + [ES]$$

$$= [ES]\left[\frac{K_m}{[S]} + \frac{K_m [I]}{[S] K_I} + 1\right]$$

$$\Rightarrow [ES] = \frac{[E]_0}{1 + \frac{K_m}{[S]} + \frac{K_m [I]}{[S] K_I}}$$

$$R = \frac{d[P]}{dt} = k_2 [ES] = \frac{k_2 [E]_0}{1 + \frac{K_m}{[S]} + \frac{K_m [I]}{[S] K_I}}$$

$$R = \frac{k_2 [S][E]_0}{[S] + K_m\left(1 + \frac{[I]}{K_I}\right)}$$

$$R_0 = \frac{k_2 [S]_0 [E]_0}{[S]_0 + K_m\left(1 + \frac{[I]}{K_I}\right)}$$

⇒ in inhibition new, apparent Micha~~ete~~elis constant ~~con~~ K_m^* can be used:

$$K_m^* = K_m\left(1 + \frac{[I]}{K_I}\right)$$

$$\rightarrow \quad R_0 = \frac{R_{max} [S]_0}{[S]_0 + K_m^*} \qquad R_{max} = k_2 [E]_0$$

inversion: Lineweaver-Burk plot:

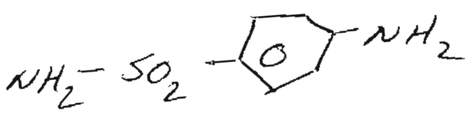
$$\frac{1}{R_0} = \frac{1}{R_{max}} + \frac{K_m^*}{R_{max}} \cdot \frac{1}{[S]_0}$$

Fig. ~~38.6~~ 36.8 p. 967

many drugs: inhibitors for bacterial enzymes


HOOC–C₆H₄–NH₂ p-aminobenzoic acid:

substrate of dihydropteroate synthetase to produce folate which bacteria need or they die.


$NH_2-SO_2-C_6H_4-NH_2$ sulfanilamid

can block enzyme → no folate → bacteria die

people make folate in another way, so sulfinilamid is non-toxic for people but deadly for bacteria

homogeneous catalyst acts in the same phase as the substrates, for example all in solution or in gas mixtures

heterogeneous catalyst for example surfaces of solids

Next, assuming that k_1, k_{-1}, k_3, and $k_{-3} \gg k_2$ the preequilibrium approximation is applied using Equations (36.58) and (36.60), yielding

$$K_s = \frac{[\mathrm{E}][\mathrm{S}]}{[\mathrm{ES}]} \approx K_m \tag{36.62}$$

$$K_i = \frac{[\mathrm{E}][\mathrm{I}]}{[\mathrm{EI}]} \tag{36.63}$$

In Equation (36.62), the constant describing the enzyme and substrate is written as K_m (Equation 36.40) when $k_{-1} \gg k_2$. With these relationships, Equation (36.61) can be written as

$$\begin{aligned}[\mathrm{E}]_0 &= \frac{K_m[\mathrm{ES}]}{[\mathrm{S}]} + \frac{[\mathrm{E}][\mathrm{I}]}{K_i} + [\mathrm{ES}] \\ &= \frac{K_m[\mathrm{ES}]}{[\mathrm{S}]} + \left(\frac{K_m[\mathrm{ES}]}{[\mathrm{S}]}\right)\frac{[\mathrm{I}]}{K_i} + [\mathrm{ES}] \\ &= [\mathrm{ES}]\left(\frac{K_m}{[\mathrm{S}]} + \frac{K_m[\mathrm{I}]}{[\mathrm{S}]K_i} + 1\right)\end{aligned} \tag{36.64}$$

Solving Equation (36.64) for [ES] yields

$$[\mathrm{ES}] = \frac{[\mathrm{E}]_0}{1 + \dfrac{K_m}{[\mathrm{S}]} + \dfrac{K_m[\mathrm{I}]}{[\mathrm{S}]K_i}} \tag{36.65}$$

Finally, the rate of product formation is given by

$$R = \frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ES}] = \frac{k_2[\mathrm{E}]_0}{1 + \dfrac{K_m}{[\mathrm{S}]} + \dfrac{K_m[\mathrm{I}]}{[\mathrm{S}]K_i}} = \frac{k_2[\mathrm{S}][\mathrm{E}]_0}{[\mathrm{S}] + K_m\left(1 + \dfrac{[\mathrm{I}]}{K_i}\right)}$$

$$R \cong \frac{k_2[\mathrm{S}]_0[\mathrm{E}]_0}{[\mathrm{S}]_0 + K_m\left(1 + \dfrac{[\mathrm{I}]}{K_i}\right)} \tag{36.66}$$

In Equation (36.66), the assumption that [ES] and [P] $\ll$ [S] has been employed so that $[\mathrm{S}] \cong [\mathrm{S}]_0$, consistent with the previous treatment of uninhibited catalysis. Comparison of Equation (36.66) to the corresponding expression for the uninhibited case of Equation (36.54) illustrates that with competitive inhibition, a new apparent Michaelis constant can be defined:

$$K_m^* = K_m\left(1 + \frac{[\mathrm{I}]}{K_i}\right) \tag{36.67}$$

Notice that K_m^* reduces to K_m in the absence of inhibitor ($[\mathrm{I}] = 0$). Next, using the definition of maximum reaction rate defined earlier in Equation (36.55), the reaction rate in the case of competitive inhibition can be written as

$$R_0 \cong \frac{R_{max}[\mathrm{S}]_0}{[\mathrm{S}]_0 + K_m^*} \tag{36.68}$$

In the presence of inhibitor, $K_m^* \geq K_m$, and more substrate is required to reach half the maximum rate in comparison to the uninhibited case. The effect of inhibition can also be observed in a Lineweaver–Burk plot of the following form:

$$\frac{1}{R_0} = \frac{1}{R_{max}} + \frac{K_m^*}{R_{max}}\frac{1}{[\mathrm{S}]_0} \tag{36.69}$$

Because $K_m^* > K_m$, the slope of the Lineweaver–Burk plot will be greater with inhibitor compared to the slope without inhibitor. Figure 36.8 presents an illustration of this effect.

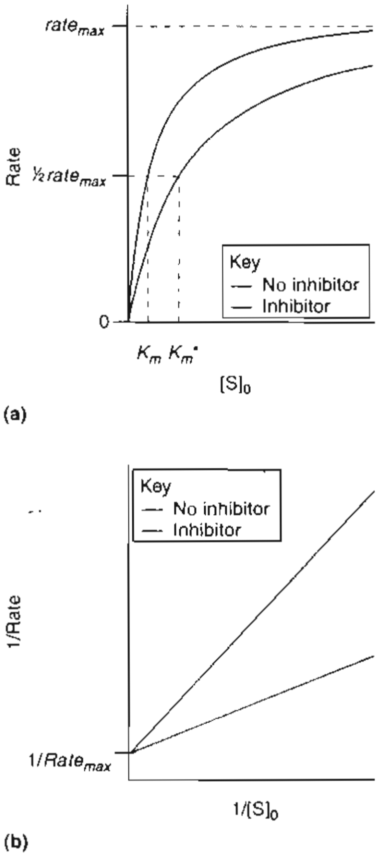
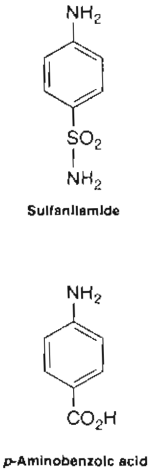


FIGURE 36.8
Comparison of enzymatic reaction rates in the presence and absence of a competitive inhibitor. **(a)** Plot of rate versus initial substrate concentration. The location of K_m and K_m^* is indicated. **(b)** Reciprocal plots ($1/R$ versus $1/[\mathrm{S}]_0$). Notice that $1/R_{max}$ is identical in the presence and absence of a competitive inhibitor.



Sulfanilamide

p-Aminobenzoic acid

FIGURE 36.9
Structural comparison of the antibacterial drug sulfanilamide, a competitive inhibitor of the enzyme dihydropteroate synthetase, and the active substrate, *p*-aminobenzoic acid. The change in functional group from $-CO_2H$ to $-SO_2NH_2$ is such that sulfanilamide cannot be used by bacteria to synthesize folate, and the bacterium starves.

Competitive inhibition has been used in drug design for antiviral, antibacterial, and antitumor applications. Many drugs are molecules that serve as competitive inhibitors for enzymes required for viral, bacterial, or cellular replication. For example sulfanilamide (Figure 36.9) is a powerful antibacterial drug. This compound is similar to *p*-aminobenzoic acid, the substrate for the enzyme dihydropteroate synthetase that participates in the production of folate. When present, the enzyme in bacteria cannot produce folate, and the bacteria die. However, humans do not possess this enzyme; they obtain folate from other sources. Therefore, sulfanilamide is not toxic.

36.4.5 Homogeneous and Heterogeneous Catalysis

A **homogeneous catalyst** is a catalyst that exists in the same phase as the species involved in the reaction, and a **heterogeneous catalyst** exists in a different phase. Enzymes serve as an example of a homogeneous catalyst: they exist in solution and catalyze reactions that occur in solution. A famous example of gas-phase catalysis is the catalytic depletion of stratospheric ozone by atomic chlorine. In the mid-1970s, F. Sherwood Rowland and Mario Molina proposed that Cl atoms catalyze the decomposition of stratospheric ozone by the following mechanism:

$$Cl + O_3 \xrightarrow{k_1} ClO + O_2 \qquad (36.70)$$

$$\underline{ClO + O \xrightarrow{k_2} Cl + O_2} \qquad (36.71)$$

$$O_3 + O \rightarrow 2\,O_2 \qquad (36.72)$$

In this mechanism, Cl reacts with ozone to produce chlorine monoxide (ClO) and molecular oxygen. The ClO undergoes a second reaction with atomic oxygen, largely formed by O_3 photolysis, resulting in the reformation of Cl and the product of O_2. The sum of these reactions leads to the net conversion of O_3 and O to 2 O_2. Notice that the Cl is not consumed in the net reaction.

The catalytic efficiency of Cl can be determined using standard techniques in kinetics. The experimentally determined rate law expression for the uncatalyzed reaction of Equation (36.72) is

$$R_{uc} = k_{uc}[O][O_3] \qquad (36.73)$$

The stratospheric temperature where this reaction occurs is roughly 220 K, at which temperature k_{uc} has a value of $3.30 \times 10^5\ M^{-1}\ s^{-1}$. For the Cl catalyzed decomposition of ozone, the rate constants at this temperature are $k_1 = 1.56 \times 10^{10}\ M^{-1}\ s^{-1}$ and $k_2 = 2.44 \times 10^{10}\ M^{-1}\ s^{-1}$. To employ these rates in determining the overall rate of reaction, the rate law expression for the catalytic mechanism must be determined. Notice that both Cl and ClO are intermediates in this mechanism. Applying the steady-state approximation, the concentration of intermediates is taken to be a constant such that

$$[Cl]_{total} = [Cl] + [ClO] \qquad (36.74)$$

where $[Cl]_{total}$ is defined as the sum of reaction intermediate concentrations, a definition that will prove useful in deriving the rate law. In addition, the steady-state approximation is applied in evaluating the differential rate expression for [Cl] as follows:

$$\frac{d[Cl]}{dt} = 0 = -k_1[Cl][O_3] + k_2[ClO][O]$$

$$k_1[Cl][O_3] = k_2[ClO][O]$$

$$\frac{k_1[Cl][O_3]}{k_2[O]} = [ClO] \qquad (36.75)$$

㊱ - 76

gas-phase catalysis:

depletion of O_3 in stratosphere by atomic Cl:

$$Cl + O_3 \xrightarrow{k_1} ClO + O_2$$

$$ClO + O \xrightarrow{k_2} Cl + O_2$$

overall; $O_3 + O \longrightarrow 2O_2$

O from O_3 photolysis

Cl <u>not</u> consumed ⇒ catalyst

not catalyzed reaction: nc

$$R_{nc} = k_{nc}[O][O_3]$$

reaction happens at around 220 K

then $k_{nc} = 3{,}3 \cdot 10^{5} \frac{1}{Ms}$

$k_1 = 1{,}56 \cdot 10^{10} \frac{1}{Ms}$, $k_2 = 2{,}44 \cdot 10^{10} \frac{1}{Ms}$

Cl and ClO are intermediates ⇒ SSA

$[Cl]_{total} := [Cl] + [ClO] = \text{const.}$ (SSA)

$$\frac{d[Cl]}{dt} \overset{SSA}{=} 0 = -k_1[Cl][O_3] + k_2[ClO][O]$$

$$k_1[Cl][O_3] = k_2[ClO][O]$$

$$[ClO] = \frac{k_1[Cl][O_3]}{k_2[O]}$$

$$\Rightarrow [Cl] = \frac{k_2[Cl]_{total}[O]}{k_1[O_3] + k_2[O]}$$

$$R_{cat} = -\frac{d[O_3]}{dt} = k_1 [Cl][O_3]$$

$$= \frac{k_1 k_2 [Cl]_{total} [O][O_3]}{k_1[O_3] + k_2[O]}$$

stratosphere: $[O_3] \gg [O]$, together with values of k_1 and k_2: $k_2[O]$ in denominator can be neglected: $k_1[O_3] \gg k_2[O]$

→ rate of catalyzed reactions

$$R_{cat} = k_2 [Cl]_{total} [O]$$

$$\Rightarrow \frac{R_{cat}}{R_{nc}} = \frac{k_2 [Cl]_{total}}{k_{nc}[O_3]}$$

stratosphere: $[O_3] \approx 10^3 [Cl]_{total}$

$$\Rightarrow \frac{R_{cat}}{R_{nc}} = \frac{k_2}{k_{nc}} \cdot 10^{-3} = \frac{2{,}44 \cdot 10^{10} \frac{1}{Ms}}{3{,}30 \cdot 10^{5} \cdot \frac{1}{Ms}} \cdot 10^{-3} \approx 74$$

⇒ catalyzed rate of O_3 depletion is about 2 orders larger the direct non-catalyzed one

in stratosphere Cl comes from photolysis of $CFCl_3$ and CF_2Cl_2
previously commonly used in refrigerators as cooling gases. They are very stable
When released they rise to the stratosphere where photolysis sets in and produce Cl
⇒ therefore chlorofluorocarbons were forbidden because O_3 filters UV from sunlight

solid heterogeneous catalysts are very important in industry

e.g. NH_3 synthesis from $N_2 + H_2$ is catalyzed by Fe(s)

Important step: adsorption (binding) of reactants to the solid surface

and adsorbed reactants can react!

adsorption without change of chemical bonding is called physisorption

→ equilibrium between free and surface bound adsorbate

adsorbate: chemical that becomes adsorbed

adsorbens: adsorbing solid

fractional coverage θ:

$$\theta = \frac{\text{number of adsorption sites occupied}}{\text{number of all possible adsorption sites}}$$

Fig. 36.10 illustrates adsorption sites on surface

$$\Theta = \frac{V_{ads}}{V_m}$$

V_{ads}: adsorbed volume of gase

V_m: volume of gas that must be adsorbed to cover the surface one time completely (monolayer coverage)

needed for study to measure θ as f(P) at constant temperatures: adsorption isotherm θ(P) at T = const.

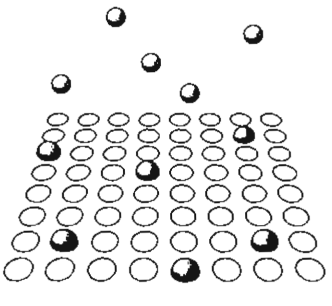


FIGURE 36.10
Illustration of fractional coverage θ. The surface (orange parallelogram) contains a series of adsorption sites (white circles). The reactant (blue spheres) exists in an equilibrium between free reactants and adsorbates. The fractional coverage is the number of occupied adsorption sites divided by the total number of sites on the surface.

Studies of adsorption involve measuring the extent of adsorption or θ as a function of reactant-gas pressure at a specific temperature. The variation in θ with pressure at fixed temperature is called an **adsorption isotherm.** The simplest kinetic model describing the adsorption process is known as the **Langmuir model,** where adsorption is described by the following mechanism:

$$\mathrm{R}(g) + \mathrm{M}\,(surface) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \mathrm{RM}\,(surface) \tag{36.80}$$

In Equation (36.80), R is reagent, M (surface) is an unoccupied adsorption site on the surface of the catalyst, RM (surface) is an occupied adsorption site, k_a is the rate constant for adsorption, and k_d is the rate constant for desorption. Three approximations are employed in the Langmuir model:

1. Adsorption is complete once monolayer coverage has been reached.
2. All adsorption sites are equivalent, and the surface is uniform.
3. Adsorption and desorption are uncooperative processes. The occupancy state of the adsorption site will not affect the probability of adsorption or desorption for adjacent sites.

With these approximations, the rate of change in θ will depend on the rate constant for adsorption k_a, reagent pressure P, and the number of vacant sites, which is equal to $N(1 - \theta)$ or the total number of adsorption sites N times the fraction of sites that are open $(1 - \theta)$:

$$\left(\frac{d\theta}{dt}\right)_{abs} = k_a PN(1 - \theta) \tag{36.81}$$

The corresponding change in θ due to desorption is related to the rate constant for desorption k_d and the number of occupied adsorption sites $N\theta$ as follows:

$$\left(\frac{d\theta}{dt}\right)_{des} = -k_d N\theta \tag{36.82}$$

At equilibrium, the change in fractional coverage with time is equal to zero so we can write

$$\frac{d\theta}{dt} = 0 = k_a PN(1 - \theta) - k_d N\theta$$

$$(k_a PN + k_d N)\theta = k_a PN$$

$$\theta = \frac{k_a P}{k_a P + k_d}$$

$$\theta = \frac{KP}{KP + 1} \tag{36.83}$$

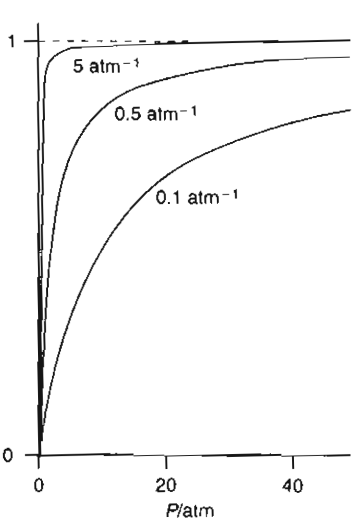


FIGURE 36.11
Langmuir isotherms for a range of k_a/k_d.

where K is the equilibrium constant defined as k_a/k_d. Equation (36.83) is the equation for the **Langmuir isotherm.** Figure 36.11 presents Langmuir isotherms for various values of k_a/k_d. Notice that as the rate constant for desorption increases relative to adsorption, higher pressures must be employed to reach $\theta = 1$, and this behavior can be understood based on the competition between the kinetics for adsorption and desorption. Correspondingly, if the rate constant for desorption is small, the coverage becomes independent of pressure for lower values of pressure.

In many instances adsorption is accompanied by dissociation of the adsorbate, a process that is referred to as **chemisorption** and described by the following mechanism:

$$\mathrm{R}_2(g) + 2\mathrm{M}\,(surface) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} 2\mathrm{RM}\,(surface)$$

Kinetic analysis of this mechanism (see the end-of-chapter problems) yields the following expression for θ:

$$\theta = \frac{(KP)^{1/2}}{1 + (KP)^{1/2}} \tag{36.84}$$

Inspection of Equation (36.84) reveals that the extent of surface coverage should demonstrate weaker pressure dependence compared to physisorption. Figure 36.12 provides a simplest; Langmuir model:

$$R(g) + M(\text{surface}) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} RM(\text{surface})$$

$R(g)$ free reactant

M(surface) free surface site

RM(surface) reactant adsorbed on surface site

k_a: rate constant for adsorption

k_d: rate constant for desorption (when the adsorbed reactant breaks free from the surface)

Langmuir model: 3 approximations needed:

1. adsorption is complete when 1 monolayer is covered: no adsorption on top of already adsorbed reactants (~~multilayer~~)
   no multilayer adsorption.
2. all sites are equal, surface is uniform
3. adsorption in a site is independent from other sites.

   If a molecule is adsorbed or not on a site is indepent of the occupancy of neighboring sites.

   number of occupied sites: $N\theta$

   number of free sites $N(1-\theta)$

   N: number of all adsorption sites

$$\left(\frac{d\theta}{dt}\right)_{ads} \sim k_{a_1} P_1 (1-\theta)$$

$1-\theta$ because adsorption only possible in free site

$$\left(\frac{d\theta}{dt}\right)_{ads} = k_a P N (1-\theta)$$

change of θ because of desorption proportional to k_d and number of occupied sites:

$$\left(\frac{d\theta}{dt}\right)_{des} = -k_d N \theta$$

equilibrium: $\frac{d\theta}{dt} = 0$

$$\frac{d\theta}{dt} = k_a P N (1-\theta) - k_d N \theta = 0$$

$$(k_a P N + k_d N)\,\theta = k_a P N$$

$$\rightarrow \quad \theta = \frac{k_a P}{k_a P + k_d} = \frac{\cancel{k_d}\,(k_a/k_d)\,P}{(k_a/k_d)\,P + 1}$$

adsorption equilibrium constant $K = k_a/k_d$

$$\Rightarrow \boxed{\theta = \frac{KP}{KP+1}}$$

Langmuir ~~d~~adsorption isotherm

Fig 36.11 p. 970

many cases: adsorption leads to dissociation of the reactants: chemisorption

$$R_2(g) + 2M(\text{surface}) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} 2RM(\text{surface})$$

$$\Rightarrow \quad \theta = \frac{\sqrt{KP}}{\sqrt{KP}+1} \qquad K = k_a / k_d$$

comparison of the 2 cases Fig. 36.12, p. 971

isotherms measured at different T

→ van't Hoff plot of $\ln K$ vs $\frac{1}{T}$

straight line

~~sole~~ slope $= -\frac{\Delta H_{ads}}{R}$

→ heat of adsorption ΔH_{ads}

<u>example</u> Kr on charcoal at 193.5 K

V_{ads} (cm³/g)	P (Torr)
5.98	2.45
7.76	3.5
10.1	5.2
12.35	7.2
16.45	11.2
18.05	12.8
19.72	14.6
21.1	16.1

θ related to V_{ads} ㊱−82

plot of V_{ads} vs P

→ isotherm

Fig. on p. 971

inverse of $\theta = \frac{KP}{KP+1}$ → linear plot

$$\frac{1}{V_{ads}} = \left(\frac{1}{KV_m}\right)\cdot\frac{1}{P} + \frac{1}{V_m}$$

→ $\frac{1}{V_{ads}}$ vs $\frac{1}{P}$ linear

itercept $= \frac{1}{V_m}$

slope $= \frac{1}{KV_m}$

$\theta = \frac{V_{ads}}{V_m}$ (see before)

$$\frac{V_{ads}}{V_m} = \frac{KP}{KP+1}$$

$$V_{ads} = \frac{KPV_m}{KP+1}$$

$$\frac{1}{V_{ads}} = \frac{1}{V_m} + \left(\frac{1}{KV_m}\right)\cdot\frac{1}{P}$$

plot on p. 972

intercept $= 0.0293\ g/cm^3$

$\Rightarrow V_m = 34.1\ cm^3/g$

slope $= 0{,}3449$

wit V_m

$\rightarrow K = 8{,}38\cdot 10^{-2}\ \frac{1}{Torr}$

comparison of the isotherms predicted using nondissociative and dissociative mechanisms corresponding to the same ratio of k_a/k_d. Finally, different Langmuir isotherms can be collected and evaluated over a range of temperatures to determine K as a function of T. With this information, a van't Hoff plot of ln$K$ versus $1/T$ should provide a straight line of slope $-\Delta H_{ads}/R$. Through this analysis, the enthalpy of adsorption ΔH_{ads} can be determined.

The assumptions employed in the Langmuir model may not be rigorously obeyed in real heterogeneous systems. First, surfaces are generally not uniform, resulting in the presence of more than one type of adsorption site. Second, the rate of adsorption and desorption may depend on the occupation state of nearby adsorption sites. Finally, it has been established that adsorbed molecules can diffuse on the surface and then adsorb corresponding to a kinetic process of adsorption that is more complicated than the Langmuir mechanism envisions.

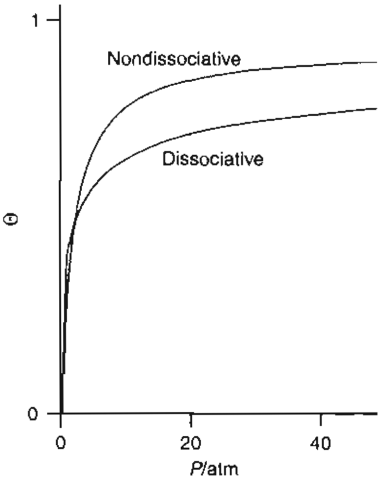


FIGURE 36.12
Comparison of Langmuir isotherms for nondissociative and dissociative adsorption with $k_a/k_d = 0.5\ \text{atm}^{-1}$.

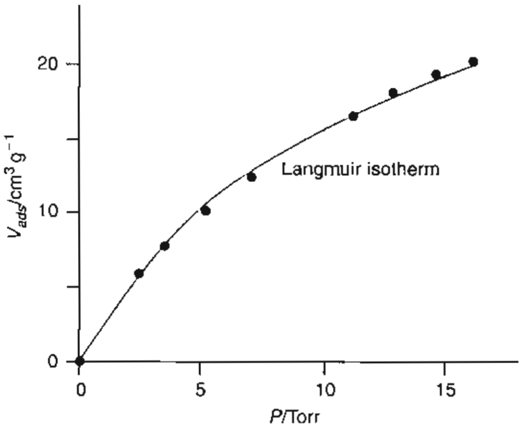
EXAMPLE PROBLEM 36.2

The following data were obtained for the adsorption of Kr on charcoal at 193.5 K. Using the Langmuir model, construct the adsorption isotherm, and determine V_m and the equilibrium constant for adsorption/desorption.

V_{ads} (cm^3 g^{-1})	P (Torr)
5.98	2.45
7.76	3.5
10.1	5.2
12.35	7.2
16.45	11.2
18.05	12.8
19.72	14.6
21.1	16.1

Solution

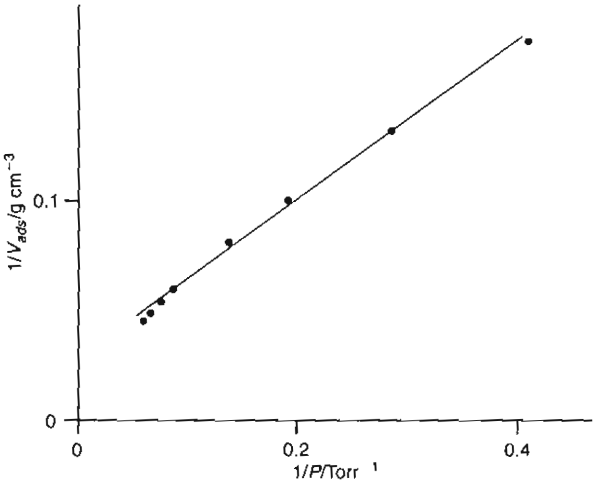
The fractional coverage is related to the experimentally measured V_{ads}. The adsorption isotherm is given by a plot of V_{ads} versus P, which can be compared to the behavior predicted by Equation (36.83) as illustrated here:



Although the comparison of the adsorption isotherm to Equation (36.83) illustrates that the Langmuir model is consistent with the adsorption of Kr on charcoal, determination of the Langmuir parameters is difficult because parameters such as V_m are unknown. This information is more readily determined by using the reciprocal of Equation (36.83):

$$\frac{1}{V_{ads}} = \left(\frac{1}{KV_m}\right)\frac{1}{P} + \frac{1}{V_m}$$

This equation demonstrates that a plot of $(V_{ads})^{-1}$ versus $(P)^{-1}$ should yield a straight line with slope equal to $(KV_m)^{-1}$ and y intercept equal to $(V_m)^{-1}$. A plot of the data in reciprocal form with the best fit line is shown next:



The y intercept obtained from the best fit line is 0.0293 g cm^{-3} such that $V_m = 34.1$ cm^3 g^{-1}. The slope of the best fit line is 0.3449 Torr g cm^{-3}. Using V_m determined from the y intercept, K is found to be 8.38×10^{-2} Torr^{-1}.

36.5 Radical-Chain Reactions

Radicals are chemical species that contain an unpaired electron. Due to the presence of the unpaired electron, radicals tend to be extremely reactive. In 1934, Rice and Herzfeld were able to demonstrate that the kinetic behavior of many organic reactions was consistent with the presence of radicals in the reaction mechanism. An example of a radical-mediated reaction is the thermal decomposition of ethane:

$$C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g) \tag{36.85}$$

Small amounts of methane (CH_4) are also produced in this decomposition. The decomposition mechanism proposed by Rice and Herzfeld is as follows:

$$\text{Initiation} \quad C_2H_6 \xrightarrow{k_1} 2\,CH_3\cdot \tag{36.86}$$

$$\text{Propagation} \quad CH_3\cdot + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5\cdot \tag{36.87}$$

$$C_2H_5\cdot \xrightarrow{k_3} C_2H_4 + H\cdot \tag{36.88}$$

$$H\cdot + C_2H_6 \xrightarrow{k_4} C_2H_5\cdot + H_2 \tag{36.89}$$

$$\text{Termination} \quad H\cdot + C_2H_5\cdot \xrightarrow{k_5} C_2H_6 \tag{36.90}$$

In this section, we include a dot ($\cdot$) in the formula of a compound to indicate that the species is a radical. The first elementary step in the mechanism involves the creation of two methyl radicals, referred to as an **initiation step** [Equation (36.86)]. In an initiation step, radicals are produced from a precursor species. The next three steps in the mechanism [Equations (36.87) through (36.89)] are referred to as **propagation steps** in which a radical reacts with another species to produce radical and nonradical products, and the radical products go on to participate in subsequent reactions. The final step in the mechanism is a **termination step** in which two radicals recombine to produce a nonradical product.

Radical Chain Reactions

Radicals contain unpaired electrons and thus are ~~higly~~ highly reactive.

1934: Rice and Herzberg found that many organic reactions have radicals in their mechanism

example: thermal decomposition of ethane:

$$C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)$$

as side-product small amounts of CH_4 are also produced. Side products indicate many times radical mechanisms

Initiation: $C_2H_6 \xrightarrow{k_1} 2CH_3^{\bullet}$

$^{\bullet}$ indicats unpaired electron thus a radical

the initiation creates the radicals in the ~~mechan~~ mechanism, ~~her 2~~ here 2 methyl radicals

Propagation radicals react to produce other radicals and non-radical products

$$CH_3^{\bullet} + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5^{\bullet}$$

$$C_2H_5^{\bullet} \xrightarrow{k_3} C_2H_4 + H^{\bullet}$$

$$H^{\bullet} + C_2H_6 \xrightarrow{k_4} C_2H_5^{\bullet} + H_2$$

Termination $H^{\bullet} + C_2H_5^{\bullet} \xrightarrow{k_5} C_2H_6$

in the termination 2 radicals combine to a non-radical

rate of consumption of ethanes

$$\nearrow \text{only } 1\ C_2H_6 \text{ involved} \Rightarrow \underline{\text{no}}\ 2k_1 \text{ but } k_1$$

$$-\frac{d[C_2H_6]}{dt} = k_1[C_2H_6] + k_2[C_2H_6][CH_3^\bullet] + k_4[C_2H_6][H^\bullet] - k_5[C_2H_5^\bullet][H^\bullet]$$

all radicals are intermediates and must be eliminated for a final rate law

Since $CH_3^\bullet$ is also an intermediate $\Rightarrow$ SSA

$$\frac{d[CH_3^\bullet]}{dt} \overset{SSA}{=} 0 = 2k_1[C_2H_6] - k_2[C_2H_6][CH_3^\bullet] \quad (1)$$

because $2CH_3^\bullet$ in reaction 1

$$\left(\frac{1}{2}\frac{d[CH_3^\bullet]}{dt}\right)_1 = k_1[C_2H_6] \Rightarrow \left(\frac{d[CH_3^\bullet]}{dt}\right)_1 = 2k_1[C_2H_6]$$

$$[CH_3^\bullet] = \frac{2k_1}{k_2}$$

SSA for $C_2H_5^\bullet$ and $H^\bullet$ intermediates:

$$\frac{d[C_2H_5^\bullet]}{dt} = 0 = k_2[CH_3^\bullet][C_2H_6] - k_3[CH_3^\bullet][C_2H_6] + k_4[C_2H_6][H^\bullet] - k_5[H^\bullet][C_2H_5] \quad (2)$$

$$\frac{d[H\cdot]}{dt} = 0 = k_3[C_2H_5\cdot] - k_4[C_2H_6][H\cdot] - k_5[C_2H_5\cdot][H\cdot] \quad (3)$$

(1) + (2) + (3):

left side: 0 + 0 + 0 = 0

$2k_1[CH_3\cdot]$ does not cancel (it is in (1))

$k_2[C_2H_6][CH_3\cdot]$ cancels from (1)+(2)

$k_3[C_2H_5\cdot]$ cancels from (2)+(3)

$k_4[C_2H_6][H\cdot]$ cancels also from (2)+(3)

$k_5[C_2H_5\cdot][H\cdot]$ is in (2) and (3) but with the same sign

$$\Rightarrow (1)+(2)+(3) = 2k_1[C_2H_6] - 2k_5[C_2H_5\cdot][H\cdot] = 0$$

$$\Rightarrow [H\cdot] = \frac{k_1[C_2H_6]}{k_5[C_2H_5\cdot]}$$

into (3):

$$0 = k_3[C_2H_5\cdot] - k_4[C_2H_6]\frac{k_1[C_2H_6]}{k_5[C_2H_5\cdot]} - k_5\underset{\checkmark}{[C_2H_5\cdot]}\frac{k_1[C_2H_6]}{k_5\underset{\checkmark}{[C_2H_5\cdot]}}$$

$$\Rightarrow 0 = k_3[C_2H_5\cdot] - \frac{k_4k_1[C_2H_6]^2}{k_5[C_2H_5\cdot]} - k_1[C_2H_6] \quad \Big| \cdot [C_2H_5\cdot]\cdot\frac{1}{k_3}$$

$$0 = [C_2H_5\cdot]^2 - \frac{k_4k_1}{k_3k_5}[C_2H_6]^2 - \frac{k_1}{k_3}[C_2H_6]\cdot[C_2H_5\cdot]$$

~~36~~ (86)
(36)-86

quadratic equation in $[C_2H_5^\bullet]$:

$$a x^2 + b x + c = 0$$

with $x = [C_2H_5^\bullet]$, $a = 1$

$$b = -\frac{k_1}{k_3}[C_2H_6], \quad c = \frac{k_4 k_1}{k_5 k_3}[C_2H_6]^2$$

$$\Rightarrow x_{1,2} = \frac{1}{2}\left(-b \pm \sqrt{b^2 - 4c}\right) \quad a = 1\,!$$

$$= \frac{k_1}{2k_3}[C_2H_6] \pm \frac{1}{2}\sqrt{\frac{k_1^2 [C_2H_6]^2}{k_3^2} + \frac{4 k_4 k_1}{k_5 k_3}[C_2H_6]^2}$$

$$= [C_2H_6]\left[\frac{k_1}{2k_3} \overset{+}{(-)} \sqrt{\left(\frac{k_1}{2k_3}\right)^2 + \frac{k_4 k_1}{k_5 k_3}}\right]$$

$x = [C_2H_5^\bullet]$ so the $-$ solution is ~~in~~ excluded,
it would result in a negative concentration

$$[C_2H_5^\bullet] = [C_2H_6]\left[\frac{k_1}{2k_3} + \sqrt{\left(\frac{k_1}{2k_3}\right)^2 + \frac{k_1 k_4}{k_3 k_5}}\right]$$

Experiment k_1 is small
$\Rightarrow$ only lowest power in k_1 is kept,
because e.g. $k^2 \ll k_1$ if k_1 is small

first term $\sim k_1$

first term in root $\sim k_1$

seecond term in root $\sim \sqrt{k_1}$ this is kept

$$\Rightarrow [C_2H_5^\bullet] = \sqrt{\frac{k_1 k_4}{k_3 k_5}}\,[C_2H_6]$$

$$\Rightarrow [H\cdot] = \frac{k_1[C_2H_6]}{k_5[C_2H_5\cdot]}$$

$$= \frac{k_1}{k_5}[C_2H_6]\cdot\sqrt{\frac{k_3k_5}{k_1k_4}}\cdot\frac{1}{[C_2H_6]}$$

$$[H\cdot] = \frac{k_1}{k_5}\sqrt{\frac{k_3k_5}{k_1k_4}} = \sqrt{\frac{k_1k_3}{k_4k_5}}$$

$$\Rightarrow R = -\frac{d[C_2H_6]}{dt} = k_1[C_2H_6] + k_2[C_2H_6][CH_3\cdot] + k_4[C_2H_6][H\cdot] - k_5[C_2H_5\cdot][H\cdot]$$

$$= k_1[C_2H_6] + k_2[C_2H_6]\cdot\frac{2k_1}{k_3} + k_4[C_2H_6]\sqrt{\frac{k_1k_3}{k_4k_5}} - k_5\sqrt{\frac{k_1k_4}{k_3k_5}}[C_2H_6]\cdot\sqrt{\frac{k_1k_3}{k_4k_5}}$$

$$= [C_2H_6]\left[k_1 + \frac{2k_1k_2}{k_3} + \sqrt{\frac{k_1k_3k_4}{k_5}} - \sqrt{\frac{k_1k_4k_5}{k_3}}\sqrt{\frac{k_1k_3}{k_4k_5}}\right]$$

k_1 small $\quad \sim k_1 \quad \sim k_1 \quad \sim\sqrt{k_1}$ keep $\quad \sim k_1$ neglect!

$$R = [C_2H_6]\sqrt{\frac{k_1k_3k_4}{k_5}}$$

$$R = -\frac{d[C_2H_6]}{dt} = \sqrt{\frac{k_1k_3k_4}{k_5}}\,[C_2H_6]$$

⇒ 1. order in C_2H_6 as in experiment

→ mechanism ok

example

$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$

experiment: order $\frac{1}{2}$ in Cl_2

following mechanism consistent with this?

$$Cl_2 \xrightarrow{k_1} 2Cl\cdot$$

$$Cl\cdot + CH_4 \xrightarrow{k_2} HCl + CH_3\cdot$$

$$CH_3\cdot + Cl_2 \xrightarrow{k_3} CH_3Cl + Cl\cdot$$

$$2Cl\cdot \xrightarrow{k_4} Cl_2$$

$$R = \frac{d[HCl]}{dt} = k_2[Cl\cdot][CH_4]$$

$Cl\cdot$ is intermediate → cannot be in final rate!

$$\frac{d[Cl\cdot]}{dt} = 2k_1[Cl_2] - k_2[Cl\cdot][CH_4] + k_3[CH_3][Cl_2] - 2k_4[Cl\cdot]^2$$

↗ $2Cl\cdot$ formed

↑ $2Cl\cdot$ consumed

$$\frac{d[CH_3\cdot]}{dt} = k_2[Cl\cdot][CH_4] - k_3[CH_3\cdot][Cl_2]$$

SSA for $CH_3\cdot$:

$$0 = k_2[Cl\cdot][CH_4] - k_3[CH_3\cdot][Cl_2]$$

$$[CH_3\cdot] = \frac{k_2[Cl\cdot][CH_4]}{k_3[Cl_2]}$$

SSA in $Cl\cdot$ ~~eq~~ :

$$0 = 2k_1[Cl_2] - k_2[Cl\cdot][CH_4] + k_3[CH_3\cdot][Cl_2] - 2k_4[Cl\cdot]^2$$

$$0 = 2k_1[Cl_2] - k_2[Cl\cdot][CH_4] + k_3\frac{k_2[Cl\cdot][CH_4]}{k_3[Cl_2]}[Cl_2] - 2k_4[Cl\cdot]^2$$

$$0 = 2k_1[Cl_2] - k_2[Cl\cdot][CH_4] + k_2[Cl\cdot][CH_4] - 2k_4[Cl\cdot]^2$$

$$0 = 2k_1[Cl_2] - 2k_4[Cl\cdot]^2$$

$$[Cl\cdot] = \sqrt{\frac{k_1}{k_4}[Cl_2]}$$

$R = k_2[Cl\cdot][CH_4] = k_2\sqrt{\frac{k_1}{k_4}}\,[CH_4]$ [illegible] $\cdot\sqrt{[Cl_2]}$

$\Rightarrow \frac{1}{2}$ order in Cl_2 as in experiment

→ mechanism consistent!

radical polymerization

a monomer is activated by reaction with a radical initiator I → monomer radical which reacts with another monomer M → radical dimer and so on

$$I \xrightarrow{k_I} 2R\cdot$$

$$R\cdot + M \xrightarrow{k_1} M_1\cdot$$

$M_n\cdot$: n indicates number of monomers in the polymer chain.

assumption: rate constant k_p equal for each propagation step;

$$M_1^\bullet + M \xrightarrow{k_p} M_2^\bullet$$

$$M_2^\bullet + M \xrightarrow{k_p} M_3^\bullet$$

$$\vdots$$

$$M_{n-1}^\bullet + M \xrightarrow{k_p} M_n^\bullet$$

termination:

$$M_m^\bullet + M_n^\bullet \rightarrow M_{m+n}$$

$$\left(\frac{d[M\cdot]}{dt}\right)_{\text{production}} = 2\phi k_I [I]$$

ϕ: probability that the radical R· from the initiator creates a radical chain

activated monomers can can combine and terminate the polymerization

$$\rightarrow \left(\frac{d[M\cdot]}{dt}\right)_{\text{decay}} = -2k_t [M\cdot]^2$$

k_t: rate constant for termination

$$\Rightarrow \frac{d[M\cdot]}{dt} = 2\phi k_I [I] - 2k_t [M\cdot]^2 \overset{SSA}{=} 0$$

because M· is intermediate

$$[M\cdot] = \sqrt{\frac{\phi k_I}{\cancel{\phi} k_t}}\sqrt{[I]}$$

→ monomer consumption

$$\frac{d[M]}{dt} = -k_p [M\cdot][M] = -k_p \sqrt{\frac{\phi k_I}{k_t}}\sqrt{[I]}\,[M]$$

efficiency of polymerization is measured by kinetic chain length ν

$$\nu = \frac{\text{average number of monomers in polymer produced}}{\text{number of active monomers}}$$

$$\nu = \frac{k_p[M\cdot][M]}{2\phi k_I[I]} = \frac{k_p[M\cdot][M]}{2k_t[M\cdot]^2} = \frac{k_p[M]}{2k_t[M\cdot]}$$

SSA yielded: $2\phi k_I[I] = 2k_t[M\cdot]^2$

expression for $[M\cdot]$ into ν

$$\rightarrow \nu = \frac{k_p[M]}{2k_t\sqrt{\frac{\phi k_I}{k_t}}\sqrt{[I]}} = \frac{k_p M}{2\sqrt{\phi k_I k_t}\sqrt{[I]}}$$

ν increases when k_I or $[I]$ are decreased

change in k_I not possible

but if polymerization is done at smallest possible $[I]$ (which keeps $[M\cdot]$ small) gives large chain length!

Photo chemistry

Initiation of a reaction by absorption of a photon of light, $h\nu$

vision starts with photon absorption by a pigment

Photosynthesis: plants an bacteria use light absoption for nutrient synthesis (sugars e.g.)

Ozone production and decomposition in the upper atmosphere needs photon absorption

Planck equation: energy in a photon:

$$E_{Photon} = h\nu = \frac{hc}{\lambda}$$

h: Planck's constant

c: speed of light in vacuum

ν: frequency of light

λ: wavelength of light

$\nu\lambda = c$ (in vacuum)

1 mol of photons is called 1 Einstein

$$E_{1\,Einstein} = N_A\, E_{Photon}$$

$$\text{intensity of light} = \frac{\text{energy}}{\text{aerea} \cdot \text{time}}$$ units: W/cm²

$$1\,W = 1\,J/s = 1\,\frac{VAs}{s} = 1\,VA$$

simplest $A \xrightarrow{h\nu} P$

rate of reactant excitations

$$R = -\frac{d(A)}{dt} = \frac{I_{abs} \cdot 1000}{l}$$

I_{abs} intensity of absorbed light

$$[I_{abs}] = 1 \frac{\text{Einstein}}{cm^2\, s}$$

l: light path length in the sample

1000: for conversion cm^3 to L

Light intensity transmitted through sample:

Beer-Lambert law

$$I_{trans} = I_0\, 10^{-\varepsilon l [A]}$$

I_0: incident intensity

ε: molar absorptivity of A

[A] reactant concentration

$$I_{abs} = \underset{\substack{\nearrow \\ \text{incoming}}}{I_0} - \underset{\substack{\uparrow \\ \text{outgoing}}}{I_{trans}}$$

$$\rightarrow I_{abs} = I_0 \left(1 - 10^{-\varepsilon l [A]}\right)$$

Taylor series of the ~~expo~~ exponential:

$$10^{-\varepsilon l [A]} = 1 - 2.303\, \varepsilon l [A] + \frac{(2.303\, \varepsilon l [A])^2}{2!} + \dots$$

if [A] is kept small, only 1. term needed

since in I_{abs} $1 - 10^{-\varepsilon l (A)}$ occurs, 1 is out:

$$I_{abs} = I_0 \cdot 2.303\, \varepsilon l [A]$$

into rate of photo excitation:

$$[A] = [A]_0 \, e^{-I_0 \, 2{,}303 \, \varepsilon t} = [A]_0 \, e^{-kt}$$

A: no of molecules

→ in terms of molecules:

$$-\frac{dA}{dt} = I_0 \frac{2{,}303\varepsilon}{N_A} A$$

$$\Rightarrow A = A_0 \, e^{-I_0 \frac{2{,}303\varepsilon}{N_A} t} = A_0 \, e^{-I_0 \sigma_A t}$$

σ_A = absorption cross section

excitation rate constant $k_a = I_0 \sigma_A$

absorption of light occurs when the photon energy is equal to the energy difference of two states in a molecule

Fig 36,17 Jablonski diagram

vertical axis: increasing energy

electronic states here: ground state Singlet S_0, excited singlet: S_1, excited triplet T_1

singlet states: all electrons paired

$\Rightarrow$ spin multiplicity = 1 = singlet (for 1)

triplet states: two unpaired electrons

$\Rightarrow$ spin multiplicity = 3 = triplet (for 3)

subscripts: energy ordering: $E(S_0) < E(S_1) < E(S_2)$

where A represents the number of molecules of reactant and N_A is Avogadro's number. Integrating Equation (36.155), we obtain

$$A = A_0 e^{-I_0(2303\varepsilon/N_A)t} = A_0 e^{-I_0\sigma_A t} \qquad (36.156)$$

where σ_A is known as the **absorption cross section** and the rate constant for excitation k_a is equal to $I_0\sigma_A$ with I_0 in units of photons cm^{-2} s^{-1}.

The absorption of light may occur when the photon energy is equal to the energy difference between two energy states of the molecule. A schematic of the processes that occur following photon absorption resulting in an electronic energy-level transition (or "elec- onic transition") is given in Figure 36.17. Such diagrams are referred to as **Jablonski igrams** after Aleksander Jablonski, a Polish physicist who developed these diagrams for cribing kinetic processes initiated by electronic transitions. In a Jablonski diagram, the tical axis represents increasing energy. The electronic states depicted are the ground-ite singlet S_0, first excited singlet S_1, and triplet T_1. In the singlet states, the electrons are in paired such that the spin multiplicity is one (i.e., a "singlet"), and in the triplet state wo electrons are unpaired such that the spin multiplicity is three (a "triplet"). The subscripts indicate the energy ordering of the states. Because triplets are generallv formed by electronic excitation, the lowest energy triplet state is labeled T_1 as opposed to T_0 (the lowest energy spin configuration of molecular oxygen is a triplet, a famous exception to this generality). Finally, the lowest vibrational level for each electronic state is indicated by dark horizontal lines, with higher vibrational levels indicated by the lighter horizontal lines. In addition, a manifold of rotational states will exist for each vibrational level; however, the rotational energy levels have been suppressed for clarity in Figure 36.17.

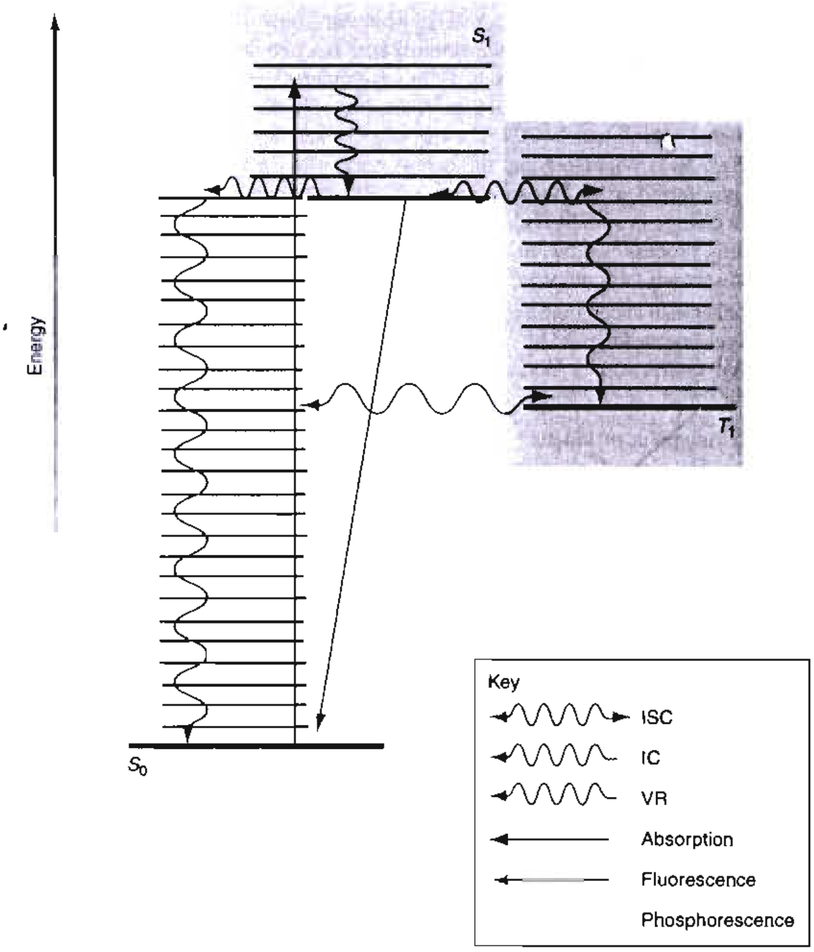


FIGURE 36.17
A Jablonski diagram depicting various photophysical processes, where S_0 is the ground electronic singlet state, S_1 is the first excited singlet state, and T_1 is the first excited triplet state. Radiative processes are indicated by the straight lines. The nonradiative processes of intersystem crossing (ISC), internal conversion (IC), and vibrational relaxation (VR) are indicated by the wavy lines.

for must molecules the ground state is a singlet, so S_0 is the singlet ground state since triplets are usually not ground states, normally there is <u>no</u> T_0, only T_1 and higher

exceptions <u>O_2</u> where the ground state is a triplet

so O_2 ground state is T_0 and in O_2 there is <u>no</u> S_0

lighter horizontal lines: vibrational levels of the electronic states

rotational levels are left out in the digram.

Transition indicated by solid and wavy lines in the Jablonski diagram are photophysical processes, because no chemical changes happen

light absorption → ~~die~~ decrease of the population of the ground state S_0 = depletion of S_0 and population of S_1 is increased

transition usually to a higher vibrational level according to the largest Frank-London factor (integral ~~ab~~ over S_0 and S_1 wave functions with the transition dipole moment between them)

<u>then</u>: thermal equilibration among the S_1 vibrational levels to a Boltzmann distribution

= vibrational relaxation is very fast (≈ 100 fs)

vibrational energy level spacings usually ㊱-96
so large that only the lowest level is
significantly populated

decay of S_1 population back to S_0 occurs by
one of three main paths:

1) Path 1: $S_1 \rightarrow S_0 + h\nu$ photon emission
= radiative transition
This is ~~po~~ spontaneous light emission and fast
= fluorescence

2) Path 2: Intersystem Crossing (ISC): population
of T_1, $S_1 \rightarrow T_1$ is spin forbidden and thus
ISC is much slower than vibrational relaxation
but is ~~so~~ on similar time-scale as fluorescence
when T_1 is populated already
then relaxation to the vibrational ground
state of T_1 happens
then again radiative transition $T_1 \rightarrow S_0 + h\nu$
can happen since $T_1 \rightarrow S_0$ is again ~~a~~ involving
a change of spin multiplicity it is forbidden
and happens much later than fluoresance.
The $T_1 \rightarrow S_0 + h\nu$ emission is called phosphorescence
very slow: phoshorescence: 10^{-6} s to seconds
fluorescence: $\simeq 10^{-9}$ s

The solid and wavy lines in Figure 36.17 represent a variety of processes that couple the electronic states. These processes, including the absorption of light and subsequent energetic relaxation pathways, are referred to as **photophysical processes** because the structure of the molecule remains unchanged. In fact, many of the processes of interest in "photochemistry" do not involve photochemical transformation of the reactant at all but are instead photophysical in nature. The absorption of light decreases the population in the lowest energy singlet state S_0, referred to as a depletion. Correspondingly, the population in the first excited singlet S_1 is increased. The absorption transition depicted in Figure 36.17 is to a higher vibrational level in S_1, with the probability of transition to a specific vibrational level determined by the Franck–Condon factor between the lowest energy vibrational level in S_0 and the vibrational states in S_1.

After populating S_1, thermal equilibration of the vibrational energy will occur, a process referred to as vibrational relaxation. Vibrational relaxation is extremely rapid (~100 fs), and when complete, the vibrational state population in S_1 will be governed by the Boltzmann distribution. The vibrational energy-level spacings are assumed to be sufficiently large such that only the lowest vibrational level of S_1 is populated to a significant extent after equilibration. Decay of S_1 resulting in repopulation of S_0 can occur through one of three paths:

1. *Path 1*: Loss of excess electronic energy through the emission of a photon. Such processes are referred to as **radiative transitions.** The process by which photons are emitted in the radiative transitions between S_1 and S_0 is referred to as **fluorescence.** This process is equivalent to spontaneous emission.
2. *Path 2*: **Intersystem crossing** (ISC in Figure 36.14) resulting in population of T_1. This process involves a change in spin state, a process that is forbidden by quantum mechanics. As such, intersystem crossing is significantly slower than vibrational relaxation, but it is competitive with fluorescence in systems where the triplet state is populated to a significant extent. Following intersystem crossing, vibrational relaxation in the triplet vibrational manifold occurs, resulting in population of the lowest energy vibrational level. From this level, a second radiative transition can occur where S_0 is populated and the excess energy is released as a photon. This process is referred to as **phosphorescence.** Because the $T_1 - S_0$ transition also involves a change in spin, it is also forbidden by spin selection rules. Therefore, the rate for this process is slow, and phosphorescence occurs over longer timescales (10^{-6} s to seconds) as compared to fluorescence ($\sim 10^{-9}$ s).
3. *Path 3*: Rather than undergoing a radiative transition, decay from S_1 to a high vibrational level of S_0 can occur followed by rapid vibrational relaxation. This process is referred to as **internal conversion** or nonradiative decay. Nonradiative decay can also occur through the triplet state by intersystem crossing to S_0 followed by vibrational relaxation.

From the viewpoint of kinetics, the absorption of light and subsequent relaxation processes can be viewed as a collection of reactions with corresponding rates. Figure 36.18 presents a modified version of the Jablonski diagram that focuses on these processes and corresponding rate constants. The individual processes, reactions, and notation for the reaction rates are provided in Table 36.1.

TABLE 36.1 Photophysical Reactions and Corresponding Rate Expressions

Process	Reaction	Rate
Absorption/excitation	$S_0 + h\nu \rightarrow S_1$	$k_a[S_0]$ $(k_a = I_0\sigma_A)$
Fluorescence	$S_1 \rightarrow S_0 + h\nu$	$k_f[S_1]$
Internal conversion	$S_1 \rightarrow S_0$	$k_{ic}[S_1]$
Intersystem crossing	$S_1 \rightarrow T_1$	$k_{isc}^S[S_1]$
Phosphorescence	$T_1 \rightarrow S_0 + h\nu$	$k_p[T_1]$
Intersystem crossing	$T_1 \rightarrow S_0$	$k_{isc}^T[T_1]$

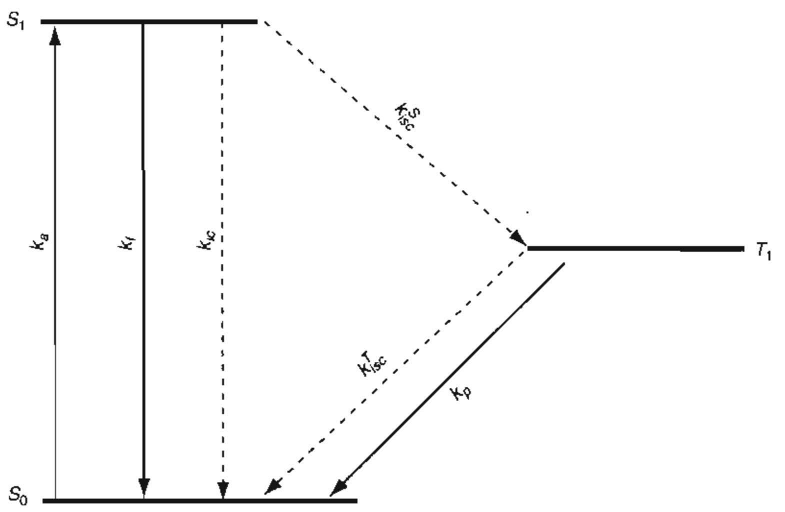


FIGURE 36.18
Kinetic description of photophysical processes. Rate constants are indicated for absorption (k_a), fluorescence (k_f), internal conversion (k_{ic}), intersystem crossing from S_1 to T_1 (k^S_{isc}), intersystem crossing from T_1 to S_0 (k^T_{isc}), and phosphorescence (k_p).

36.9.2 Fluorescence and Fluorescence Quenching

The photophysical processes outlined in Table 36.1 are present for any molecular system. To study excited state lifetimes, another photophysical process is introduced: **collisional quenching.** In this process, a collision occurs between a species Q and a molecule populating an excited electronic state. The result of the collision is the removal of energy from the molecule with the accompanying conversion of the molecule from S_1 to S_0:

$$S_1 + Q \xrightarrow{k_q} S_0 + Q \tag{36.157}$$

The rate expression for this process is

$$R_q = k_q[S_1][Q] \tag{36.158}$$

By studying the rate of collisional quenching as a function of [Q], it is possible to determine the k_f. To demonstrate this procedure, we begin by recognizing that in the kinetic scheme illustrated in Figure 36.18, S_1 can be considered an intermediate species. Under constant illumination, the concentration of this intermediate will not change. Therefore, we can write the differential rate expression for S_1 and apply the steady-state approximation:

$$\frac{d[S_1]}{dt} = 0 = k_a[S_0] - k_f[S_1] - k_{ic}[S_1] - k^S_{isc}[S_1] - k_q[S_1][Q] \tag{36.159}$$

The **fluorescence lifetime** τ_f is defined as

$$\frac{1}{\tau_f} = k_f + k_{ic} + k^S_{isc} + k_q[Q] \tag{36.160}$$

Using this definition of τ_f, Equation (36.159) becomes

$$\frac{d[S_1]}{dt} = 0 = k_a[S_0] - \frac{[S_1]}{\tau_f} \tag{36.161}$$

Equation (36.161) is readily solved for $[S_1]$:

$$[S_1] = k_a[S_0]\tau_f \tag{36.162}$$

3) Path 3 ; S_1 can make also a radiation less transition to a high S_0 vibrational level and then fast vibrationl relaxation :— internal conversion

Fig 36.18, p. 985 illustrates the processes

Table 36.1, p. 989 lists the processes

Quenching

Quenching happens when in the mixture a Quencher Q is added which can collide with an excited S_1 molecule (collissional quenching) and overtake its excitation energy ~~in~~ as thermal (kinetic) energy:

$$S_1 + Q \xrightarrow{k_q} S_0 + Q$$

rate: $R_q = k_q [S_1][Q]$

by a study of R_q as a function of $[Q]$ the fluorescence rate constant k_f and thus the fluorescence lifetime τ_f can be determined

S_1 is like an intermediate $\Rightarrow$ SSA

$$\frac{d[S_1]}{dt} = 0 = k_a[S_0] - k_f[S_1] - k_{ic}[S_1] - k^{S}_{isc}[S_1] + k_q[Q][S_1]$$

↗ absorbtion under constant light illumination

$$\Rightarrow \frac{1}{\tau_f} = k_f + k_{ic} + k^{S}_{isc} + k_q[Q]$$

$$\Rightarrow \frac{d[S_1]}{dt} = 0 = k_a[S_0] - \frac{[S_1]}{\tau_f}$$

$$[S_1] = k_a[S_0]\tau_f$$

$\Rightarrow$ fluorescence intensity I_f:

$$I_f = k_f[S_1] = k_a[S_0]k_f\tau_f$$

$$\Rightarrow k_f\tau_f = \frac{k_f}{k_f + k_{ic} + k^{S}_{isc} + k_q[Q]} = \phi_f$$

so fluorescence decay is like a branching reaction

ϕ_f: quantum yield of fluorescence

Inversion + definition of τ_f:

$$\frac{1}{I_f} = \frac{1}{k_a[S_0]}\left(1 + \frac{k_{ic} + k^{S}_{isc}}{k_f}\right) + \frac{k_q[Q]}{k_a[S_0]k_f}$$

when $\phi_f \to 1$, $k_f \gg k_{ic}, k^{S}_{isc}$

I_f^0 fluorescence intensity without quencher

$$\Rightarrow \frac{I_f^0}{I_f} = 1 + \frac{k_q}{k_f}[Q]$$

$\Rightarrow$ plot of $\frac{I_f^0}{I_f}$ vs $[Q]$ gives a straight line with slope $= \frac{k_q}{k_f}$;

Stern - Volmer plot

Fig. 36.19, p 986: Stern-Volmer plot

before continous illumination was assumed

$\Rightarrow$ before: SSA for $[S_1]$

usually: excitation by a short light pulse

must be shorter than τ_f !

pulses as short as 4 fs ($4 \cdot 10^{-15}$ s) can be used nowadays

in this case $I_0 = 0$ after the pulse, also $k_a[S_0] = 0$ after the pulse (no more absorption after the pulse)

$$\Rightarrow \frac{d[S_1]}{dt} = -k_f[S_1] - k_{ic}[S_1] - k_{isc}^S[S_1] - k_q[Q][S_1]$$

$$\frac{d[S_1]}{dt} = -\frac{[S_1]}{\tau_f}$$

The fluorescence intensity I_f depends on the rate of fluorescence given by

$$I_f = k_f[\mathrm{S}_1] \tag{36.163}$$

Substituting Equation (36.162) into Equation (36.163) results in

$$I_f = k_a[\mathrm{S}_0]k_f\tau_f \tag{36.164}$$

Inspection of the last two factors in Equation (36.164) illustrates the following relationship:

$$k_f\tau_f = \frac{k_f}{k_f + k_{ic} + k_{isc}^S + k_q[\mathrm{Q}]} = \Phi_f \tag{36.165}$$

The product of the fluorescence rate constant and fluorescence lifetime is equivalent to the radiative rate constant divided by the sum of rate constants for all processes leading to the decay of S_1. In effect, S_1 decay can be viewed as a branching reaction, and the ratio of rate constants contained in Equation (36.165) can be rewritten as the quantum yield for fluorescence Φ_f, similar to the definition of reaction yield provided in Section 35.8. The fluorescence quantum yield is also defined as the number of photons emitted as fluorescence divided by the number of photons absorbed. Comparison of this definition to Equation (36.165) demonstrates that the fluorescence quantum yield will be large for molecules in which k_f is significantly greater than other rate constants corresponding to S_1 decay. Inverting Equation (36.164) and using the definition of τ_f, the following expression is obtained:

$$\frac{1}{I_f} = \frac{1}{k_a[\mathrm{S}_0]}\left(1 + \frac{k_{ic} + k_{isc}^S}{k_f}\right) + \frac{k_q[\mathrm{Q}]}{k_a[\mathrm{S}_0]k_f} \tag{36.166}$$

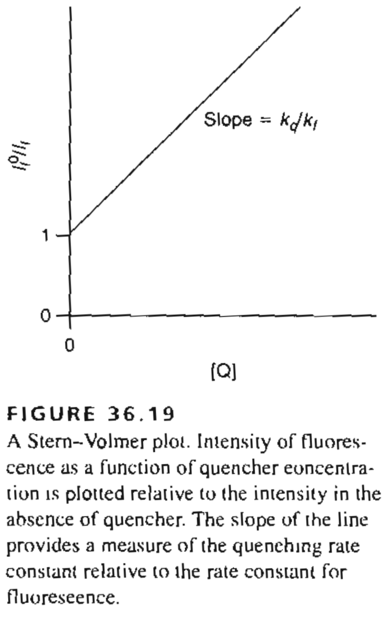


FIGURE 36.19
A Stern–Volmer plot. Intensity of fluorescence as a function of quencher concentration is plotted relative to the intensity in the absence of quencher. The slope of the line provides a measure of the quenching rate constant relative to the rate constant for fluoresecence.

For a fluorophore with a quantum yield approaching unity, $k_f \gg k_{ic}$ and k_{isc}^S. In fluorescence quenching experiments, fluorescence intensity is measured as a function of [Q]. Measurements are generally performed by referencing to the fluorescence intensity observed in the absence of quencher I_f^0 such that

$$\frac{I_f^0}{I_f} = 1 + \frac{k_q}{k_f}[Q] \tag{36.167}$$

Equation (36.167) reveals that a plot of the fluorescence intensity ratio as a function of [Q] will yield a straight line, with slope equal to k_q/k_f. Such plots are referred to as **Stern–Volmer plots,** an example of which is shown in Figure 36.19.

36.9.3 Measurement of τ_f

In the development presented in the preceding subsection, it was assumed that the system of interest was subjected to continuous irradiation so that the steady-state approximation could be applied to $[\mathrm{S}_1]$. However, it is often more convenient to photoexcite the system with a temporally short burst of photons or pulse of light. If the temporal duration of the pulse is short compared to the rate of S_1 decay, the decay of this state can be measured directly by monitoring the fluorescence intensity as a function of time. Optical pulses as short as 4 fs (4×10^{-15} s) can be produced that provide excitation on a timescale that is significantly shorter than the decay time of S_1.

After excitation by a temporally short optical pulse, the concentration of molecules in $[\mathrm{S}_1]$ will be finite. In addition, the rate constant for excitation is zero because $I_0 = 0$; therefore, the differential rate expression for S_1 becomes

$$\frac{d[\mathrm{S}_1]}{dt} = -k_f[\mathrm{S}_1] - k_{ic}[\mathrm{S}_1] - k_{isc}^S[\mathrm{S}_1] - k_q[\mathrm{Q}][\mathrm{S}_1]$$

$$\frac{d[\mathrm{S}_1]}{dt} = -\frac{[\mathrm{S}_1]}{\tau_f} \tag{36.168}$$

$$\Rightarrow [S_1] = [S_1]_0 \, e^{-t/\tau_f}$$

when $k_f \gg k_{ic}, k_{isc}^{S}$

then

$$\lim_{k_f \gg k_{ic}, k_{ic}^{S}} \tau_f = \frac{1}{k_f + k_q[Q]}$$

$$\frac{1}{\tau_f} = k_f + k_q[Q]$$

plot of $\frac{1}{\tau_f}$ vs $[Q]$ is a straight line where

intercept = k_f, slope = k_q

example: fluorescence quenching of pyrene in solution, quencher C_6Br_6:

$[C_6Br_6]$ in M	τ_f (s)
0.0005	$2.66 \cdot 10^{-7}$
0.001	$1.87 \cdot 10^{-7}$
0.002	$1.17 \cdot 10^{-7}$
0.003	$8.50 \cdot 10^{-8}$
0.005	$5.51 \cdot 10^{-8}$

Figure on p. 987 : $\frac{1}{\tau_f}$ vs $[C_6Br_6]$

slope = $3.00 \cdot 10^{9} \frac{1}{s} = k_q$

intercept = $1.98 \cdot 10^{6} \frac{1}{s} = k_f$

Electron Transfer

Exchange of charge in reactions

Important in Biology, e.g. Photosynthesis:

$$6\,CO_2(g) + 6\,H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6\,O_2(g)$$

$$\Delta G^0 = 2870\ kJ$$

also occurs in bacteria, but in "green sulfur" bacteria H_2S is used instead of H_2O:

$$2\,H_2S(aq) + CO_2(g) \rightarrow CH_2O(g) + H_2O(l) + \underset{\text{rhombic}}{2S(rh)}$$

$$\Delta G^0 = 88\ kJ$$

also transfer and use of light energy involves electron transfer

echange of an electron from a donor molecule (D) to an acceptor molecule (A)

$$D + A \rightleftarrows D^+ + A^-$$

Equation (36.168) can be solved for $[S_1]$ resulting in

$$[S_1] = [S_1]_0 e^{-t/\tau_f} \tag{36.169}$$

Because the fluorescence intensity is linearly proportional to $[S_1]$ per Equation (36.163), Equation (36.169) predicts that the fluorescence intensity will undergo exponential decay with time constant τ_f. In the limit where $k_f \gg k_{ic}$ and $k_f \gg k_{isc}^S$, τ_f can be approximated as follows:

$$\lim_{k_f \gg k_{ic}, k^S_{isc}} \tau_f = \frac{1}{k_f + k_q[Q]} \tag{36.170}$$

In this limit, measurement of the fluorescence lifetime at a known quencher concentration combined with the slope from a Stern–Volmer plot is sufficient to uniquely determine k_f and k_q. Taking the reciprocal of Equation (36.170), we obtain

$$\frac{1}{\tau_f} = k_f + k_q[Q] \tag{36.171}$$

Equation (36.171) demonstrates that a plot of $(\tau_f)^{-1}$ versus [Q] will yield a straight line with y intercept equal to k_f and slope equal to k_q.

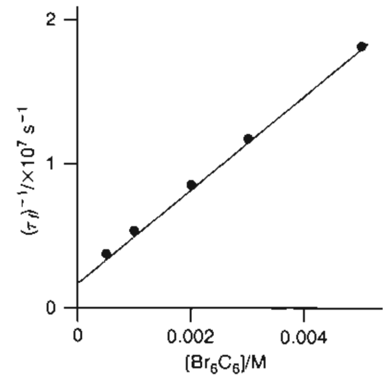
EXAMPLE PROBLEM 36.4

Thomaz and Stevens (in *Molecular Luminescence*, New York: W. A. Benjamin Inc, 1969) studied the fluorescence quenching of pyrene in solution. Using the following information, determine k_f and k_q for pyrene in the presence of the quencher Br_6C_6.

$[Br_6C_6]$ (M)	τ_f (s)
0.0005	2.66×10^{-7}
0.001	1.87×10^{-7}
0.002	1.17×10^{-7}
0.003	8.50×10^{-8}
0.005	5.51×10^{-8}

Solution

Using Equation (36.171), a plot of $(\tau_f)^{-1}$ versus [Q] for this system is as follows:



The best fit to the data by a straight line corresponds to a slope of $3.00 \times 10^9\ s^{-1}$, which is equal to k_q by Equation (36.171), and a y intercept of $1.98 \times 10^6\ s^{-1}$, which is equal to k_f.

mechanisms

First D and A collide and form a complex DA: ⇒ diffusion of A and D in solution is needed before they can form the DA complex:

$$D + A \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} DA$$

electron transfer then happens in the complex!
||
et

$$DA \underset{k_{-et}}{\overset{k_{et}}{\rightleftharpoons}} D^+A^-$$

finally D^+A^- must ~~et~~ separate:

$$D^+A^- \xrightarrow{k_{sep}} D^+ + A^-$$

⇒ rate $R = k_{sep}[D^+A^-]$

D^+A^- is intermed~~e~~iate ⇒ SSA:

$$\frac{d[D^+A^-]}{dt} \overset{SSA}{=} 0 = k_{et}[DA] - k_{-et}[D^+A^-] - k_{sep}[D^+A^-]$$

$$[D^+A^-] = \frac{k_{et}[DA]}{k_{-et} + k_{sep}}$$

DA is also an intermediate ⇒ also SSA

$$\frac{d[DA]}{dt} \overset{SSA}{=} 0 = k_d[D][A] - k_{-d}[DA] - k_{et}[DA] + k_{-et}[D^+A^-]$$

$$[DA] = \frac{k_d[D][A] + k_{-et}[D^+A^-]}{k_{-d} + k_{et}}$$

into $[D^+A^-]$ expressions

$$[D^+A^-] = \frac{k_{et}[DA]}{k_{-et} + k_{sep}}$$

$$= \frac{k_{et}}{k_{-et} + k_{sep}} \left(\frac{k_d[D][A] + k_{-et}[D^+A^-]}{k_{-d} + k_{et}} \right)$$

solution for $[D^+A^-]$

$$[D^+A^-]\left[1 - \underbrace{\frac{k_{et}k_{-et}}{k_{-d} + k_{et}}}_{\frac{k_{et}}{k_{-et} + k_{sep}}}\right] = \frac{k_{et}}{k_{-et} + k_{sep}} \frac{k_d[D][A]}{k_{-d} + k_{et}}$$

$$\Rightarrow [D^+A^-] = \frac{k_{et}k_d}{k_{-et}k_{-d} + k_{sep}k_{-d} + k_{sep}k_{et}} [D][A]$$

$$\Rightarrow R = \frac{k_{sep}k_{et}k_d}{k_{-et}k_{-d} + k_{sep}k_{-d} + k_{sep}k_{et}} [D][A]$$

$\Rightarrow$ 1. order in D, 1. order in A as in experiment if electron transfer much faster than DA complex dissociation: $k_{et} \gg k_{-d}$

then DA formation is rate limiting step and electron transfer is a diffusion controlled reaction

If $k_{et} \ll k_{-d}$ then electron transfer is rate limiting

and:

$$R(k_{-d} \gg k_{et}) = k_{et}\, K_{d,-d}\, [D][A] = k_{exp}\, [D][A]$$

$K_{d,\bar{d}}$: equilibrium constant of

$D + A \rightleftharpoons DA$ step