Correction to class 14, page 4

Error in book! (p. 275)

Anode

$M\overset{-1}{H}(s) + OH^- \rightarrow M^+ + 2e^- + \overset{+1}{H_2}O(l)$

$(\overset{-1}{H} \rightarrow \overset{+1}{H} + 2e^-)$

$E^\circ = 0.83\ V$

Cathode $|\cdot 2$

$\overset{+3}{Ni}OOH(s) + H_2O(l) + e^- \rightarrow \overset{+2}{Ni}(OH)_2 + OH^-(aq)$

$E^\circ = 0{,}52\ V$

overall = Anode + cathode · 2

$2\,NiOOH(s) + MH(s) + H_2O(l) \rightarrow MOH(s\ \text{or}\ aq) + 2\,Ni(OH)_2$

$E^\circ = 1.35\ V$

~~Actually Unit #2 was planned~~
~~Shifted to (16)~~

Switch from Electrochemistry to Kinetics

= Study of rates = speeds and mechanisms of chemical reaction

obj: Introduction, reaction rates, rate laws

Thermodynamics: Gibbs or Helmholtz energies
for equilibrium constants:
→ direction of a reaction
→ concentrations in equilibrium

nothing about the time scale for a reaction

reactants → products ≙ concentration changes

example reactant A → product B

[A] decreases (reactant), [B] ~~de~~ increases (product)

reaction rate: concentration change with time

important: reaction rate and dependence on system
parameters like T, concentrations, and P

→ informations about mechanism

needed: methods to measure and analyze
reaction dynamics

also theory for mechanisms & Physics involved

mechanism: sequence of elementary one-step reactions
leading from reactants to products

Reaction rates

general chemical reaction:

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

A, B, C, D, ... chemical molecules = species no. of moles of any species i at any point in time:

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

n_i: number of moles of i at any time

n_i^0: initial number of moles

ν_i: stoichiometric coefficient of i in equation (reactants $\nu_i < 0$, products $\nu_i > 0$)

ξ: extent of reaction

start of reaction $\xi = 0$, completion of reaction: $\xi = 1$

differentiation $\rightarrow$ $\frac{dn_i}{dt} = \nu_i \frac{d\xi}{dt}$, $\frac{dn_i^0}{dt} = 0$

reaction rate Rate: Rate $R = \frac{d\xi}{dt}$ R for "Rate"

$\rightarrow$ rate $Rate = \frac{1}{\nu_i} \frac{dn_i}{dt}$

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

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

no. of reactant moles decreases in time

$\rightarrow -\frac{1}{|\nu_i|}$ for reactants $\Rightarrow$ all Rates are positive

can be defined with respect to reactants and products.

4 mol NO_2 react with 1 mol O_2 to form 2 mole N_2O_5

$\Rightarrow$ rate of conversion is 4x rate of O_2 conversion

conversion rates are different, but because of $\frac{1}{\nu_i}$ th reaction rates are all equal

rates change if <u>all</u> stoichiometric coefficients in a reaction equation are multiplied (all) by the same factor

$\Rightarrow$ it is important to use 1 specified set of coefficients for a balanced reaction in the complete kinetic study

the reaction rate is extensive
(depends on amounts)

by division by an extensive quantity such as the volume V of the reaction mixture, it becomes intensive: k

$$R = \frac{1}{V}\cdot Rate = \frac{1}{V}\left(\frac{1}{\nu_i}\frac{dn_i}{dt}\right) = \frac{1}{\nu_i}\frac{dc_i}{dt}$$

$c_i = [i]$ molarity of i, also for gases

$CH_3CHO(g) \to CH_4(g) + CO(g)$ acetaldehyde decomposition

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

ideal gas law:

$$P_{CH_3CHO} = \frac{n_{CH_3CHO}}{V}RT = [CH_3CHO]\cdot RT$$

$$R = \frac{1}{V}Rate = \cancel{\frac{1}{V}n_{CH_3CHO}} = -\frac{1}{\nu_{CH_3CHO}}\frac{d[CH_3CHO]}{dt}$$

$$= -\frac{1}{RT}\frac{dP_{CH_3CHO}}{dt}\cdot\frac{1}{\nu_{CH_3CHO}}$$

$\hookrightarrow = 1$

Rate laws

In general a rate will depend on T, P, concentrations, and on the phase (l, g, s) in which a reaction occurs

homogeneous: reaction in 1 phase
heterogeneous: " " more than 1 phase (surface reactions)

for those reactions in most cases an empirical relation between rate and reactant concentrations can be written

this relation is a rate law:

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

one term for each reactant

α: order of the reaction with respect to A

overall order: sum of all orders: $\alpha + \beta + \dots$

k: rate constant of the reaction

general $k = k(P,T)$ but depends not on concentrations

an order can be an integer, a fraction, also negative

NO relation between orders and stoichiometric coefficients exists.

orders must be measured in experiments

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

experimental rate law: $R = k[NO_2]^2[O_2]$

2. order with respect to NO_2, 1. order with respect to O_2, 3. order overall

rate constant = proportionality factor between concentrations and rate

unit of reaction rate R: always M/s

unit of k changes with change in order

$R = k$ zero order $[k] = M/s = [R]$

$R = k[A]$ 1. order in A: $[k] = s^{-1}$

$R = k[A]^2$ 2. order in A: $[k] = \frac{1}{Ms}$

$R = k[A]^n$ nth order in A: $[k] = \frac{1}{M^{n-1}s}$

$R = k[A][B]$ 1. order in A and also in B: $[k] = \frac{1}{Ms}$ (2. order overall)

$R = k[A][B][C]$ 1. order in A and ~~al~~ also in B and C

→ 3. order overall: $[k] = 1/M^2s$; $1M = 1\frac{mol}{L}$

$R = k[A]^3$

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

$A \rightarrow B \quad R = -\frac{d[A]}{dt}$ ~~$R = k[A]^n$ $[k] = \frac{1}{M^{n-1} s}$~~

at some T, P: the reaction is 1 order in A and 1. order overall

while experimentally it is found that $k = 40 s^{-1}$

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

transparency [A] as measured at different times

$\frac{d[A]}{dt}$ = slope of a tangent at the concentration curve at different times

$\Rightarrow$ R depends on time

Plot of tangents at t=0 and t=30ms: ~~$[A]_0 = 1$~~

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

~~= 40~~

results: $R_{t=0} = -\frac{d[A]}{dt}\Big|_{t=0} = 40\, M/s$

$R_{t=30ms} = -\frac{d[A]}{dt}\Big|_{t=30ms} = 12\, M/s$

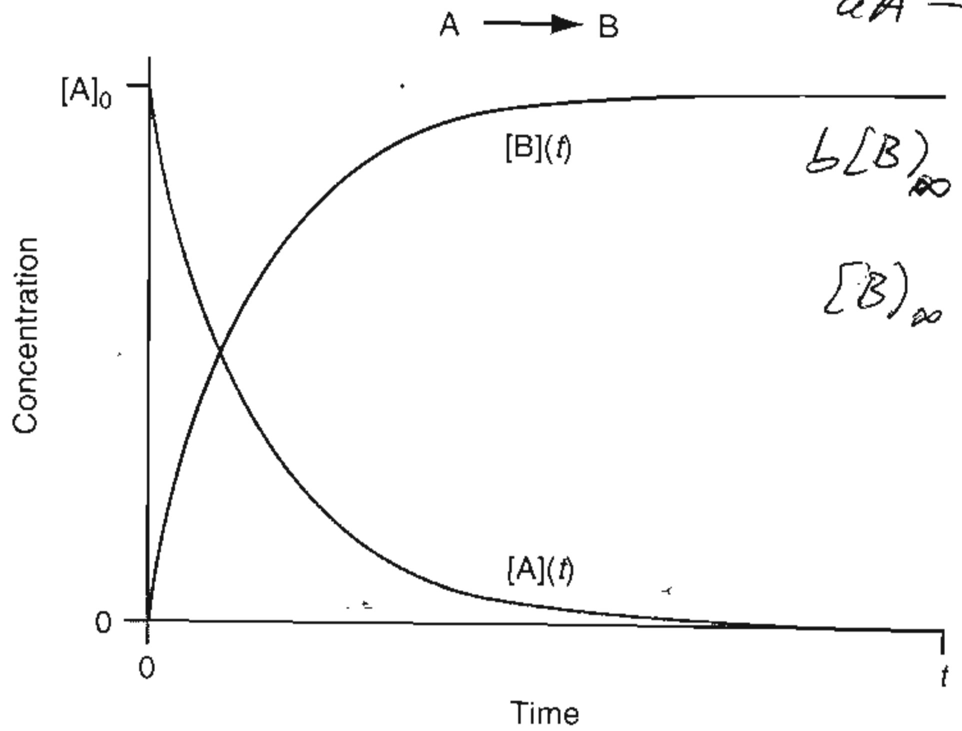
$\rightarrow$ rate decreases with time

from change of [A] with time and rate law equation:

at t=0: $[A]_{t=0} = 1M \Rightarrow R_{t=0} = 40 s^{-1}[A]_0 = 40 s^{-1}\cdot 1M$

$= 40\frac{M}{s}$

35.1
tion as a function of time
version of reactant A into
. The concentration of A at
]$_0$, and the concentration
o. As the reaction proceeds, the
esults in the production of B.



$aA \rightarrow bB$

$b[B]_\infty = a[A]_0$

$[B]_\infty = \frac{a}{b}[A]_0$

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 found at 30 ms: $[A]_{t=30\,ms}$ $.3\,M$

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

<u>convention</u> define R at the beginning before large concentration changes = <u>initial rate</u>

initial rate in example before: $R_{t=0}$

<u>always</u> rate of reaction = initial rate

However, the rate constant is independent of concentrations

$\Rightarrow$ if rate constant k, concentrations, orders of the reaction are all known

$\rightarrow$ reaction rate can be calculated at all times

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

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

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

units of k

order n:

$$(k) = \frac{1}{M^{n-1}\ s}$$

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

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

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

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

with respect to B
with respect to C
overall

---

liter.

tangent to sit

$$\frac{d[A]}{dx} = \tan\alpha$$

slope

iven by

$$\cdot\frac{d[A]}{dt} \qquad (35.12)$$

ate that at a certain temperature and pressure rall, and $k = 40\ \mathrm{s}^{-1}$ so that

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

eaction is equal to the negative of the time ar xperiment in which [A] is measured as The derivative in Equation (35.12) is simtration curve at a specific time. Therefore, t which the rate is determined. Figure 35.2 time points, $t = 0$ ms(1 ms $= 10^{-3}$ s) and is given by the negative of the slope of the h time, per Equation (35.12):

$$\frac{\text{\textbackslash]}}{-} = 40\ \mathrm{M\,s^{-1}}$$

is

$$\frac{[\mathrm{A}]}{d'} = 12\ \mathrm{M\,s^{-1}}$$

with time. This behavior is a direct conseof time, as expected from the rate law of

$$40\ \mathrm{s}^{-1}(1\ \mathrm{M}) = 40\ \mathrm{M\,s^{-1}}$$

f A has decreased to 0.3 M so that the rate is

$$= 40\ \mathrm{s}^{-1}(0.3\ \mathrm{M}) = 12\ \mathrm{M\,s^{-1}}$$

ɔnt an important issue in kinetics: how does s with time? One convention is to define the ve undergone any substantial change from ned under such conditions is known as the example is that determined at $t = 0$. In the

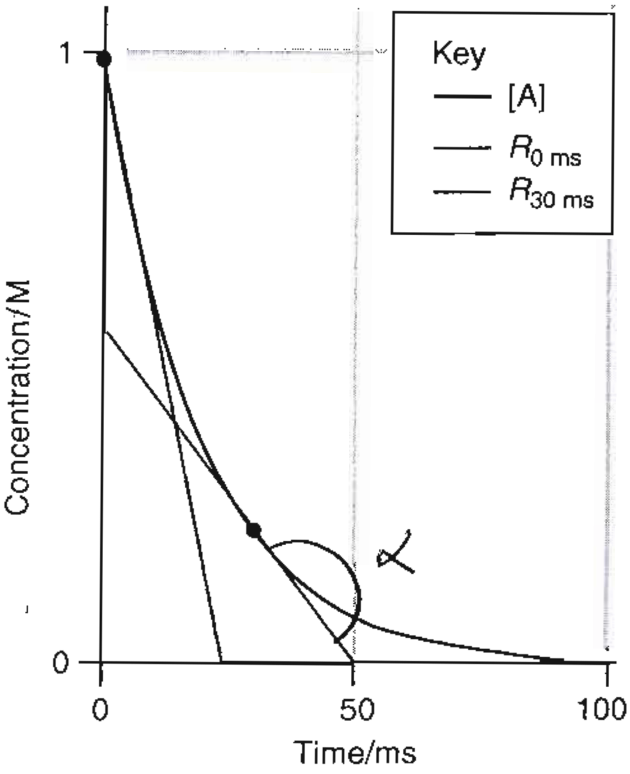


FIGURE 35.2
Measurement of the reaction rate. The concentration of reactant A as a function of time is presented. The rate R is equal to the slope of the tangent of this curve. This slope depends on the time at which the tangent is determined. The tangent determined 30 ms into the reaction is presented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

- Determination of reaction orders
- Mechanisms

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

the rate law is $R = k[A]^{\alpha}[B]^{\beta}$

$\Rightarrow$ rate measurement for 1 set of concentrations is not enough, because then 1 equation, but 2 unknowns α, β

$\Rightarrow$ measurement of rates at different sets of concentrations $[A], [B]$ needed

1. Isolation Method

all reactants in excess = with large concentrations
<u>only</u> 1 reactant with a small concentration

$\rightarrow$ only the small reactant concentration will change much during reaction

$A + B \rightarrow C$, e.g. $[A]_0 = 1.00\,M$, $[B]_0 = 0.01\,M$

$R = 0$ when all $[B]_0$ has reacted

then $[A]$ will be $0.99\,M$ = only a small change

excess $[A]$ will be practically const. in time

$\Rightarrow$ easier rate law: $R = k'[B]^{\beta}$, $k' = k[A]_0^{\alpha}$

$k' =$ const : $k =$ const., $[A] =$ const. (changed very little)

order β for $[B]$ can be obtained with different values for $[B]$,

for α: $[B]$ large, $[A]$ small

2. Initial Rates Method

for 1 reactant $[R]_0$ is changed, all other reactants $[R']_0$ = const.

and initial rates are determined

e.g. $[A]_0$ is changed, $[B]_0$ = const.

then for 2 values of $[A]_0$ with $[B]_0$ = const.:

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

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

$[B]_0$, k = const. ⇒ they cancel

for B: 2 initial rates at $[A]_0$ = const. at different $[B]_1$, $[B]_2$

determine orders and rate constants for

	[A]/M	[B]/M	initial rate / M/s
(1)	$2.30\cdot10^{-4}$	$3.10\cdot10^{-5}$	$5.25\cdot10^{-4}$
(2)	$4.60\cdot10^{-4}$	$6.20\cdot10^{-5}$	$4.20\cdot10^{-3}$
(3)	$9.20\cdot10^{-4}$	$6.20\ 10^{-5}$	$1.68\cdot10^{-2}$

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

$$\ln\frac{4.20\cdot10^{-3}}{1.68\cdot10^{-2}} = \alpha\cdot\ln\frac{4.60\cdot10^{-4}}{9.20\cdot10^{-4}} \quad , \quad -1.386 = \alpha(-0.693)$$

→ $\alpha = 2$ (round to next nearest integer)

$$\frac{R_1}{R_2} = \frac{k[A_x]_1^{2}\,(B)_1^{\beta}}{k\,[A]_2^{2}\,[B]_2^{\beta}} \qquad \frac{5.25\cdot10^{-4}}{4.20\cdot10^{-3}} = \left(\frac{2.30\cdot10^{-4}}{4.60\cdot10^{-4}}\right)^{2}\left(\frac{3.10\cdot10^{-5}}{6.20\cdot10^{-5}}\right)^{\beta}$$

$$\rightarrow 0.125 = 0.25\cdot(0.500)^{\beta}$$

$$0.500 = (0.500)^{\beta}$$

$$\ln 0.5 = \beta \cdot \ln 0.5 \rightarrow \beta = 1$$

2. order in A, 1. order in B, 3. order overall

k can be obtained for (1), (2), or (3), does not matter which one!

e.g. (1): $R_1 = k[A]_1^2[B]_1$

$$k = \frac{5.25 \cdot 10^{-4}\ M/s}{(2.30 \cdot 10^{-4} M)^2 (3.10 \cdot 10^{-5} M)} = 3.20 \cdot 10^{8} \frac{1}{M^2 s}$$

error in book, p. 915: <u>not</u> 3.17 but 3.20!

$$R = \left(3.20 \cdot 10^{8} \frac{1}{M^2 s}\right)[A]^2[B]$$

at different times t, stop the reaction in a sample of the reaction mixture by rapid cooling or by a reaction which removes one of the reactants

usually not easy and can be used only for slow r.

mostly: monitoring a physical property of the system with time, like P or V when the number of gas molecules changes:

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

because in reaction 1 mol gas → 2 mol gas

⇒ P and V will increase as reaction proceeds

= P increase when container volume = const.

Spectroscopic methodes can yield [ ] = f(t) directly e.g. by electronic absorption (color change) with the ~~Lamb~~ Lambert-Beer law $A \sim \varepsilon l [\ ]_{abs}$

A = absorbance: $A = \frac{I_0}{I}$, l light path, ε = const.

also NMR or IR or Raman Spectroscopy
can be used vibrational Spectr.

important for ps (10^{-12}s) or fs (10^{-15}s) reactions

ms (10^{-3}s): stopped flow methods for solutions

transperancy: stopped flow
reactants A and B mixed in reaction chamber
detector used at different times for measurement
use is limited by mixing times

flash photolysis for reactions which can be
started by a light pulse
short light pulse → reaction starts
pulses of ≈ 10 fs (10^{-14}s) duration possible
3000 cm^{-1} vibrations need ≈ 10 fs for a period
→ femto second chemistry with 10 fs pulses

ultrafast processes are e.g.
vision, photosynthesis, atmospheric processes,
charge carrier dynamics in semi conductors
now also for X-rays fs pulses possible
for photo initiated structure changes:
vibrational spectroscopy in 100 fs time scale
NMR useful for µs (10^{-6}s) time scales

Perturbation - Relaxation Methods

System in equilibrium is brought out of
equilibrium by a P, T, or pH jump and then the
relaxation to the new equilibrium is followed

syringes, and the reactants are mixed at the junction indicated in the figure. The reac tion is monitored by observing the change in absorbance of the reaction mixture as function of time. The temporal resolutions of stopped-flow techniques are generall 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 th reaction. Ultrafast light pulses as short as 10 femtoseconds (10 fs = 10^{-14} s) in the visi ble region of the electromagnetic spectrum are available such that reaction dynamics o this extremely short or ultrafast timescale can be studied. For reference, a 3000 cm vibrational mode has a period of roughly 10 fs; therefore, using short optical pulse reactions can be initiated on the same timescale as vibrational molecular motion, and thi capability has opened up many exciting fields in chemical kinetics, referred to a **femtochemistry.** This capability has been used to determine the ultrafast chemical kinet ics associated with vision, photosynthesis, atmospheric processes, and charge-carrie dynamics in semiconductors. Very recently, femtochemical techniques have been extende to the X-ray region of the spectrum, allowing for the direct interrogation of photoinitiate structural changes using time-resolved scattering techniques. Recent references to som of this work are included in the "For Further Reading" section at the end of this chapter

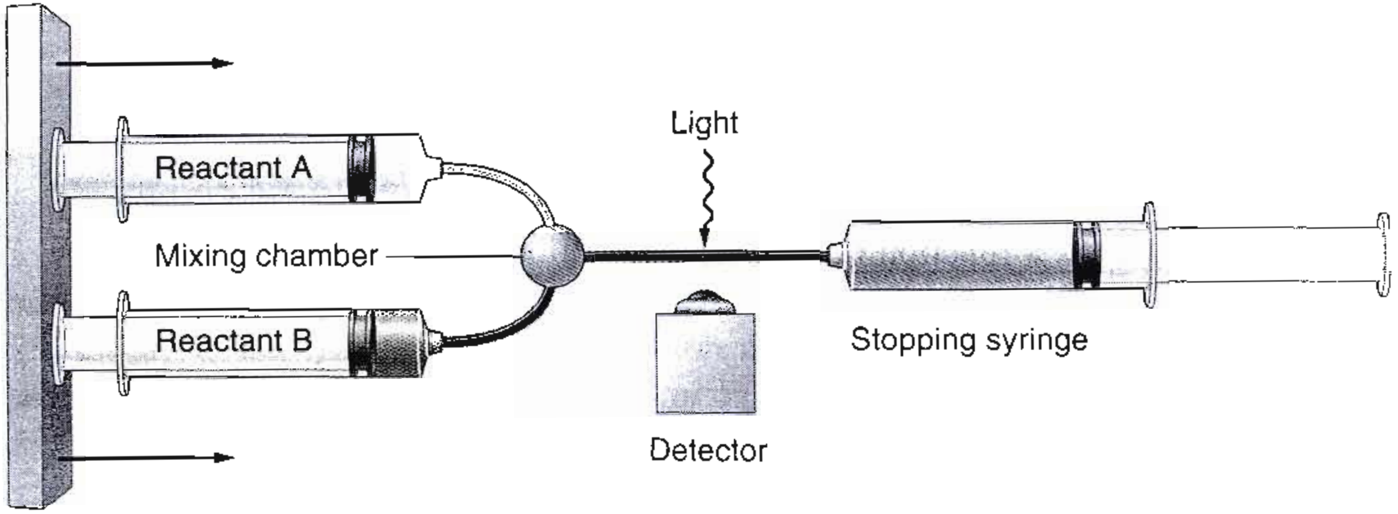


FIGURE 35.3
Schematic of a stopped-flow experiment. Two reactants are rapidly introduced into the mixing chamber by syringes. After mixing, the reaction kinetics are monitored by observing the change in sample concentration versus time, in this example by measuring the absorption of light as a function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

stoichiometric coefficients in reaction equations
≠ orders of the reaction

the balanced overall equations gives no information about the mechanism

mechanism: series of elementary reaction steps from reactants to products

a correct mechanism contains only elementary (1 step) reactions

the rate law and thus the orders depend strongly on the mechanim of a reaction

mechanism: series of elementary reaction steps

elementary: reactions which occur in 1 single step

molecularity of such a step: no. of molecules involved in the step

unimolecular reaction steps: only 1 molecule involved
e.g. decompositions of diatomic molecules are mostly unimolecular: $I_2 \xrightarrow{k} 2I$

but enthalpy changes in the reaction lead to heat transport by collisions with other molecules (Chap. 36, Sec. 3)

bimolecular reaction steps: 2 molecules involved

$NO + O_3 \xrightarrow{k} NO_2 + O_2$ bimolecular

important rate law of such a step follows directly from its molecularity unimolecular steps : 1. order reactions

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

bimolecular steps : 2. order reactions

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

only for elementary (1 step) reactions,
order of reaction = stoichiometric coefficients

but order = molecularity
only for elementary reactions
if order = molecularity then the reaction is not sure elementary (only can be)

common problem to identify the correct mechanism among the proposed ones

the design of experiments which can decide between proposed mechanism can be very difficult

general: sometimes it is possible to rule out a mechanism as incorrect, but it is never possible to prove for sure that a mechanism is correct

A → P can be a simple 1. order reaction with just 1 elementary reaction step

or it can be that first A forms an intermediate I
intermediates I cancel from overall reaction equation and they are no reactants and no products, but they are formed by a step and consumed in another one

so the mechanism could also be $A \to I$, $I \to P$

<u>check</u> detection of I in the reaction mixture (e.g. by spectroscopy)

<u>but</u> if $I \to P$ is very fast as compared to $A \to I$, then $[I]$ will be very small and it can be difficult to detect

When $I \to P$ is very fast, then the overall kinetics are the same as for a onestep mechanism

<u>usual</u> procedure: the simplest mechanism that yields the correct orders (experimental) is considered as correct,

until a clever chemist finds a way to prove the stepwise nature of a reaction

if orders of a reaction predicted by a mechanism = measured orders, then the mechanism can be correct

if the orders from mechanim ≠ ords from experiment

$\Rightarrow$ mechanism is wrong!

Integrated Rate Laws

1. order

decay of reactant: $A \xrightarrow{k} P$

if 1. order in A (many decay reactions, all radioactive decays), then rate $R = k[A]$

k: rate constant, further:

$R = -\frac{d[A]}{dt}$ rate of consumption (−) since

A decay $\Rightarrow \frac{d[A]}{dt} < 0$, $R > 0$

both expressions for R are the same

$$\Rightarrow \frac{d[A]}{dt} = -k[A] \quad (- \text{ to other side})$$

homogenous first order differential equation (no term without [A] = homogeneous)

→ separation of variables:

all with [A] to the left, all with t (dt) to the right:

$$\frac{d[A]}{[A]} = -k\,dt \quad k = \text{const.} \Rightarrow \text{integration}$$

$$[A]_{t=0} = [A]_0, \quad [A]_t = [A]$$

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

$$\Rightarrow \ln[A] - \ln[A]_0 = -k(t-0) = -kt$$

$$\Rightarrow \ln\frac{[A]}{[A]_0} = -kt \Rightarrow [A] = [A]_0\, e^{-kt}$$

when we start with only $[A] = [A]_0$

then for each P formed, 1 A is consumed

$\Rightarrow [A]_0 = [P] + [A]$, $[P] = [A]_0 - [A]$

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

$[A]$: exponential decay with time

must be checked by experiment if 1. order is correct.

e.g. measure $[A]$ at different times

then since $\ln [A] = \ln [A]_0 - kt$

if 1. order decay is correct

and a plot of $\ln [A]$ vs t must give a straight line if 1. order decay

with slope $= -k$, intercept $= \ln [A]_0$

Transperancy $\frac{[A]}{[A]_0}$ vs t, $\ln\left(\frac{[A]}{[A]_0}\right)$ vs t

$[A] = f(t)$ must be measured over the full time range of the reaction to be sure about 1. order decay

since sometimes it happens that at later times also the products P take part in the reaction

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

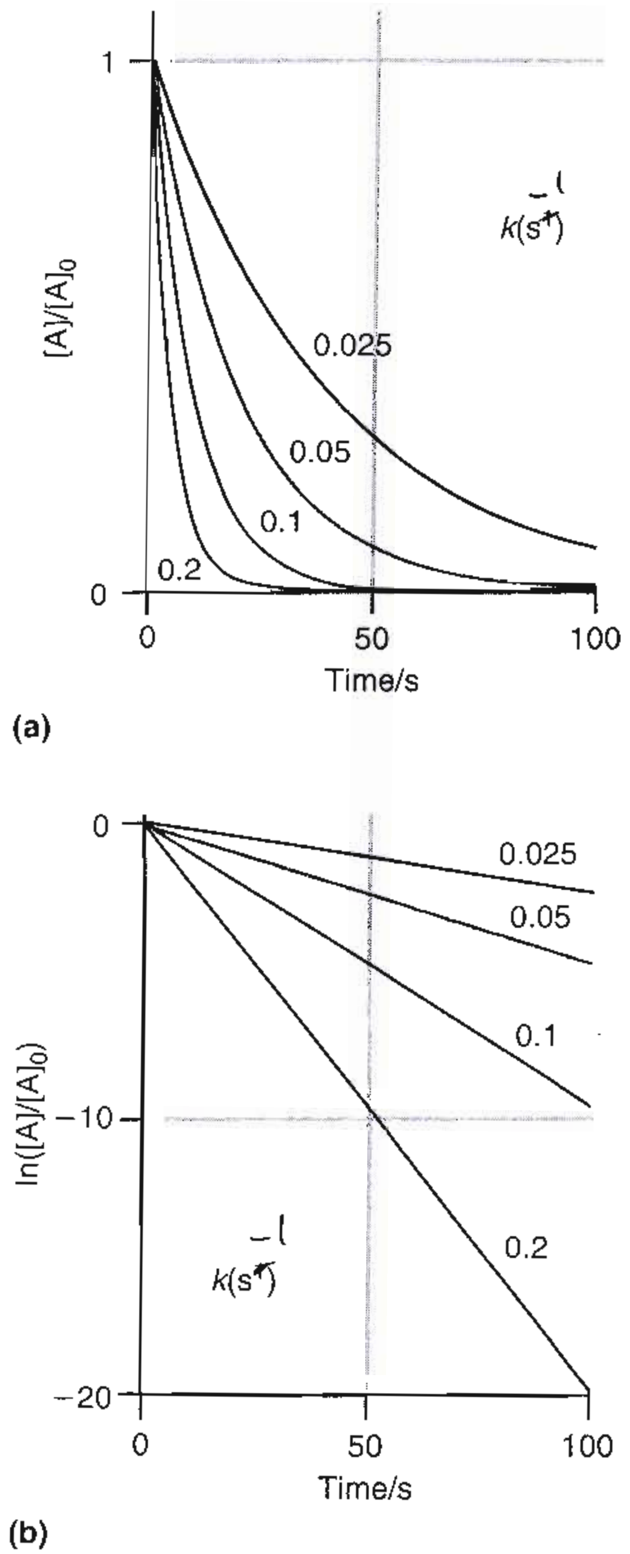


FIGURE 35.4
Reactant concentration as a function of time for a first-order chemical reaction as given by Equation (35.27). (**a**) Plots of [A] as a function of time for various rate constants *k*. The rate constant of a given curve is provided in the figure. (**b**) The natural log of reactant concentration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

Equation (35.29) predicts that for a first-order reactant concentration versus time will be a s equal to the natural log of the initial concentra of the concentration dependences predicted by order reactions. It is important to note that the integrated rate law expression requires that the accurately known over a wide range of reac indeed follows a certain order dependence.

35.5.2 Half-Life and First-Order F

The time it takes for the reactant concentrati value is called the **half-life** of the reaction and tion, substitution of the definition for $t_{1/2}$ into E

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

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

Notice that the half-life for a first-order reactio tion, and only the rate constant of the reaction

EXAMPLE PROBLEM 35.3

The decomposition of N_2O_5 is an important pr half-life for the first-order decomposition of th will it take for a sample of N_2O_5 to decay to 6

Solution

Using Equation (35.29), the rate constant for t the half-life as follows:

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{2.05 \times 10^4}$$

The time at which the sample has decayed to mined using Equation (35.27):

$$[N_2O_5] = 0.6[N_2O_5]_0 = [$$

$$0.6 = e$$

$$\frac{-\ln(0.6)}{} =$$

⇒ as long as ~~the~~ the organism is alife, its ^{14}C level is constant, which corresponds to 15,3 decays / m

after death: no more exchange and ^{14}C decays in the dead organism

fossilized wood (turned to stone) shows 2,40 ^{14}C decays per minute, how old is the wood?

When the tree died: $[^{14}C]_0$

decay ratio: $\frac{[^{14}C]}{[^{14}C]_0} = \frac{2{,}40\ m^{-1}}{15{,}3\ m^{-1}} = 0{,}157$

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{5760\,y} = \frac{\ln 2}{1{,}82 \cdot 10^{11} s} = 3{,}81 \cdot 10^{-12} s^{-1}$$

$$5760\,y \cdot 365{,}25 \frac{d}{y} \cdot 24 \frac{h}{d} \cdot 60 \frac{m}{h} \cdot 60 \frac{s}{m} = 1{,}82 \cdot 10^{11} s$$

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

$$t = -\frac{1}{k} \ln\left(\frac{[^{14}C]}{[^{14}C]_0}\right) = -\frac{\ln(0{,}157)}{3{,}81 \cdot 10^{-12} s^{-1}} = 4{,}86 \cdot 10^{11} s$$

$$\approx 15400\,y$$

2. order reactions : 2 types

~~a~~ type I

$$2A \xrightarrow{k} P$$

type I: 2. order with 1 reactant A

type II: 2. order with 2 reactants A and B for type I: $R = k[A]^2 = -\frac{1}{2}\frac{d[A]}{dt}$

$\nu A \rightarrow$: $R = -\frac{1}{\nu}\frac{d[A]}{dt}$ (consumption $\Rightarrow -$)

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

separation of variables:

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

$$\rightarrow -\int_{[A]_0}^{[A]}\frac{d[A]}{[A]^2} = 2k\int_0^t dt \qquad \int\frac{dx}{x^2} = -\frac{1}{x} + C$$

$\Rightarrow$ − sign cancels

$$\frac{1}{[A]} - \frac{1}{[A]_0} = 2kt$$

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

Transpar. $\frac{[A]}{[A]_0}$ vs t and $\left(\frac{[A]}{[A]_0}\right)^{-1}$ vs t

if 2. order type I, then

plot of $\frac{1}{[A]}$ vs t must give a straight line:

slope $= 2k$, intercept $= \frac{1}{[A]_0}$

$\frac{[A]_0}{[A]}$ vs t: straight line also, but

slope $= 2k[A]_0$, intercept $= 1$

$$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt \;\Big|\; \cdot[A]_0 \quad \underset{\left(\frac{[A]}{[A]_0}\right)^{-1}}{\underset{\parallel}{\frac{[A]_0}{[A]}}} = 1 + 2k[A]_0 t$$

Half-life $t_{1/2}$: time it takes for $\frac{1}{2}[A]_0$ to be consumed

⇒ put $t_{1/2}$ for t and $\frac{1}{2}[A]_0$ for $[A]$

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

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

<u>only</u> for 1. order reactions $t_{1/2}$ does not depend on $[A]_0$ and <u>so</u> does not increase lateron

after $\frac{\ln 2}{k}$, $[A]_0 \rightarrow \frac{1}{2}[A]_0$

after again $\frac{\ln 2}{k}$, $\frac{1}{2}[A]_0 \rightarrow \frac{1}{4}[A]_0$

tropospheric chemistry: decomposition of N_2O_5

half-life of N_2O_5 (1. order decay): $2{,}05 \cdot 10^4\,s$

how long does ist take for 60% $[N_2O_5]_0$ to decompose?

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{2{,}05 \cdot 10^4\,s} = 3{,}38 \cdot 10^{-5}\,s^{-1}$$

60% decay:

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

$$0.6 = \exp(-3{,}38 \cdot 10^{-5} s^{-1} \cdot t)$$

$$t = \frac{-\ln(0.6)}{3{,}38 \cdot 10^{-5} s^{-1}} = 1.51 \cdot 10^4\,s = 252\,m = 4.19\,h$$

the radioactive ^{14}C nucleus decays with $t_{1/2} = 5760\,y$

living organisms exchange C with the surroundings (e.g. as CO_2 into plants, by eating into animals)

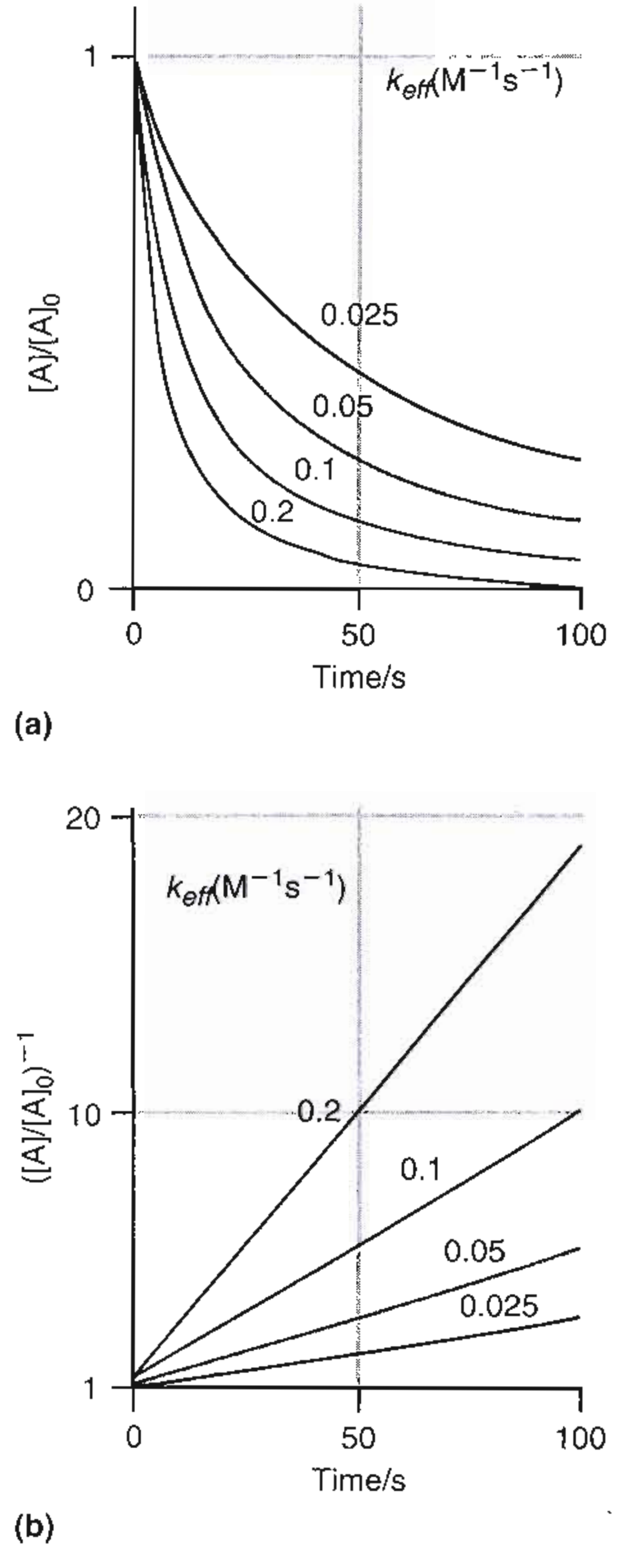


FIGURE 35.5
Reactant concentration as a function of time for a type I second-order chemical reaction. (**a**) Plots of [A] as a function of time for various rate constants. The rate constant of a given curve is provided in the figure. (**b**) The inverse of reactant concentration as a function of time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

Equation (35.35) demonstrates that for a seco
reactant concentration versus time will result
and y intercept of $1/[A]_0$. Figure 35.5 present
for a second-order reaction and $1/[A]$ versus
Equation (35.35) is evident.

35.5.4 Half-Life and Reactions o

Recall that "half-life" refers to when the conce
value. With this definition, the half-life for a t

$$t_{1/2} = \frac{}{k_{eff}}$$

In contrast to first-order reactions, the half-life
on the initial concentration of reactant, with a
ing in a decrease in $t_{1/2}$. This behavior is consi
through a unimolecular process, whereas the
process that involves the interaction of two spe
such, the concentration dependence of the reac

35.5.5 Second-Order Reaction (T

Second-order reactions of type II involve two

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

Assuming that the reaction is first order in bot

$$R = k[A$$

In addition, the rate with respect to the time de

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

The loss rate for the reactants is equal, so

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

Equation (35.40) provides a definition for [B] i
concentration, $[B]_0 - [A]_0$, denoted as Δ. Begi
the initial concentrations of A and B are not
(35.39) equal results in the following expressio

Half-life for 2. order, type I :

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

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

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

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

bimolecular reaction : collision of 2 reactants necessary → $t_{1/2} \sim \frac{1}{[A]_0}$ expected

$t_{1/2}$ increases as $[A]_0$ decreases

⇒ during reaction $[A]_0$ gets smaller

→ $t_{1/2}$ gets longer

2. order, type II

2 reactants

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

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

loss rate equal for ~~A~~ A and B

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

$$\rightarrow [B] = [B]_0 - [A]_0 + [A] \quad , \quad \Delta = [B]_0 - [A]_0$$

$$\Delta + [A] = [B]$$

case $[A]_0 \neq [B]_0 \Rightarrow \Delta \neq 0$

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

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

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

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

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

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

$\Delta + [A] = [B]$

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

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

good for $[A]_0 \neq [B]_0$, not for $[A]_0 = [B]_0$ $\left(\frac{1}{\Delta} = \frac{1}{0}\right)$

then $[A] = [B]$ at all times

$$\rightarrow -\frac{d[A]}{dt} = k[A][B] = k[A]^2$$

goes same way as type I

$\Rightarrow$ well defined $t_{1/2}$ exists only if there is a stoichiometric mixture, i.e. $[A]_0 = [B]_0$

however, a $t_{1/2}$ different for different reactants could be defined

-Numerical Methods

- Sequential 1. order reactions

In a large number of kinetic problems it is not possible to derive an integrated Rate Law

Then how is comparison to experiment possible? Numerical methods can help.

Example: 1. ord reactions where integration can be done for comparison

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

time derivative: change in [A] per infinitesimally small time interval

Thus for a finite time Δt (small, but not infinitesimally small as dt) it is:

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

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

[A]: concentration at time t

$$\ln\frac{[A]}{[A]_0} = -kt$$

⇒ change of $[A] = \Delta[A]$ in time Δt

⇒ [A] at time $t + \Delta t$

⇒ is used again for next Δt until reaction is finished

$$\begin{aligned}[A]_{t+\Delta t} &= [A]_t + \Delta[A] \\ &= [A]_t - k[A]_t\,\Delta t \\ &= (1 - k\Delta t)[A]_t\end{aligned}$$

$[A]_t$: concentration of [A] at the beginning t of interval Δt

$[A]_{t+\Delta t}$: concentration of [A] at the end of Δt: $t+\Delta t$

Transp. Illustration of Method

roaches

preceding section, an integrated rate law /ever, there is a wide variety of kinetic prob- pression cannot be obtained. How can one in the absence of an integrated rate law? In nother approach by which to determine the ted by a kinetic model. To illustrate this :r reaction:

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

action is

$$= -k[\text{A}] \qquad (35.43)$$

iange in [A] for a time duration that is infini- ι state that for a finite time duration Δt, the

$$= -k[\text{A}]$$

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

ation of [A] at a specific time. Therefore, we iange in the concentration of A, or $\Delta[\text{A}]$, over n...ion change to determine the concentration v concentration can be used to determine the time period, and this process is continued until /,

$$\text{A}]_t + \Delta[\text{A}]$$

$$\text{A}]_t - k\Delta t[\text{A}]_t \qquad (35.45)$$

ration at the beginning of the time interval, and of the time interval. This process is illustrated in ncentration is used to determine $\Delta[\text{A}]$ over the this next time point, $[\text{A}]_1$, is used to determine

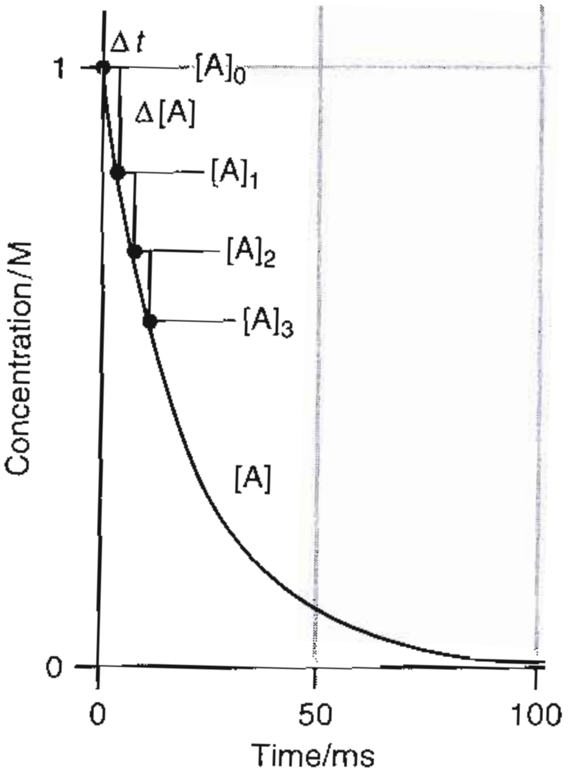


FIGURE 35.6
Schematic representation of the numerical evaluation of a rate law.

For the use of the numerical method (IJ) - L we must ~~no~~ know the time-scale in which the reaction happens

to be able to select Δt small enough to obtain all details of the reaction in the reaction time

Transp. comparison of different Δt + integrated time law

When Δt gets smaller, the accuracy is getting better.

One has to reduce Δt until convergence = no more changes in $[A](t)$ on further decrease of Δt

Euler's Methode used is the simplest one and quite bruteforce, because Δt must be small enough to get the desired accuracy

$\Rightarrow$ it is possible that a very large number of iterations is needed

→ long calculations

better are more sophisticated methods like the Runge-Kutta method which allows larger Δt

Sequential 1. order reactions

= series of steps one after the other (step 2 cannot occur before step 1 has happened);

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

I = intermediate: no reactant and also no product in the overall reaction ($A \to P$)

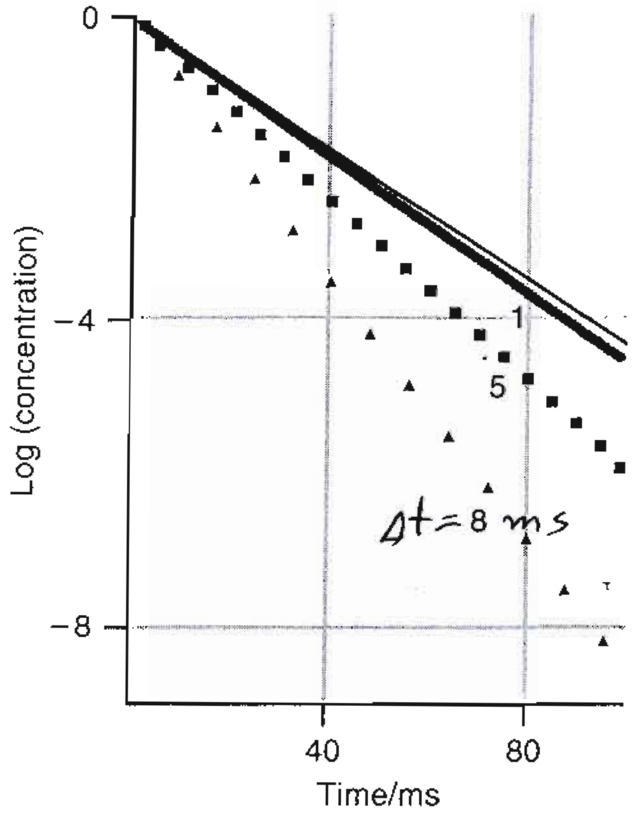


FIGURE 35.7
Comparison of the numerical approximation method to the integrated rate law expression for a first-order reaction. The rate constant for the reaction is 0.1 M s^{-1}. The time evolution in reactant concentration determined by the integrated rate law expression of Equation (35.27) is shown 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.

Δ[A] over the next time interval, resulting
tinued until the entire concentration profile

The specific example discussed here i
numerically integrating differential equatio
of Euler's method requires some knowledg
tion of a time interval Δt that is sufficiently
tion. Figure 35.7 presents a comparison of
the integrated rate law expression for a firs
cally for three different choices for Δt. Th
method is highly dependent on an appropri
of the numerical model is demonstrated by
evolution in concentrations does not change

The numerical method can be applied t
rate expressions can be prescribed. Euler's
way by which to predict how reactant and
cific kinetic scheme. However, this method
time step must be chosen to accurately cap
time steps may be quite small, requiring a
duce the full time course of the reaction. A
ally demanding. More elegant approaches,
allow for larger time steps to be performed
reader is encouraged to investigate these ap

35.7 Sequential Firs

Many chemical reactions occur in a series
into products through multiple sequential e
sider the following **sequential reaction** sch

$$A \xrightarrow{k_A}$$

In this scheme, the reactant A decays to
undergoes subsequent decay resulting in th
as an **intermediate.** The sequential reacti
involves a series of elementary first-order
rate expressions for each species can be wr

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

$$\frac{d[I]}{\;} = k_A$$

I cancels for the overall equation

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

$$\frac{d[I]}{dt} = \underbrace{k_A[A]}_{\substack{I\text{ formed}\\ \to \oplus}} - \underbrace{k_I[I]}_{\substack{I\text{ consumed}\\ \to \ominus}}$$

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

These follow from the elementary steps of the mechanism. The decay of A into I and the formation of P from I are both elementary 1. order processes

I ~~appears~~ plays a role both in the decay of A and in the formation of P

beginning: <u>only</u> $[A]_0$ at $t=0$: $[A]_0 \neq 0$, $[I]_0 = [P]_0 = 0$

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

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

inhomogeneous differential equation

solution by variation of constant:

1. Solve homogeneous part $\frac{d[I]}{dt} = -k_I[I]$
2. Then put your homogeneous solution back into the full equation, assuming that the integration constant C depends on time: $C = C(t)$ and solve for $C(t)$ $\Rightarrow$

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

Since only A at $t=0$

$\Rightarrow [A]_0$ = sum of <u>all</u> concentrations at $t>0$:

$$[A]_0 = [A] + [I] + [P] \quad , \quad [P] = [A]_0 - [A] - [I]$$

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

<u>Transp.</u> [ ] as f(t)

(a) $k_A = 2k_I$

[A] falls of exponentially → rise of [I] from 0

after maximum of [I], it decays when forming P

(b) $k_A = 8k_I$ ($k_A \gg k_I$)

$[I]_{max}$ is larger than before because now A decays faster than before

→ rise of [I] is more quick

$[P] = [A]_0$ always at the end of reaction

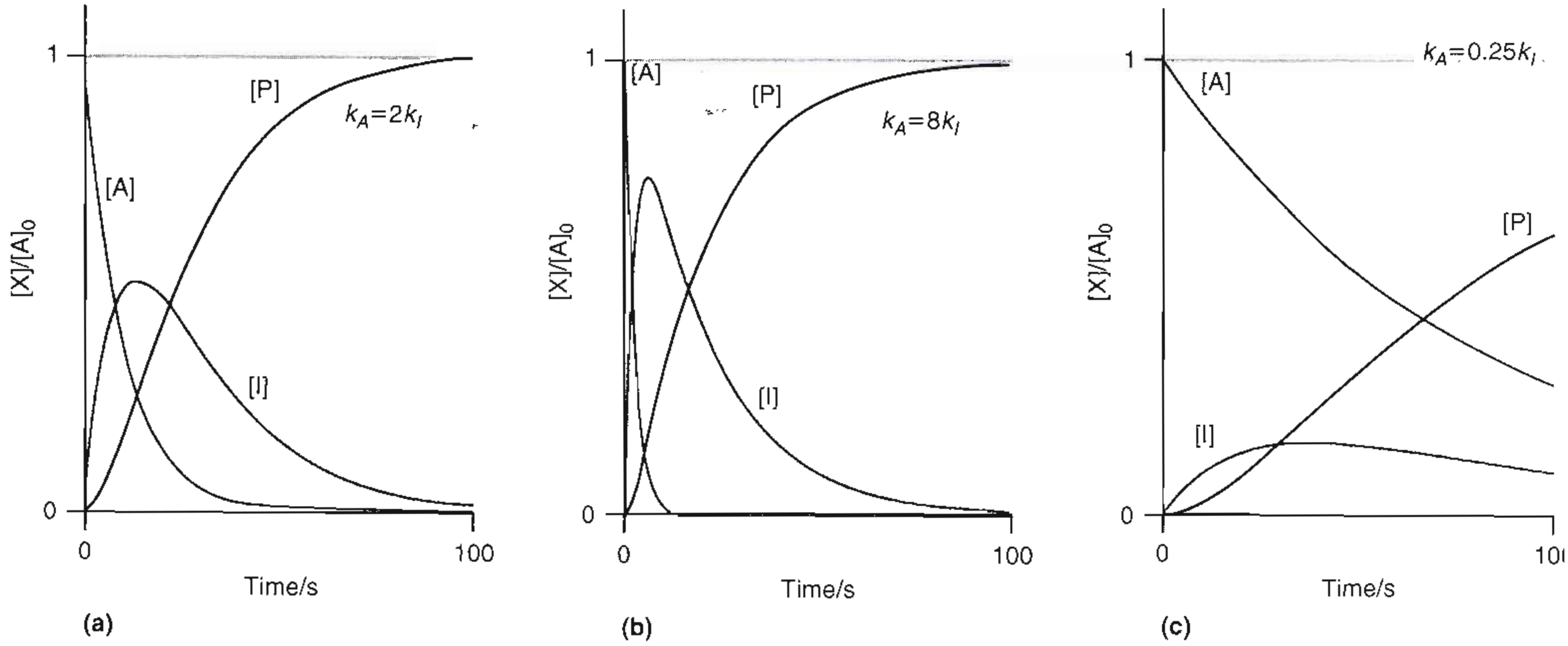
(no equilibrium ⇒ reaction until complete)

(c) $k_A = 0{,}25\,k_I$, $k_A < k_I$

[I] much lower than when $k_A > k_I$, because now it I is formed slowly, then it decays very ~~fat~~ fast immediately after its formation

⇒ [I] will rise to a small and almost not changing value throughout the reaction time = <u>steady state</u>

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.



reaction in which the reactant (A, bl line) forms an intermediate (I, purple line) that undergoes subsequent deca to form the product (P, red line) where **(a)** $k_A = 2k_I = 0.1\ s^{-1}$and **(b)** $k_A = 8k_I = 0.4\ s^{-1}$. Notice that both the maximal amount of I in addi tion to the time for the maximum is changed relative to the first panel. **(c)** $k_A = 0.025k_I = 0.0125\ s^{-1}$. In thi case, very little intermediate is forme and the maximum in [I] is delayed re tive to the first two examples.

$[I]_{max}$

(I) is maximum, when $\frac{d[I]}{dt}\Big|_{t=t_m} = 0$

$$\rightarrow t_m = \frac{1}{k_A - k_I} \ln \frac{k_A}{k_I}$$

determine t_m when $k_A = 2k_I = 0.1\,s^{-1}$ as in (a)

$$t_m = \frac{1}{0,1\,s^{-1} - 0,05\,s^{-1}} \ln \frac{0.1}{0.05} = 13,9\,s$$

$$\frac{d[I]}{dt}\Big|_{t=t_m} = \frac{k_A}{k_I - k_A} \underbrace{\left[-k_A e^{-k_A t_m} + k_I e^{-k_I t_m} \right]}_{=0} [A]_0 = 0$$

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

$$-k_A e^{-k_A t_m} + k_I e^{-k_I t_m} = 0$$

$$k_A e^{-k_A t_m} = k_I e^{-k_I t_m}$$

$$e^{(k_I - k_A)t_m} = \frac{k_I}{k_A}$$

~~t_m~~

$$(k_I - k_A)\,t_m = \ln \frac{k_I}{k_A}$$

$$t_m = -\frac{1}{k_A - k_I}\left(-\ln \frac{k_A}{k_I}\right)$$

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

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

homogeneous part: $\frac{d[I]}{dt} = -k_I [I]$

$$\int \frac{d[I]}{[I]} = -k_I \int_0 dt$$

$$\ln[I] = -k_I t + c$$

$$[I] = C e^{-k_I t}$$

assume $C = C(t)$ and insert in full equation:

$$\underbrace{\frac{dC(t)}{dt} e^{-k_I t} - k_I C e^{-k_I t}}_{d[I]/dt} \checkmark = k_A [A]_0 e^{-k_A t} - k_I C e^{-k_I t}$$

$$= k_A [A]_0 e^{-k_A t} \quad - k_1 [I]$$

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

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

$$\Rightarrow \int dC = k_A [A]_0 \int e^{+(k_I - k_A)t} dt$$

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

$$[I] = \cancel{k_A} \frac{k_A}{k_I - k_A} [A]_0 e^{(k_I - k_A)t} e^{-k_I t} + D e^{-k_I t}$$

(since $[I] = C e^{-k_I t}$)

$$[I] = \frac{k_A}{k_1 - k_A} e^{-k_A t} [A]_0 + D \cdot e^{-k_I t}$$

$$[I]_{t=0} = 0 \Rightarrow 0 = \frac{k_A [A]_0}{k_I - k_A} + D$$

$$D = -\frac{k_A [A]_0}{k_I - k_A}$$

<u>turn</u>

- rate ~~contre~~ determining step

- steady state approximation (SSA)

In the sequential reaction before: the rate of formation of product P depends on the time-scales for the formation and decay of the Intermediate I

1. limit $k_I \gg k_A$

every I molecule formed decays fast to P

⇒ rate of I formation from reactant decay (k_A small) slow, while formation of P from I fast

2. limit: $k_A \gg k_I$

Intermediate formation (k_A) much faster than I decay

A produces I fast, but decay of I to P is slow

⇒ rate determining or rate limiting step:

if 1 step of a sequence is much slower than all others, the slow step will control the rate of P formation

⇒ slow step (small k) is rate determining

$k_A \gg k_I$ I decay is slow and rate limiting

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

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

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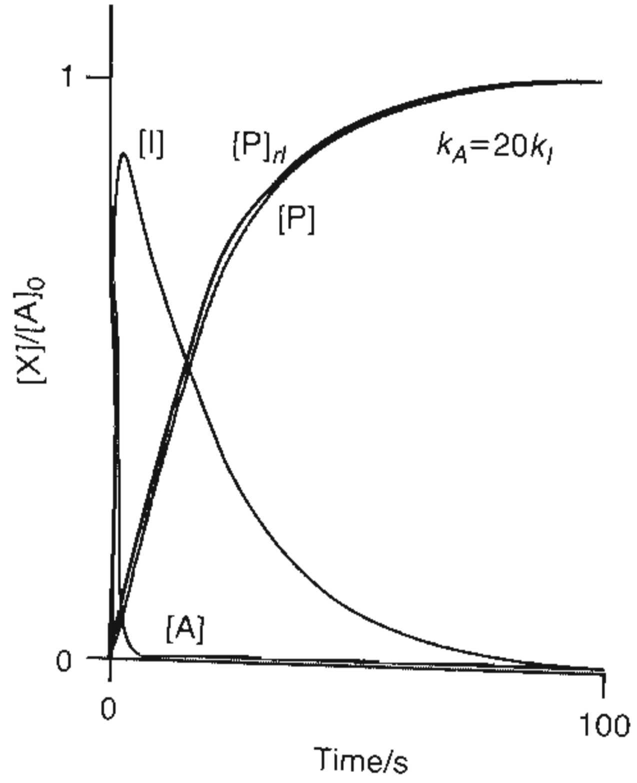
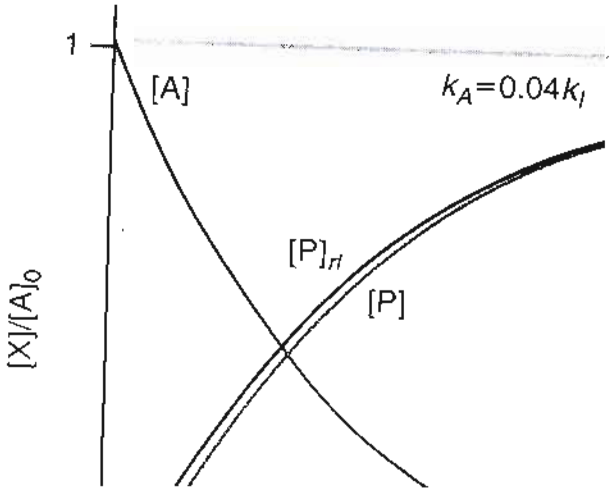


(a)



0)
ıe-
:
1)
2)

$e^{-k_A t} \ll e^{-k_I t}$ and $k_A \gg k_I \Rightarrow$ [illegible]

$$\lim_{k_A \gg k_I} [P] \approx \left(\frac{k_A e^{-k_I t}}{-k_A} + 1 \right) [A]_0$$

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

$[P](t)$ when I decay is limiting step, same as in a 1. order decay $I \rightarrow P$

<u>2. limit</u> $k_I \gg k_A$, $e^{-k_I t} \ll e^{-k_A t}$

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

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

k_I ($\gg k_A$) must be large enough that $k_I e^{-k_A t} \gg k_A e^{-k_I t}$

then $[P](t)$ is identical to a 1. order decay of A to P, at least for the example $k_I \approx 20 k_A$

<u>Transp.</u> Comparison of $[P]_{re}$ from rate limiting step approximation with $[P]$ from the exact integration in the 2 limits

$k_A = 1 s^{-1} = 20 k_I$ (a) decay of I rate limiting in P formation: fast decay of $A \rightarrow$ large $[I]_{max}$ which then decays slow to product P

$[P]_{re}$, $[P]$ very similar $\Rightarrow$ approx. valid!

(b) $k_A = 0.004\ s^{-1}$, $k_I = 0.02\ s^{-1}$

thus $k_A \ll k_I$ Transp. →

A decay is rate limiting

→ very small [I] is formed from A

slow loss of A is mirror image of the P formation

again $[P]_{ze}$ and [P] very similar

also here approx. is valid

Steady State Approximation (SSA)

series of steps:

$$A \xrightarrow{k_A} I_1 \,,\quad I_1 \xrightarrow{k_I} I_2 \,,\quad I_2 \xrightarrow{k_2} P$$

overall: $A \rightarrow P$, I_1, I_2 are intermediates

P formation from decay and formation of intermediates I_1 and I_2

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

$$\frac{d[I_1]}{dt} = k_A[A] - k_I[I_1] \qquad \frac{d[I_2]}{dt} = k_I[I_1] - k_2[I_2]$$

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

integration not easy

1. method to use: numerical Euler method

vhen a substantial difference in rate con-
exists.

imation

heme:

$$I_2 \xrightarrow{k_2} P \qquad (35.60)$$

n the formation and decay of two interme-
xpressions for this scheme are as follows:

$$\text{A}] \qquad (35.61)$$

$$] - k_1[\text{I}_1] \qquad (35.62)$$

$$] \quad k_2[\text{I}_2] \qquad (35.63)$$

$$] \qquad (35.64)$$

rations for the species involved in this reac-
essions is not trivial; therefore, how can the
s to use Euler's method (Section 35.6) and
unction of time. The result of this approach
esented in Figure 35.10. Notice that the rel-
only modest intermediate concentrations.
t $[\text{I}_1]$ and $[\text{I}_2]$ undergo little change with
centrations is approximately equal to zero:

$$= 0 \qquad (35.65)$$

te approximation. This approximation is
ns by simply setting the time derivative of
is particularly good when the decay rate
f production so that the intermediates are
the reaction (as in the case illustrated in
roximation to I_1 in our example reaction

$$\text{A}] - k_1[\text{I}_1]_{ss}$$

$$= \frac{k_A}{k_1}[\text{A}]_0 e^{-k_A t} \qquad (35.66)$$

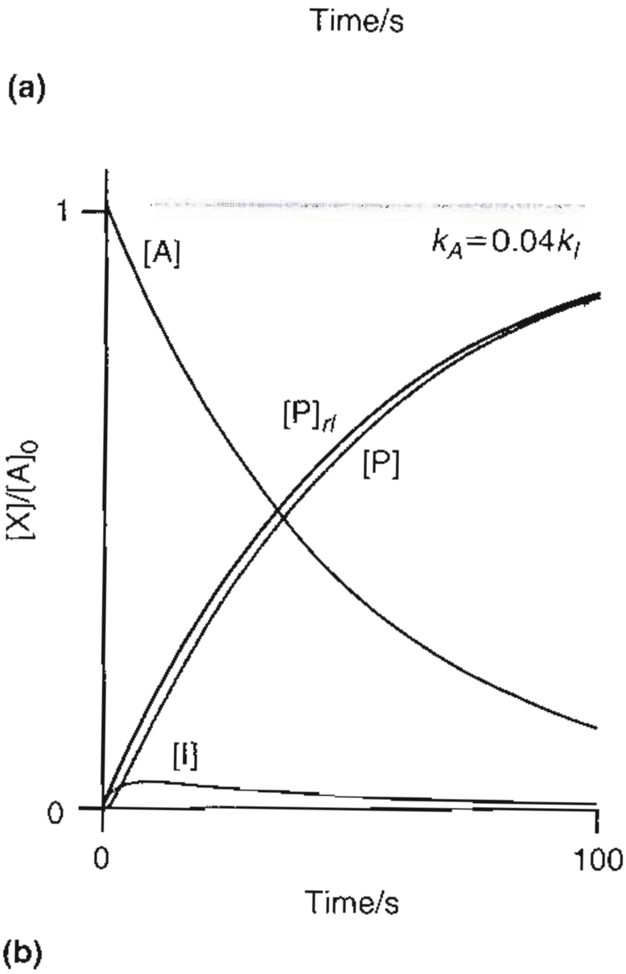


FIGURE 35.9
Rate-limiting step behavior in sequential reactions. **(a)** $k_A = 20k_I = 1\ \text{s}^{-1}$ such that the rate-limiting step is the decay of intermediate I. In this case, the reduction in [I] is reflected by the appearance of [P]. The time evolution of [P] predicted by the sequential mechanism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

Transp. Euler method for $k_A = 0.02\ s^{-1}$

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

again $k_A < k_1, k_2 \rightarrow$ only small $[I_1], [I_2]$

$[I_1], [I_2]$ do not change much in time

$$\Rightarrow \frac{d[I_1]}{dt} \approx 0, \quad \frac{d[I_2]}{dt} \approx 0$$

= Steady State Approximation (SSA)

setup rates for each intermediate and set those rates equal 0 to calculate the almost constant intermediate concentrations

($\approx$ const. in most of reaction time)

intermediate concentrations must never appear in the final rate (product formation)

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

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

expression for A, integrated with $[A]_0 \neq 0$ and $[I_1]_0 = [I_2]_0 = [P]_0 = 0$

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

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

k_1 cancels

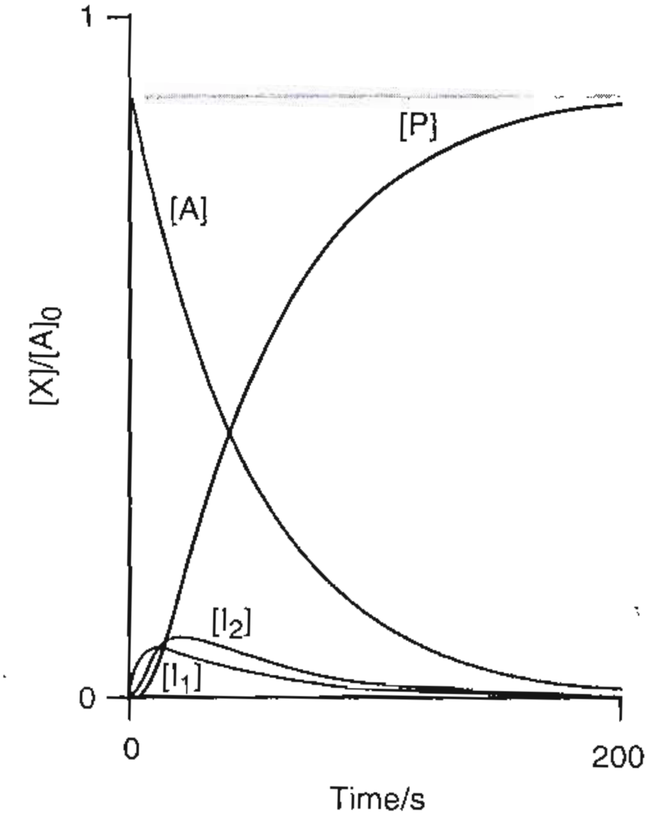
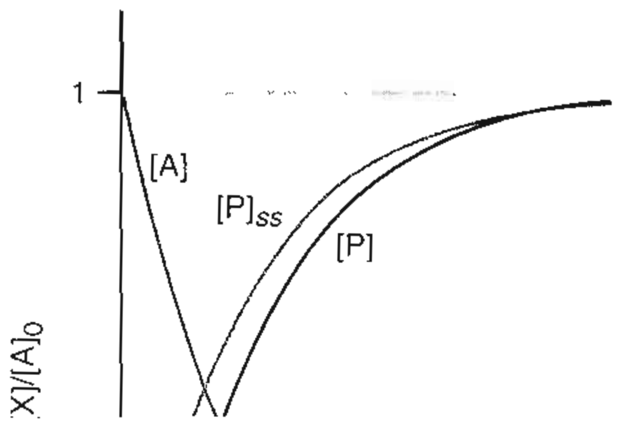


FIGURE 35.10
Concentrations determined by numerical evaluation of the sequential reaction scheme presented in Equation (35.60) where $k_A = 0.02\ \mathrm{s}^{-1}$ and $k_1 = k_2 = 0.2\ \mathrm{s}^{-1}$.



where the subscript *ss* indicates that the steady-state approximation. The final equalit tion of the differential rate expression for [A and all other initial concentrations are zer under the steady-state approximation is

$$\frac{d[\mathrm{I}_2]_{ss}}{dt} = 0 = k_1[$$

$$[\mathrm{I}_2]_{ss} = \frac{k_1}{k_2}[\mathrm{I}_1]_{ss}$$

Finally, the differential expression for *P* is

$$\frac{d[\mathrm{P}]_{ss}}{dt} = k_2[\mathrm{I}_2]$$

Integration of Equation (35.68) results in the

$$[\mathrm{P}]_{ss} = [\mathrm{A}]_0$$

Equation (35.69) demonstrates that within t dicted to demonstrate appearance kinetics co

When is the steady-state approximatio the concentration of intermediate be consta centration of the first intermediate under t derivative of $[\mathrm{I}_1]_{ss}$ is

$$\frac{d[\mathrm{I}_1]_{ss}}{dt} = \frac{d}{dt}\left(\frac{k_A}{k_1}[\mathrm{A}]_0 e^{-}\right.$$

The steady-state approximation is valid when true when $k_1 \gg k_A^2[\mathrm{A}]_0$. In other words, *k* is small at all times. Similar logic applies to I_2 valid when $k_2 \gg k_A^2[\mathrm{A}]_0$.

Figure 35.11 presents a comparison betwee and those predicted using the steady-state appr tial reaction where $k_A = 0.02\ \mathrm{s}^{-1}$ and $k_1 = k$ ditions where the steady-state approximation between [P] determined by numerical evalua value, $[\mathrm{P}]_{ss}$, is evident. For the examples prese relatively easy to implement; however, for ma intermediate concentration with time is not appr imation is difficult to implement if the intermed two of the differential rate expressions derived

EXAMPLE PROBLEM 35.6

$$\rightarrow \frac{d[P]_{SSA}}{dt} = k_2 [I_2]$$

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

$$[P]_{SSA} = k_A [A]_0 \int_0^t e^{-k_A t} \, dt = -[A]_0 \, e^{-k_A t} \Big|_0^t$$

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

looks in SSA, like P comes from a 1. order decay of A directly

When is SSA valid?

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

SSA ok, when $[I_1]_{SSA} = \text{const.} \Rightarrow$ when $\frac{d[I_1]_{SSA}}{dt} = 0$

this is the case when $k_1 \gg k_A^2 [A]_0$, and

$$\frac{d[I_2]_{SSA}}{dt} = \frac{d}{dt}\left(\frac{k_A}{k_2}[A]_0 \, e^{-k_A t}\right) = -\frac{k_A^2}{k_2}[A]_0 \, e^{-k_A t}$$

ok when $k_2 \gg k_A^2 [A]_0$

Transp. Comparison of numerical concentrations with $\left(P_{\cancel{ss}}\right)_{SSA}$, when $k_A = 0.02\,s^{-1}$, $k_1 = k_2 = 0.2\,s^{-1}$: conditions such that SSA should be ok valid when $k_2 \gg$

Figure 35.11 pre
and those predicted
tial reaction where k
ditions where the s
between [P] determ
value, $[P]_{ss}$, is evide
relatively easy to in
intermediate concent
imation is difficult to
two of the differentia

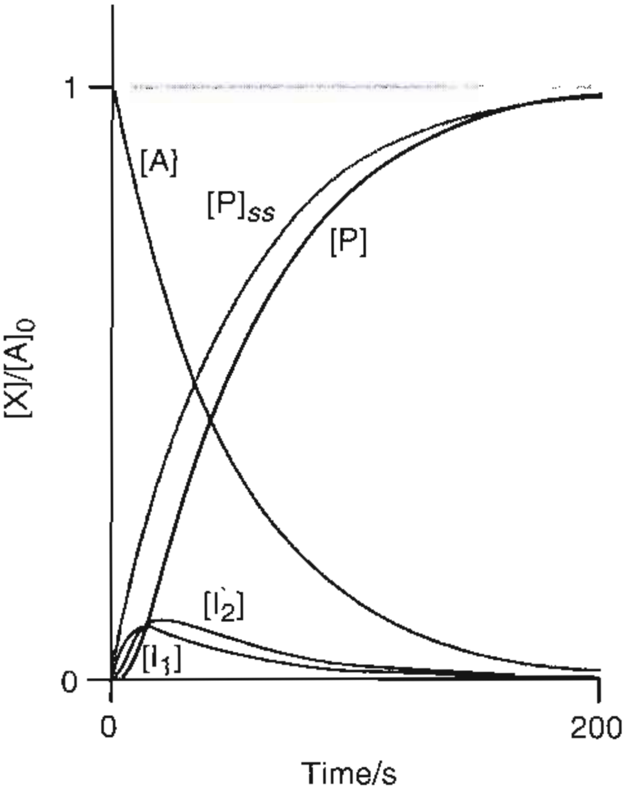


FIGURE 35.11
Comparison of the numerical and steady-state concentration profiles for the sequential reaction scheme presented in Equation (35.44) where $k_A = 0.02\ \text{s}^{-1}$ and $k_1 = k_2 = 0.2\ \text{s}^{-1}$. Curves corresponding to the steady-state approximation are indicated by the subscript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

EXAMPLE PRO

Consider the follow

Assuming that only
ence of [P] using the

Solution

The differential rate
(35.48), and (35.49):

<u>but</u> relatively large error in
$[P]_{SSA}$

<u>many</u> reactions: SSA <u>not</u> very good

SSA can also be difficult to use

$A \xrightarrow{k_A} I$, $I \xrightarrow{k_I} P$ only A at $t=0$

What is $[P]$ in SSA?

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

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

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

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

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

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

$[P]$ is same as when derived from rate limiting step (decay of A)

$\Rightarrow$ ok

- Parallel Reactions
- T dependence of rate constants

in many cases: 1 reactant yields several products

parallel reactions: each reactant A forms products B, C:

$$\begin{tikzcd} A \arrow[r, "k_B"] \arrow[dr, "k_c"'] & B \\ & C \end{tikzcd}$$

differential rate expressions:

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

both consumption

$$\frac{d[B]}{dt} = k_B[A] \qquad \frac{d[C]}{dt} = k_c[A] \quad \text{formation}$$

with $[A]_0 \neq 0$, $[B]_0 = [C]_0 = 0$:

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

$$\rightarrow \frac{d[B]}{dt} = k_B[A]_0 e^{-(k_B+k_c)t}$$

Integration:

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

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

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

Transp. (A), [B], [C] vs t for $k_B = 2k_c = 0.1 s^{-1}$

General features of such branching reactions:

1) Decay of A with effective rate constant $(k_B + k_c)$

2) The ratio of products $[B]/[C]$ is the same in all times, does not depend on time

equation: $\frac{[B]}{[C]} = \frac{k_B}{k_c}$ Rest cancels

if k of 1 of the branching reaction increases, then the product ~~of~~ [P] of that branch increases also

The extent of P formation depends on the ratio of rate constants

The larger the rate constant of a ~~brach~~ branch becomes, the more likely the product of that branch will be formed

yield ϕ_i: probability that product i is formed in the reactant decay ;

$$\phi_i = \frac{k_1}{\sum_j k_j}$$

In the figure with $k_B = 2k_c$, the yield of c

is: $\phi_c = \frac{k_c}{k_B + k_c} = \frac{k_c}{2k_c + k_c} = \frac{1}{3}$

since $\sum_i^{\text{all products}} \phi_i = 1 \Rightarrow \phi_B = \frac{2}{3}$ Figure $[B]_\infty = 2[C]_\infty$

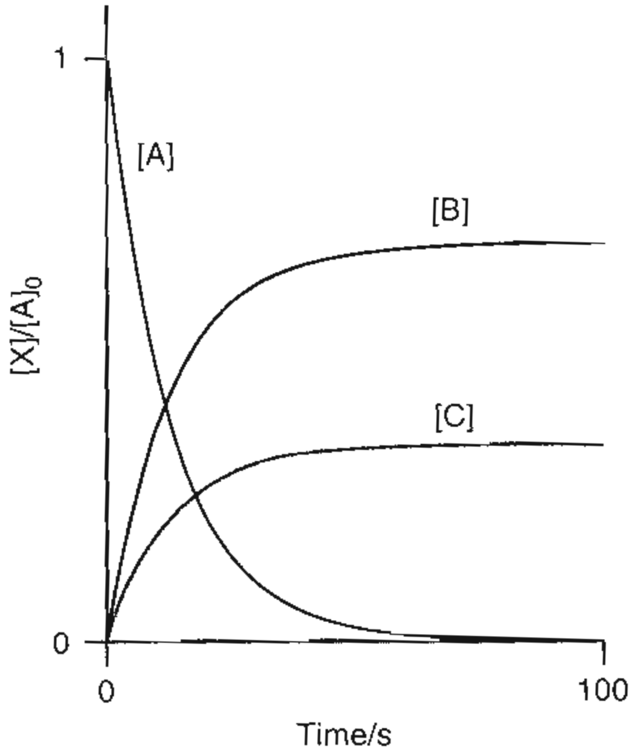


FIGURE 35.12
Concentrations for a parallel reaction where $k_B = 2k_C = 0.1\ \mathrm{s}^{-1}$.

Figure 35.12 provides an illustration of the rea
branching reaction where $k_B = 2k_C = 0.1\ \mathrm{s}^{-1}$
branching reactions are evident in the figure. Fi
an apparent rate constant equal to $k_B + k_C$, th
branch. Second, the ratio of product concentrati
time point the ratio$[B]/[C]$ is identical. This be
and (35.77) where this ratio of product concentr

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

Equation (35.78) is a very interesting result.
stant for one of the reaction branches increases
tion of the corresponding product increases as
of the product concentrations in Equation (35.
fore, the product ratio will be the same throug

Equation (35.78) demonstrates that the e
reaction is dependent on the rate constants. A
respect to probability; the larger the rate cons
that product will be formed. The **yield** Φ is de
uct will be formed by decay of the reactant:

$$\Phi_i = \frac{}{\sum_{n}}$$

In Equation (35.79), k_i is the rate constant for
product of interest indicated by the subscript i.
constants for the reaction branches. The total
each product, and it is normalized such that

$$\sum_i \Phi_i =$$

In the example reaction depicted in Figure 35.
mation of product C is

$$\Phi_C = \frac{k_C}{k_B + k_C} =$$

Because there are only two branches in
Figure 35.12 reveals that $[B] = 2[C]$, which

EXAMPLE PROBLEM 35.7

In acidic conditions, benzyl penicillin (BP) un

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

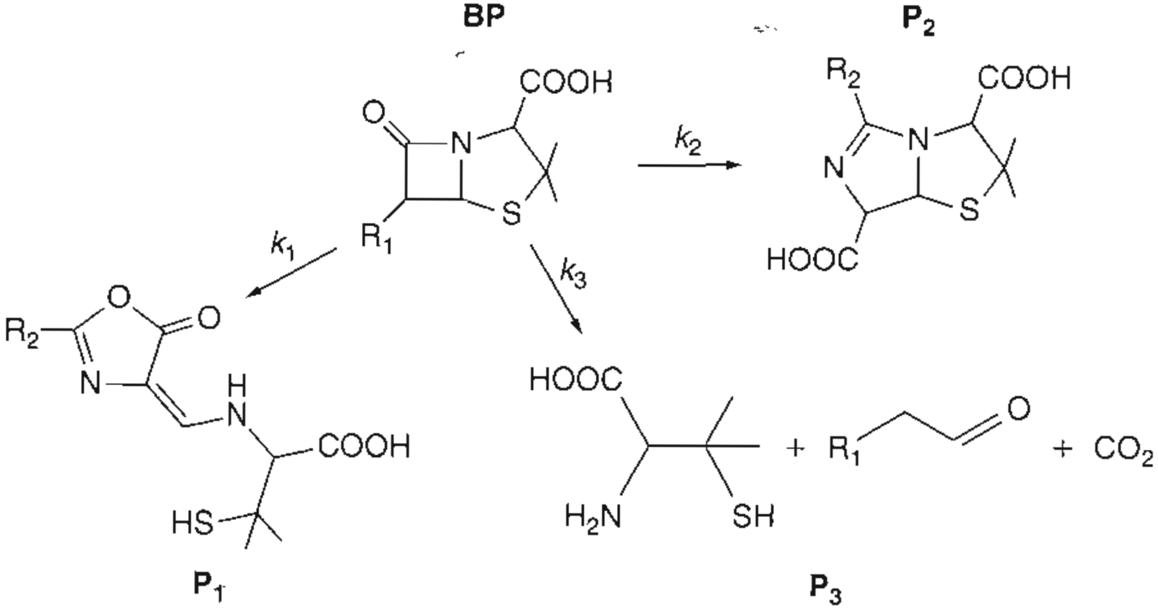
In the example reaction depicted in Figure 35.12 where $k_B = 2k_C$, the yield for the formation of product C is

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

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:



In Equation (35
preexponentia
the preexponei
depending on
mol^{-1} (for exa
lowing express

Equation (35
with slope ec
provides an a
for a reactior

EXAMPLE

The tempera
in Example
given in the
tial factor fc

Transp. Branching decay of Benzylpenicillin (BP)

R_1, R_2 are alkyl substituents $H_3C-(CH_2)_n-$

swallow BP then you get pH=3 in your stomach

At pH=3, 22°C: $k_1 = 7.0 \cdot 10^{-4}\,s^{-1}$, $k_2 = 4.1 \cdot 10^{-4}\,s^{-1}$, $k_3 = 5.7 \cdot 10^{-3}\,s^{-1}$

yield of P_1 formation?

$$\phi_{P_1} = \frac{k_1}{k_1+k_2+k_3} = \frac{7.0 \cdot 10^{-4}\,s^{-1}}{(0.70 + \underset{0.41}{\cancel{4.1}} + 5.7)\cdot 10^{-3}\,s^{-1}} = 0.067$$

$$x \cdot 10^{-4} = x \cdot 10^{-1} \cdot 10^{1} \cdot 10^{-4} = \frac{x}{10} \cdot 10^{-3}$$

→ in acid dissociation of BP, 6.7% P_1 is formed

T-dependence of k

in general a rate constant $k = f(T)$

observed for many reaction: $\ln k$ vs $\frac{1}{T}$ is linear

→ Arrhenius expression (late 1800s)

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

A = frequency factor or Arrhenius pre-exponential factor

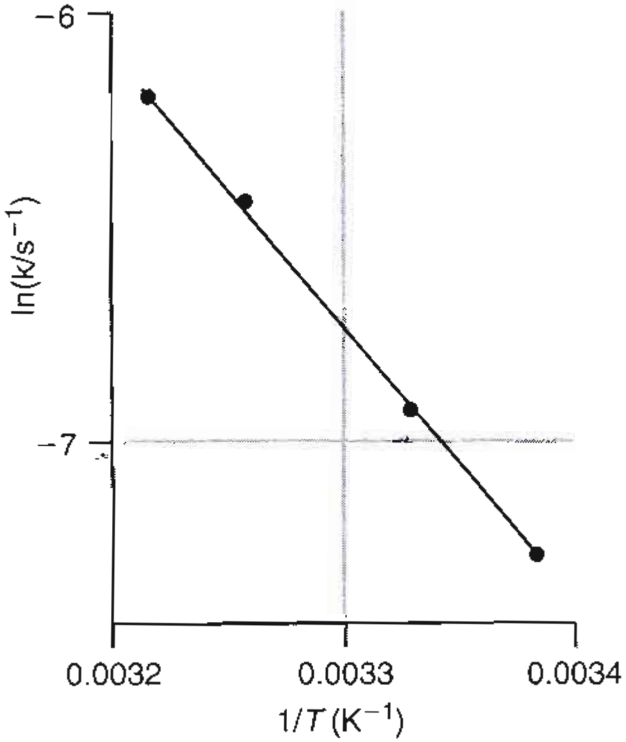
E_a = activation energy

A: unit of a rate constant ⇒ changes with order

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

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

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

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

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

$\ln k$ vs $\frac{1}{T}$: straight line

slope $= -\frac{E_a}{R}$, intercept $\ln A$

example as before: hydrolysis of BP:

t (°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	$2.0 \cdot 10^{-3}$

Transp. plot $\ln\left(\frac{k}{s^{-1}}\right)$ vs $\frac{1}{T}$

linear regression: $\ln k = (-6\,300\,K) \cdot \frac{1}{T} + 14.1$

intercept: $14.1 = \ln A \Rightarrow A = e^{14.1}\, s^{-1} = 1.33 \cdot 10^{6}\, s^{-1}$

E_a is the energy needed that a reaction can occur

Transp. Boltzmann distributions of molecular speeds at 200 K and at 500 K:

E vs fraction of molecules with $E_k = E$

+ E_{pot} vs q $\quad E(q = \text{reactants}) \rightarrow E_a \rightarrow E(q = \text{products})$

reaction coordinate q: describes changes in a molecule going from R → P = bond and geometry changes as they must happen from R to P

e.g. for $A{-}B + C \rightarrow A{-}C + B$, q can be R_{A-B} or also R_{A-C}

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

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

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

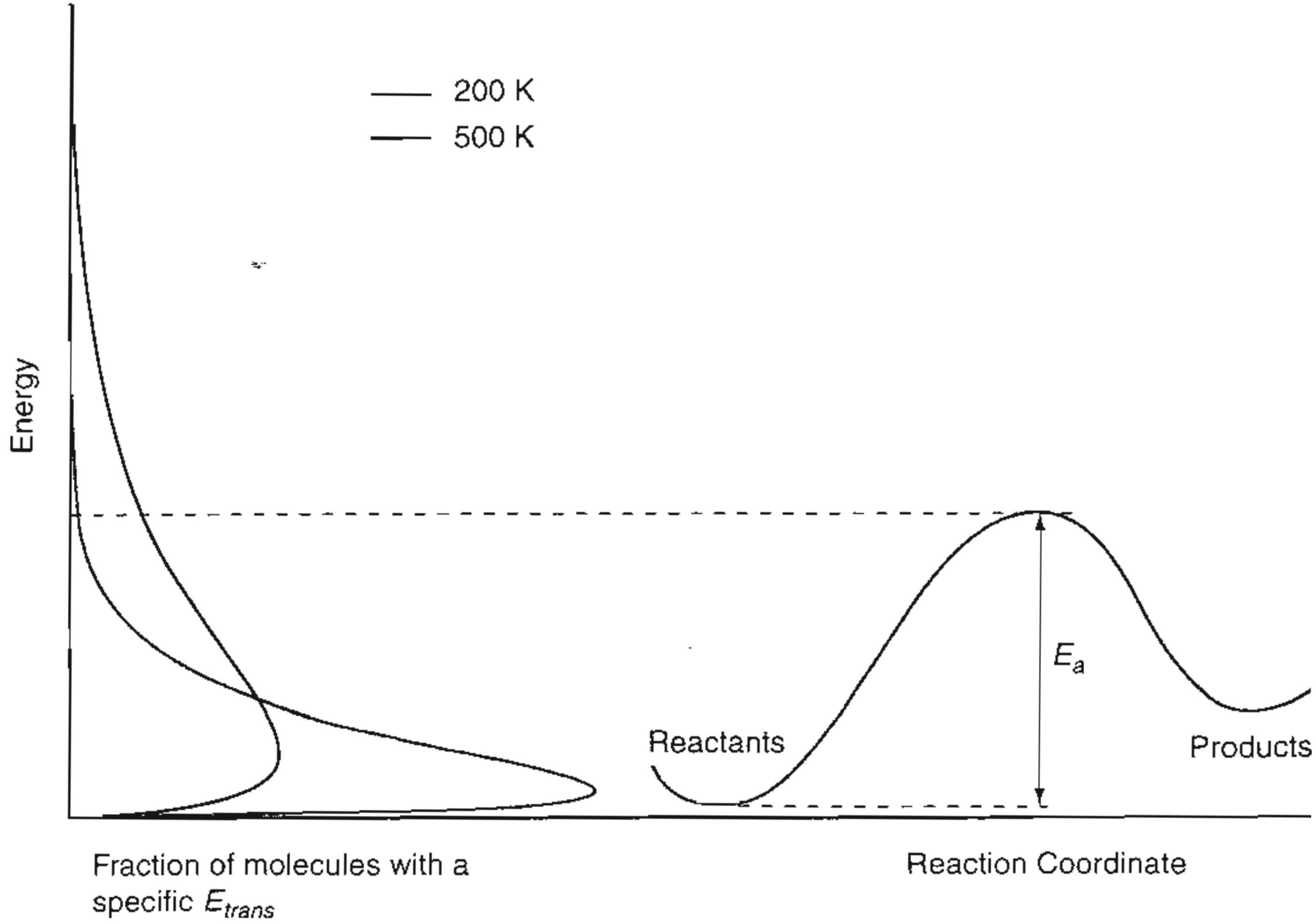


FIGURE 35.13
A schematic drawing of the energy profile for a chemical reaction. Reactants must acquire sufficient energy to overcome the activation energy E_a for the reaction to occur. The reaction coordinate represents the bonding and geometry changes that occur in the transformation of reactants into 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.

The no. of molecules with $E_k \geq E_a$ increases when T increases, fraction of molecules with $E_k \geq E_a$ is $e^{-E_a/RT}$

When at fixed T, E_a increases, then the fraction of molecules with E_k large enough for reaction decreases

<u>not all</u> reactions follow the Arrhenius law

Reason: E_a and A can be f(T) while the law assumes them to be independent of T

→ no straight line plot of ln k vs $\frac{1}{T}$

more modern theories:

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

a and E' are assumed independent of T

m can be 1, $\frac{1}{2}$, $-\frac{1}{2}$, depending on the details of the theory used

activated complex theory: m = 1 predicted

with m = 1 a plot of $\ln\left(\frac{k}{T}\right)$ vs $\frac{1}{T}$ gives a straight line with slope $= -E'/R$ and intercept $= \ln \overset{a}{\cancel{A}}$

The limitations of the Arrhenius law are clearly known and it gives a good description for a large number of reactions.

A = collision frequency factor ?

2. order in solution:

$$k_1 = 5.70 \cdot 10^{-5} \frac{L}{mol\,s} \quad , \; 25°C$$

$$k_2 = 1.64 \cdot 10^{-4} \frac{L}{mol\,s} \quad , \; 40°C$$

slope of ln k vs $\frac{1}{T}$:

$$slope = \frac{\ln k_1 - \ln k_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

$$= \frac{-9.772 - (-8.716)}{(3.354 - 3.1934) \cdot 10^{-3}\,K^{-1}} = \frac{-1.056}{0.1606} \cdot 10^{3}\,K$$

$$= -6.576 \cdot 10^{3}\,K$$

$$E_a = -R \cdot slope = 8.3145 \frac{J}{K\,mol} \cdot 6.576 \cdot 10^{3}\,K$$

$$= 54676 \frac{J}{mol} = 54.7 \frac{kJ}{mol}$$

$$k = Ae^{-Ea/RT} \qquad A = ke^{Ea/RT}$$

any 1 of the 2 given k values is ok

$$A = 1.64 \cdot 10^{-4} \frac{1}{M\,s} \exp\left[\frac{54.68 \cdot 10^{3} \frac{J}{mol}}{8.3145 \frac{J}{K\,mol} \cdot \underset{\nearrow\, 40°C}{313.15\,K}}\right]$$

$$= 1.64 \cdot 10^{-4} \frac{1}{Ms} \exp(+21)$$

$$= 1.64 \cdot 10^{-4} \frac{1}{Ms} \cdot 1.3188 \cdot 10^{9}$$

$$= 2.16 \cdot 10^{-5} \frac{1}{Ms} = 2.16 \cdot 10^{-5} \frac{L}{mol\,S}$$

$[A] = [k]$!

Reversible Reactions: Equilibrium

so far was assumed:
When product P is formed, no backward reaction takes place

Transp. $E_{pot} = f(q)$

$E_{pot}(q)$ suggests: with enough energy, the backward reaction can occur.

$R \rightarrow P$ if reactants have enough energy to overcome the activation energy E_a
then reactants form products
But, if the products have enough energy to overcome the barrier E_a'
then reaction in reverse direction occurs also:

$$P \rightarrow R$$

Then we have a reversible reaction which can occur in both directions. $R \rightleftharpoons P$

forward reaction: 1. order in A
backward reaction: 1. order in B:

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

k_A, k_B: forward and backward rate constants
differential rate equations:

$$\frac{d(A)}{dt} = \underbrace{-k_A[A]}_{\substack{\text{consumption of A} \\ \ominus \text{ sign}}} \quad \underbrace{+ k_B[B]}_{\substack{\text{formation of A} \\ \oplus \text{ sign}}}$$

A consumed with k_A $(-k_A[A])$, B consumed with k_B $(k_B[B])$ producing A again

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:

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

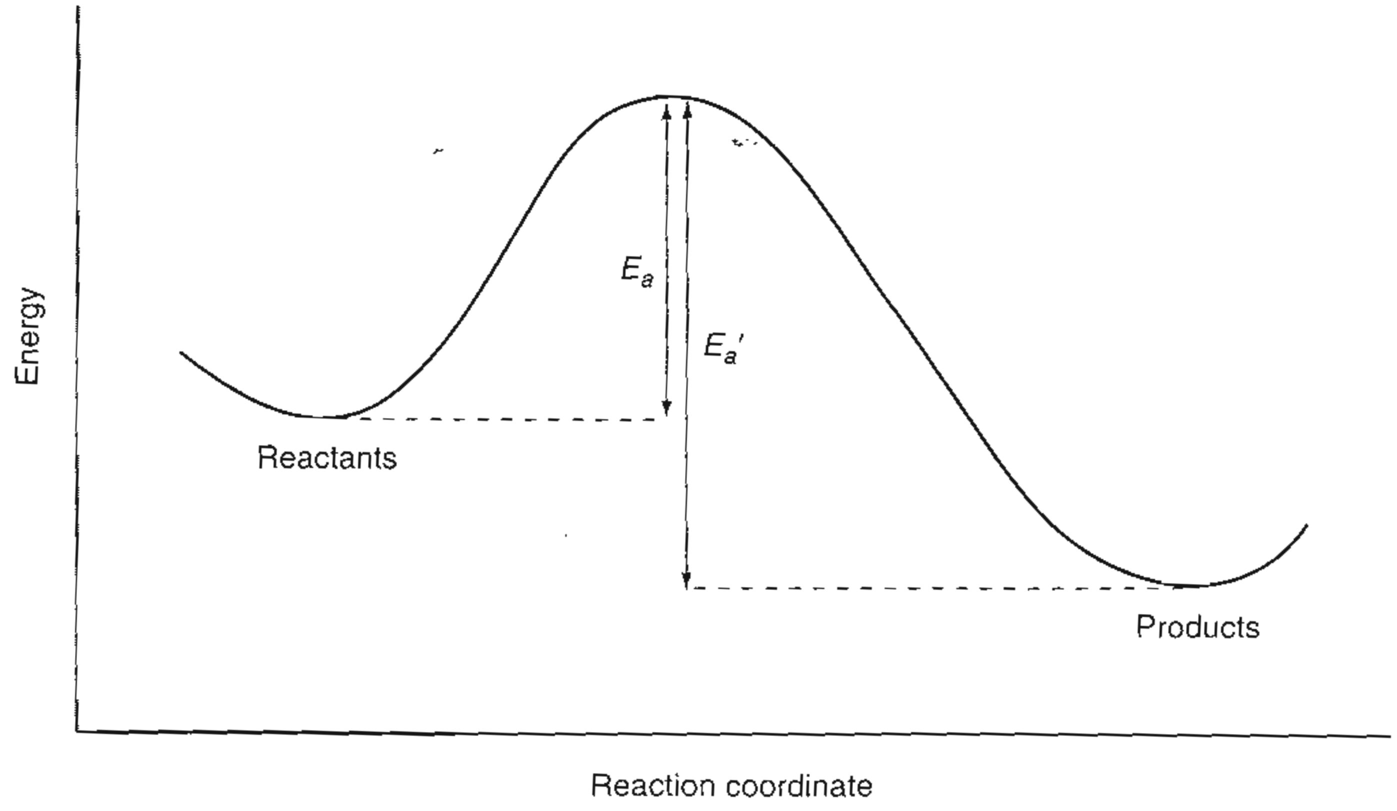


FIGURE 35.14
Reaction coordinate demc
activation energy for react
products E_a and the back
which products form reac

further: $$\frac{d(B)}{dt} = \underset{\substack{\text{formation of } B\\ \oplus}}{k_A(A)} - \underset{\substack{\text{consumption of } B\\ \ominus}}{k_B(B)}$$

1. order decay reaction was discussed before:

~~then~~ the reactant decay term $-k_A(A)$ here similar to 1. order decay reaction

but here we have a second term, $k_B(B)$, which describes reactant formation by product decay.

initially at $t=0$: $(A)_0 \neq 0$, $(B)_0 = 0$

then at all times $t>0$: $(A)_0 = (A)+(B)$

$\Rightarrow$ integration possible:

$$\frac{d(A)}{dt} = -k_A(A) + k_B(B)$$
$$= -k_A(A) + k_B((A)_0 - (A))$$
$$= -(k_A+k_B)(A) + k_B(A)_0$$

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

formula collection:

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

$$\Rightarrow \int_{(A)_0}^{(A)} \frac{d(A)}{(k_A+k_B)(A) - k_B(A)_0} = \frac{1}{k_A+k_B}\ln\frac{(k_A+k_B)(A) - k_B(A)_0}{\underbrace{(k_A+k_B)(A)_0 - k_B(A)_0}_{\text{cancel !}}}$$

$b = k_A + k_B$

$a = -k_B(A)_0$

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

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

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

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

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

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

Transp. $[A]$, $[B]$ vs t with $k_A = 2k_B = 0.06\,s^{-}$

$[A]$ decays exponentially with rate constant (k_A+k_B) and $[B]$ appears exponentially also with rate constant (k_A+k_B)

at t_{eq} the concentrations become constant and equilibrium is reached

forward+ backward reactions $\rightarrow$ $[A]_\infty, [B]_\infty \neq 0$ both not zero

equilibrium concentrations $[A]_{eq}$, $[B]_{eq}$:

$$[A]_{eq} = \lim_{t\to\infty}[A] = [A]_0 \frac{k_B}{k_A+k_B} \qquad \lim_{t\to\infty} e^{-\alpha t} = 0$$

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

at t_{eq}: $[A]$, $[B]$ so close to $[A]_{eq}$, $[B]_{eq}$ that they change only little at $t > t_{eq}$

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:

$$\begin{aligned} \frac{d[\mathrm{A}]_{eq}}{dt} &= \frac{d[\mathrm{B}]_{eq}}{dt} = 0 = -k_A[\mathrm{A}]_{eq} + k_B[\mathrm{B}]_{eq} \\ \frac{k_A}{k_B} &= \frac{[\mathrm{B}]_{eq}}{[\mathrm{A}]_{eq}} = K_c \end{aligned} \tag{35.94}$$

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

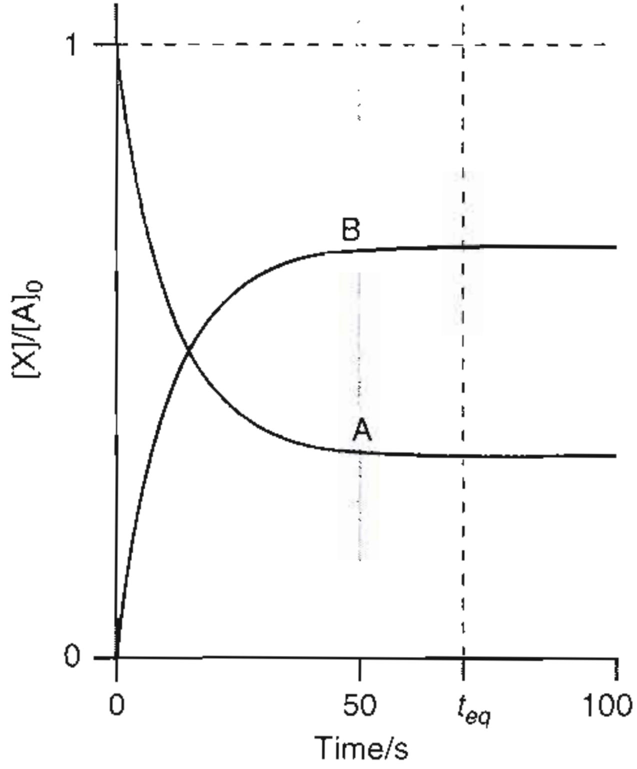


FIGURE 35.15
Time-dependent concentrations in which both forward and back reactions exist between reactant A and product B. In this example, $k_A = 2k_B = 0.06\ \mathrm{s}^{-1}$. Note that the concentrations reach a constant value at longer times ($t \geq t_{eq}$) at which point the reaction reaches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

⇒ system has practically reached equilibrium at t_{eq}

$t > t_{eq}$: $[A]$, $[B]$ constant = time independent

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

__but__ forward and backward rates are __not 0__

in equilibrium, they are just __equal__

so that $[A]_{eq}$, $[B]_{eq}$ do not change anymore in equilibrium

forward and backward ~~rates~~ reactions still happen in equilibrium, but with equal rates, so that concentrations do __not__ change for $t > t_{eq}$

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

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

The equilibrium constant in concentration form as ~~from~~ known from thermodynamics and also from statistical mechanics is now written in terms of rate constants:

the larger is k_A, the more K_c is on the product side ($[B]$)

measurement: decay / and formation rates of A and B

→ apparent rate constant $k_A + k_B$

measurement of K_c → ratio of forward and backward rate constants ⇒ k_A and k_B separately deceptively simple equation. From the kinetic standpoint, K_c is related to the ratio of forward and backward rate constants for the iction. The greater the forward ra 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.

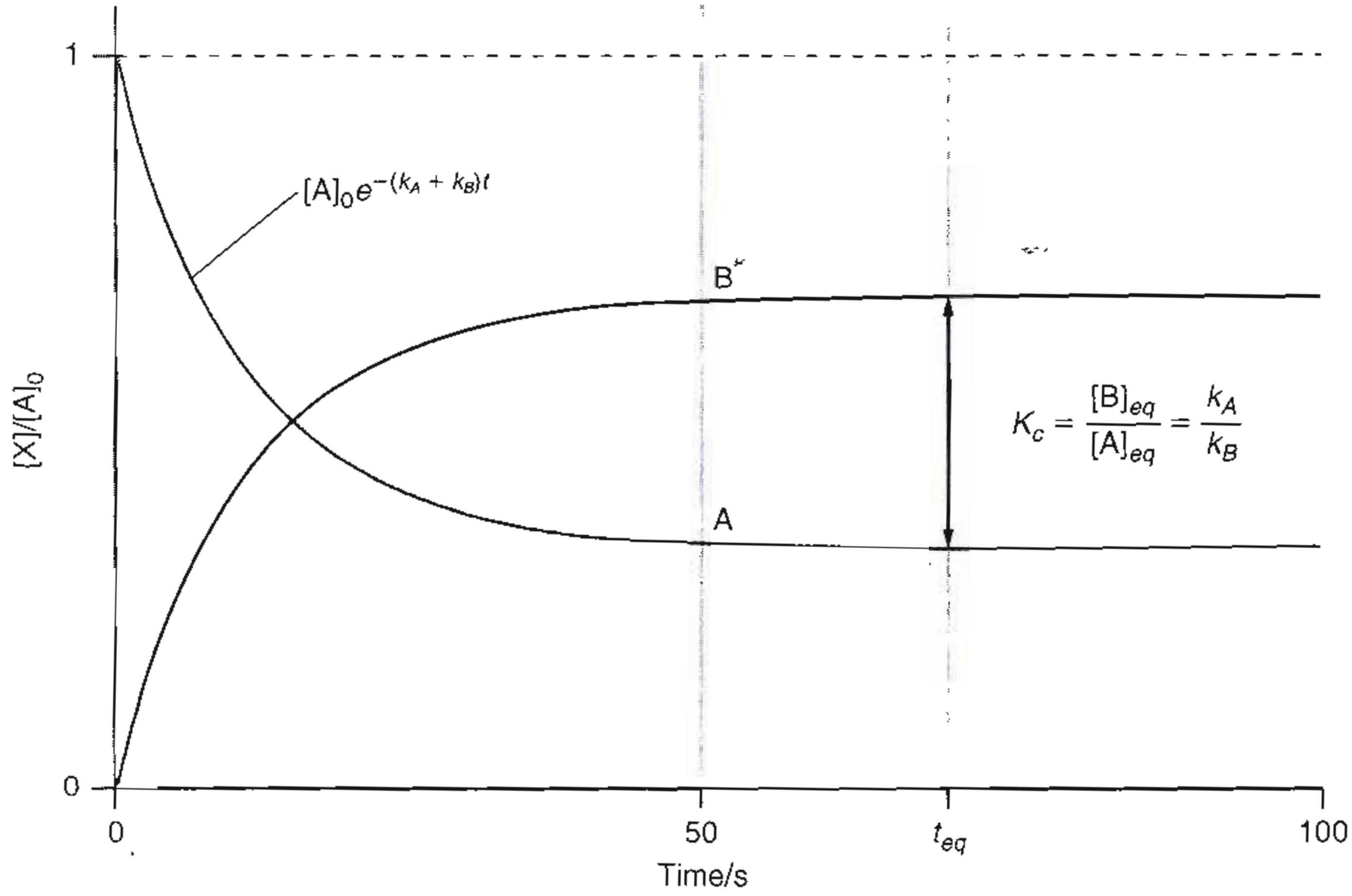
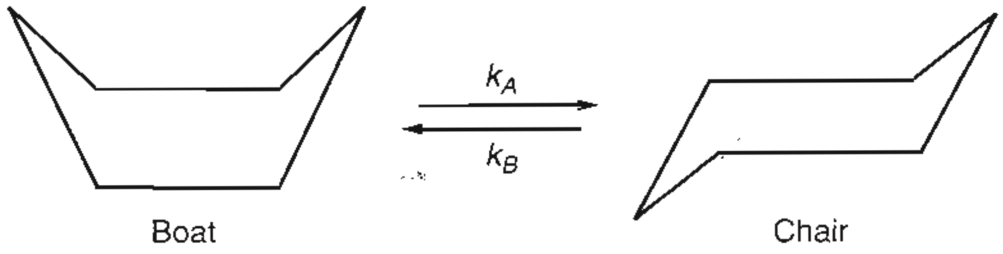


FIGURE 35.16
Methodology for determining forward and backward rate constants. The apparent rate constant for reactant decay is equal to the sum of forward k_A and backward k_B rate constants. The equilibrium constant is equal to k_A/k_B. These two measurements provide a system of two equations and two 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 $10^{12}\ \text{s}^{-1}$, what is the expected observed reaction rate constant at 298 K if one were to initiate this reaction starting with only the boat conformer?

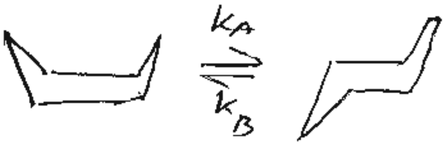
Solution

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

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

Transp. Measurement of $k_A + k_B$ from reactant decay, and of $k_A/k_B = K_C$
$\rightarrow k_A$ and k_B

Transp. boat $\underset{k_B}{\overset{k_A}{\rightleftharpoons}}$ chair



1. order forward and backward,

$$K_C = 10^4 = \frac{[\text{chair}]_{eq}}{[\text{boat}]_{eq}}$$

chair $\rightarrow$ boat $E_a = 42$ kJ/mol

Arrhenius factor $A = 10^{12}\,s^{-1}$
starting with only boat, what is the apparent rate constant $k_{app} = k_A + k_B$, 298K

E_a is for $\overset{\text{chair}}{\cancel{\text{boat}}} \rightarrow \overset{\text{boat}}{\cancel{\text{chair}}}$

$$\Rightarrow k_B = A e^{-E_a/RT}$$

$$= 10^{12}\,s^{-1} \exp\left[\frac{-42000\ J/mol}{8.314\ \frac{J}{K\,mol} \cdot 298K}\right]$$

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

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

$$k_A = 10^4 k_B = 10^4 \cdot 4.34 \cdot 10^4\ s^{-1}$$
$$= 4.34 \cdot 10^8\ s^{-1}$$

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

- Perturbation - Relaxation Methods
- Auto ionization of water

Equilibrium reactions: the concentration values near equilibrium will occur at later times than the initial rates suggest.

rate constant measurement: concentration evolutions with time + measurement of equilibrium concentrations

that is not possible if the initial conditions cannot be controlled exactly

for example: reaction start at a specific time is maybe not possible

However, one can wait for equilibrium to be established and then one perturbs the equilibrium by a fast change of P, T, or concentrations, like pH value

then after the change the system will not be in equilibrium any more: it is in old equilibrium, but new equilibrium is changed (K changed)

So the system will change (relax) ~~to~~ until a new equilibrium is reached

then the relaxation kinetics can be measured.

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

forward, backward reactions of 1. order

rapid T-jump ⇒ according to Arrhenius the rate constants will change to $\overset{+}{k}_A$ and $\overset{+}{k}_B$

(+ indicates values valid after T jump)

and there will be a new equibibrium:

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

initial T and ΔT can be fixed such that the final T is the one at which we want to do our experiment

At new equilibrium: $[A]_{eq} = \text{const.} \Rightarrow \frac{d(A)_{eq}}{dt} = 0$

$$\Rightarrow \frac{d(A)_{eq}}{dt} = 0 = -\overset{+}{k}_A (A)_{eq} + \overset{+}{k}_B (B)_{eq}$$

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

subscript eq denotes the new equilibrium after the T-jump

ξ: extent by which the pre T-jump (before T-jump) concentrations are shifted

$[A] - \xi = (A)_{eq}$ $\quad -\xi$ since A is consumed

$(B) + \xi = (B)_{eq}$

if T is higher after the jump

then $\overset{+}{k}_A$ after jump is larger than k_A before

⇒ new $(A)_{eq} < [A]$ before jump equilibrium

$$\rightarrow [A) - \xi = (A)_{eq}$$

$$\frac{d(A)}{dt} - \frac{d\xi}{dt} \cancel{= \frac{d(A)_{eq}}{dt}} = \frac{d(A)_{eq}}{dt} = 0$$

$$\rightarrow \frac{d\xi}{dt} = \frac{d(A)}{dt} = -k_A^+ (A) + k_B^+ (B)$$

rate constants are for after T-jump

$$\frac{d\xi}{dt} = -k_A^+ (\xi + (A)_{eq}) + k_B^+ (-\xi + (B)_{eq})$$

$$= \underbrace{-k_A^+ [A]_{eq} + k_B^+ [B]_{eq}}_{0} - \xi (k_A^+ + k_B^+)$$

rates equall in
new equilibrium

$$\frac{d\xi}{dt} = -\xi (k_A^+ + k_B^+)$$

relaxation time $\tau = \frac{1}{k_A^+ + k_B^+}$

<u>Transp.</u> time evolutions in T-jump experiment

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

$$\ln \frac{\xi}{\xi_0} = -t/\tau$$

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

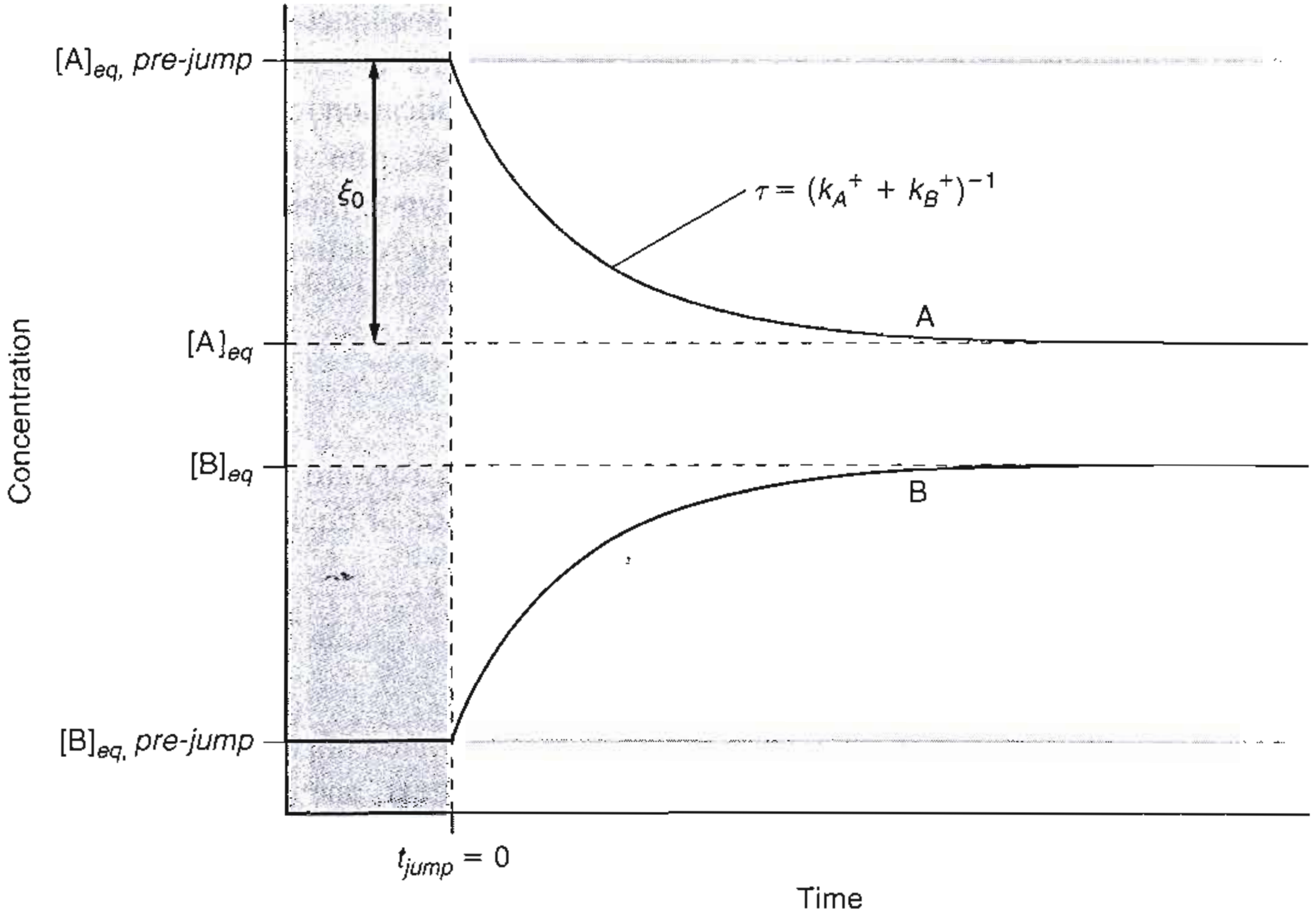
relaxation time: time it takes for ξ to reach $\frac{1}{e} \xi_0$
($\frac{1}{e}$ of its initial value)

the time ~~sch~~ scale of the relaxation is related to $k_A^+ + k_B^+$

$\Rightarrow$ measure τ, K_c (new equilibrium): $\tau = \frac{1}{k_A^+ + k_B^+}$, $K_c = \frac{k_A^+}{k_B^+}$

$k_A^+ = k_B^+ K_c \quad k_B^+ K_c + k_B^+ = \frac{1}{\tau}$, $k_B^+ = \frac{1}{\tau(1+K_c)}$, $k_A^+ = k_B^+ K_c = \frac{K_c}{\tau(1+K_c)}$

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:

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

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

Auto ionization of water :

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

forward reaction : 1. order

reverse reaction : 2. order

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

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

before

$A = H_2O$

$[A] - \xi = [A]_{eq}$

$\Rightarrow [A]_{eq} + \xi = [A]$

$-k_f[H_2O] = -k_f^+(\xi + [H_2O]_{eq})$

$[H^+] = k_r(\xi - [H^+]_{eq})$

since $[B] + \xi = [B]_{eq}$

$B = H^+$

example : pH = 7 , $\tau = 37\mu s$ after T-jump to 298K

$[B] = [B]_{eq} - \xi$

$[H^+] = (\xi - [H^+]_{eq})$

$[OH^-] = -(\xi - [OH^-]_{eq})$

after (post-) T-jump :

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

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

since $[H_2O] = \xi + [H_2O]_{eq}$

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

$\ominus \cdot \ominus = \oplus$

$$[H_2O]_{eq} \cdot \frac{k_f^+}{k_r^+} = [H^+]_{eq}[OH^-]_{eq} \quad \text{from } K_c$$

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

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

$$= -k_f^+\xi - k_r^+[H^+]_{eq}[OH^-]_{eq} \checkmark - k_r\xi([H^+]_{eq} + [OH^-]_{eq})$$

$$+ k_r^+[H^+]_{eq}[OH^-]_{eq} \checkmark + k_r^+\xi^2$$

$$k_r^+(\xi - [H^+]_{eq})(\xi - [OH^-]_{eq}) = k_r^+[H^+]_{eq}[OH^-]_{eq} + k_r^+\xi^2 - k_r^+\xi[OH^-]_{eq} - k_r^+\xi[H^+]_{eq}$$

$$\frac{d\xi}{dt} = -k_f^+\xi - k_r^+\xi\left([H^+]_{eq} + [OH^-]_{eq}\right) + \underset{\substack{\downarrow \\ \text{terms of order (with) } \xi^2}}{O(\xi^2)}$$

here: $O(\xi^2) = k_r^+\xi^2$

ξ is small <u>if</u> there is only a small perturbation of equilibrium by the T-jump

<u>then</u> the $O(\xi^2)$ term can be neglected

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

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

$\xi = f(t)$ identical to before, only new τ for k_f^+ and k_r^+: τ and K_c after jump ~~mst~~ must be measured

$$\tau = 37\,\mu s = 37\cdot 10^{-6}\,s$$

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

in equilibrium: $pH = 7 \Rightarrow [H^+]_{eq} = [OH^-]_{eq} = \overset{1.0}{\cancel{1}}\cdot 10^{-7}\,M$

$$[H_2O]_{eq} = 55.5\,M \text{ at } 298\,K$$

$$\frac{k_f^+}{k_r^+} = K_c = \frac{[H^+]_{eq}[OH^-]_{eq}}{[H_2O]_{eq}} = \frac{(1.0\cdot 10^{-7}\,M)^2}{55.5\,M} = 1.8\cdot 10^{-16}\,M$$

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

$$\frac{1}{3.7\cdot 10^{-5}\,s} = \left[\underset{K_c}{1.8\cdot 10^{-16}\,M} + \underset{[H^+]_{eq} + [OH^-]_{eq}}{2.0\cdot 10^{-7}\,M}\right] k_r^+$$

(23) - 6

$$k_r^+ = \frac{1}{3.7\cdot10^{-5}\,s \cdot 2.0\cdot10^{-7}\,M}$$

$1.8\cdot10^{-16}\,M \ll 2.0\cdot10^{-7}\,M$ is neglected

$$\rightarrow k_r^+ = 1.4\cdot10^{11}\,\frac{1}{M\,s}$$

$$k_f^+ = K_c k_r^+ = 1.4\cdot10^{11}\,\frac{1}{M\,s}\cdot1.8\cdot10^{-16}\,M$$

$$= 2.5\cdot10^{-5}\,s^{-1}$$

$k_f^+ \ll k_r^+ \Rightarrow$ small extent of autoionization in water

k_f^+, k_r^+ are $f(T)$

$\Rightarrow K_c$ is also $f(T)$

-Potential Energy Surfaces
- Activated Complex Theory

The energetics in a reaction are important to determine the rates!

reaction kinetics are related to energetics

→ Potential Energy Surfaces

Example: bimolecular reactions:

$$AB + C \rightarrow A + BC$$

AB, BC are stable, assume that ABC and AC are not formed (not very stable) in the reaction

Interaction of 3 atoms → potential energy E_p

$$E_p = f(R_{AB}, R_{BC}, \Theta = \measuredangle ABC)$$

<u>Transperancy</u> coordinates for $AB + C \rightarrow A + BC$

plotting E_p → four-dimensional plot, 3 coordinates <u>and</u> E_p

Reduction of dimensions: keeping Θ fixed at 180°

(A, B, C in linear arrangement)

above the R_{AB}, R_{BC} plane E_p is plotted: the larger is E_p the higher is the point above the plane

<u>Transp.</u> the minima in a) and b) correspond to the stable diatomics AB and BC

<u>easier</u> is a 2D contour plot (c)

view straight down on the 3D surface

lines are drawn between points of equal E_p

Notice the substantial difference between the
consistent with the modest amount of autoionize
ward and reverse rate constants are temperature
stant also demonstrates temperature dependence

35.13 Potential Energ

In the discussion of the Arrhenius equation, the
fied as an important factor determining the rate
reaction kinetics and energetics is central to the
To illustrate this concept, consider the following

$$AB + C \rightarrow A$$

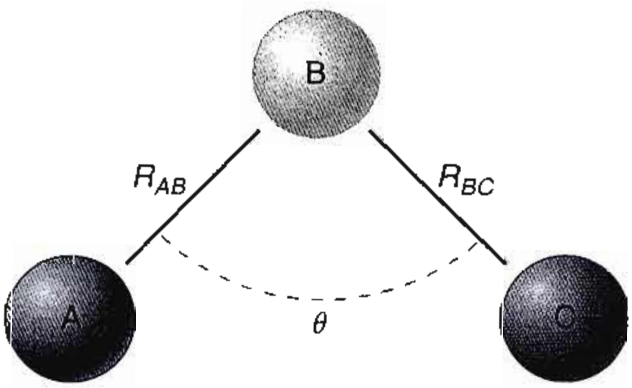


FIGURE 35.18
Definition of geometric coordinates for the AB + C → A + BC reaction.

The diatomic species AB and BC are stable,
species ABC and the diatomic species AC are nc
tion. This reaction can be viewed as the interac
energy of this collection of atoms can be defined
space. The geometric relationship between th
respect to the distance between two of the thre
formed between these two distances, as illustrate

The potential energy of the system can be e
nates. The variation of the potential energy with
then be presented as a graph or surface referr
Formally, for our example reaction this surface
geometric coordinates and energy). The dimensi
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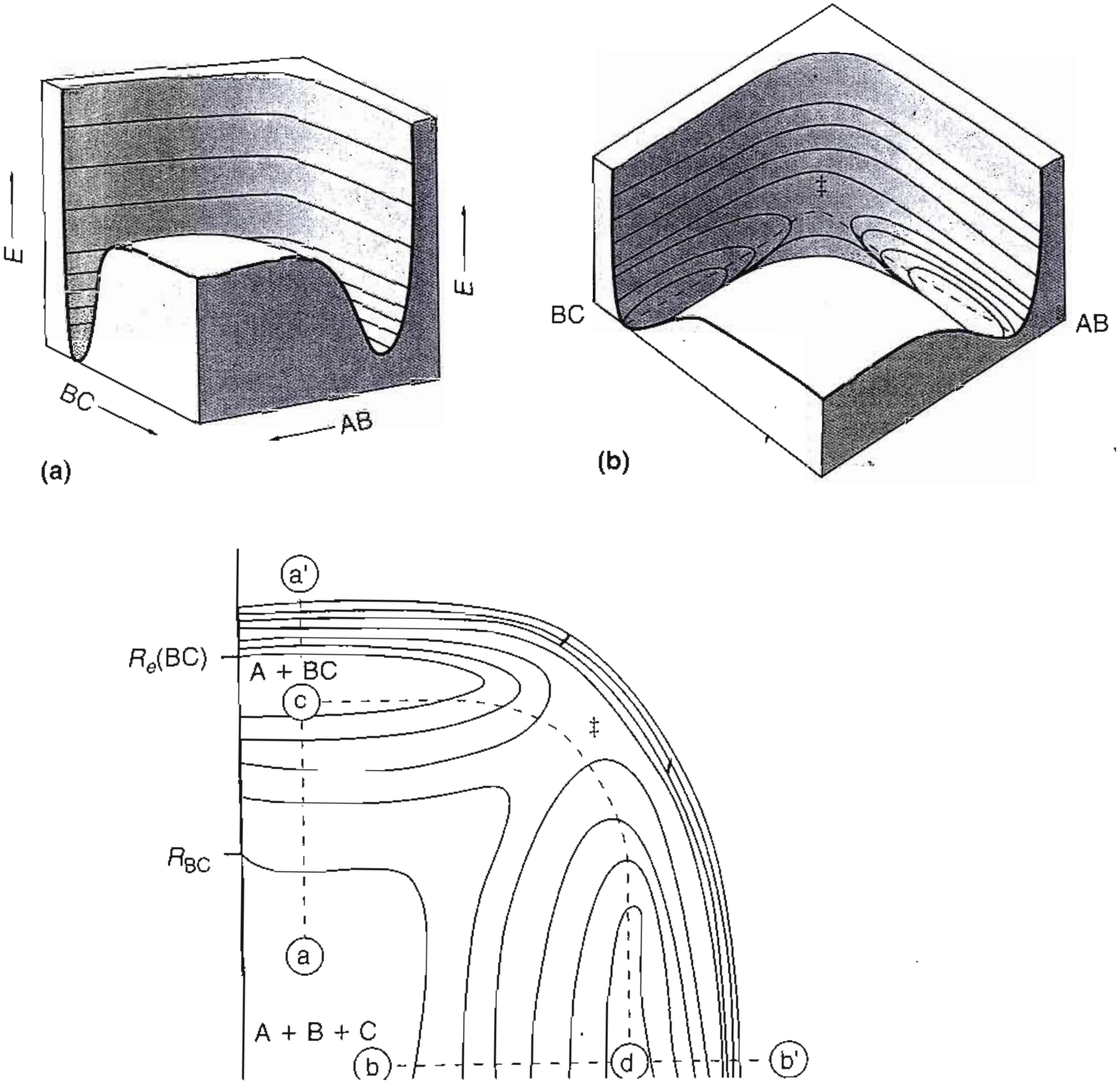
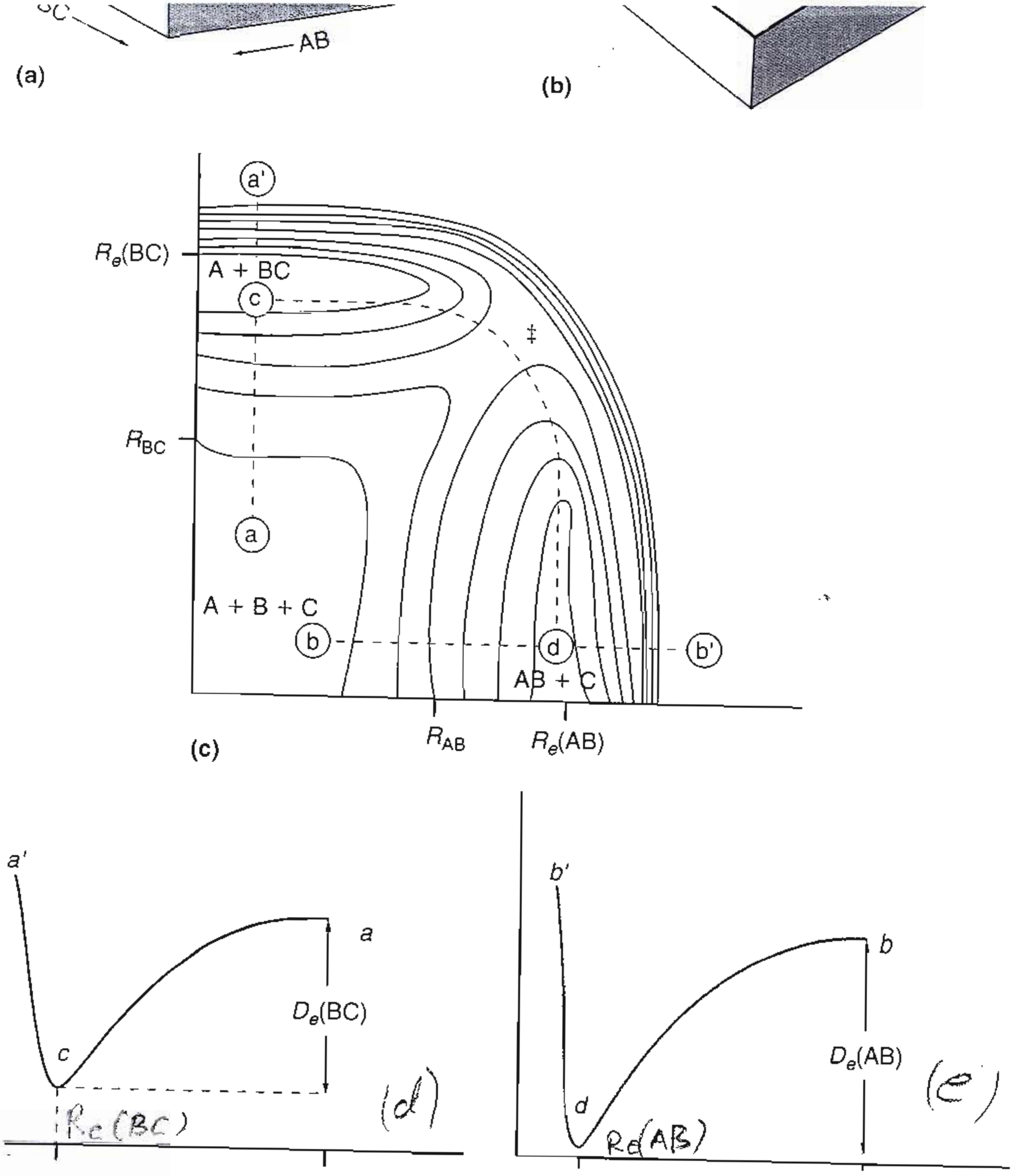


FIGURE 35.19
Illustration of a potential energy surface for the AB + C reaction at a colinear geometry (θ = 180° in Figure 35.18). **(a, b)** Three-dimensional views of the surface. **(c)** Contour plot of the surface with contours of equipotential energy. The curved dashed line represents one possible 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 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.]

lower left corner

Plateau where both R_{AB} and R_{BC} are large.

Here the atoms are separated or dissociated

$\Rightarrow A + B + C$

dashed lines: path a-a' : R_{AB} = const.

R_{BC} decreases

formation of diatomic BC at

$R_e(BC)$

$K_e(BC)$ = equilibrium value of R_{BC} in molecule BC

In (d) cross-section of the surface along a-a'

= potential energy diagram

→ dissociation energy of the diatomic BC

= depth D_e of potential

D_e = dissociation energy of BC

Minimum at $R_e(BC)$

(e) cross-section along b-b' : R(BC) = const

R(AB) decreases along b-b' :

$A + B + C \rightarrow AB + C$

E_p minimum $R_e(AB)$: equilibrium bond length of AB

note R_{BC} increases from up to down

and R_{AB} increases from right to left

the path way from AB + C to A + BC with lowest E_p

is the dashed line (curved) c-d

curved dashed line c-d
= reaction pathway (lowest energy path)

the maximum of E_p along this path is called the transition state shown by the $\ddagger$ symbol

<u>Transp.</u> E_p vs reaction coordinate q (c-d path)

transition state = maximum of E_p along the c-d pathway (reaction pathway)

⇒ TS: <u>no</u> stable intermediate but the unstable activated complex

kinetics and the yields of products depend on the energy of reactants and on the orientation of the reactants relative to eachother

<u>experimental check</u>: crossed molecular beams
reactants with well-defined energies in 1 beam, which interacts with another beam of reactants in well-defined geometrics
the products formed are then analyzed in terms of their energetics and distribution of products in space and beam geometry

= complicated and large analysis = lot of work
→ construction of a potential energy surface

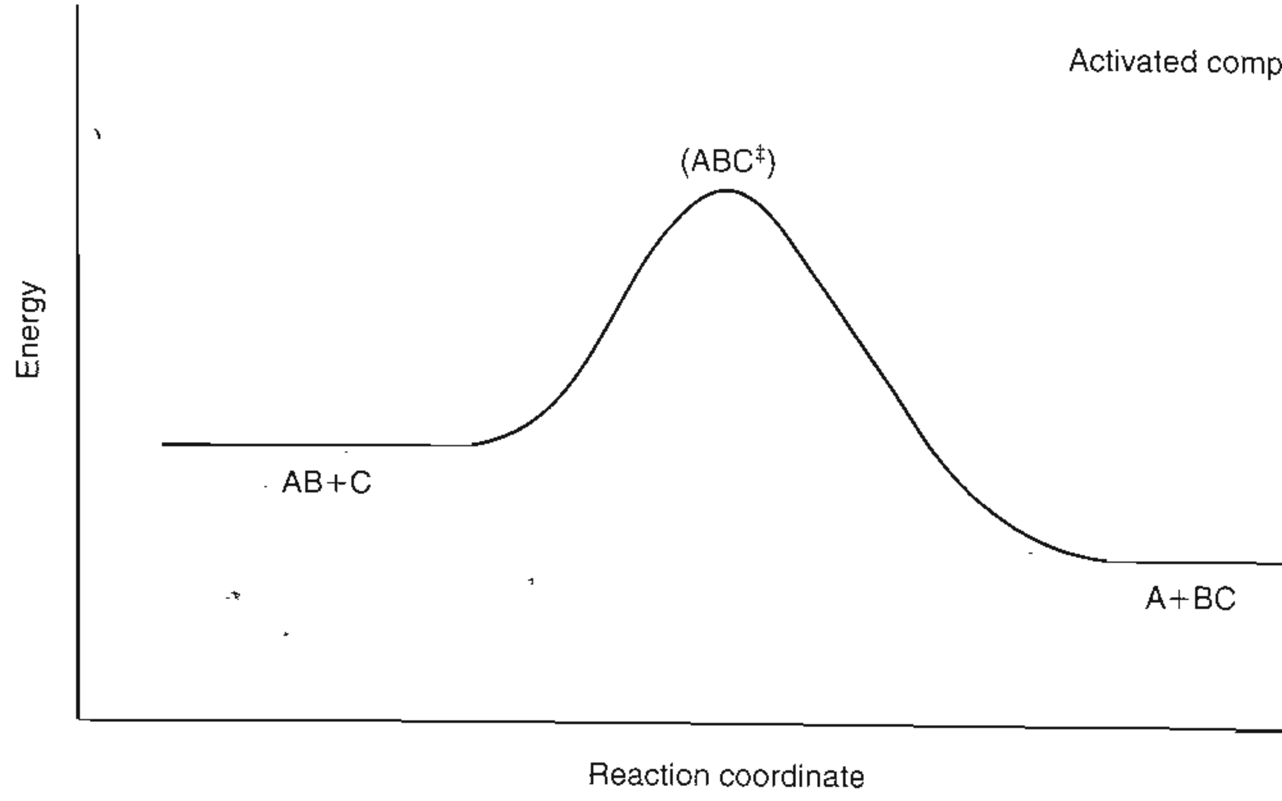


FIGURE 35.20
Reaction coordinate diagram involving an activated complex and a reactive intermediate. The graph corresponds to the reaction-coordinate derived from the dashed line between points *c* and *d* on the contour plot of Figure 35.19c. The maximum in energy along this coordinate corresponds to 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
developed principally by Henry Eyring in the 1930s. This theory, known as **acti**
complex theory or **transition state theory,** provides a theoretical description of
tion rates. To illustrate the conceptual ideas behind activated complex theory, co
the following bimolecular reaction:

Activated Complex Theory

Henry Eigen in the 1930-s

activated complex or transition state (TS) theory

bi molecular reactions : $A + B \xrightarrow{k} P$

Transp. E vs reaction coordinate q

$$A + B \rightarrow AB^{\neq}\ (TS) \xrightarrow{decay} P$$

TS is not stable; lifetime of TS = few vibrations $\cdot 10^{-14}$ s

1930, only theory, no experiments available in the fs time scale → in that time no experimental evidence for existence and nature of TS available

But now such transition complexes can be investigated

Assumptions

1. (most important): equilibrium between reactants and the TS
2. q that describes the decay of the TS can be seen as 1 degree of freedom of the TS
   e.g. if the breaking of a bond is involved in the decay, then the degree of freedom is the stretching vibration of this bond.

Kinetic mechanism:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB^{\neq} \qquad AB^{\neq} \xrightarrow{k_2} P$$

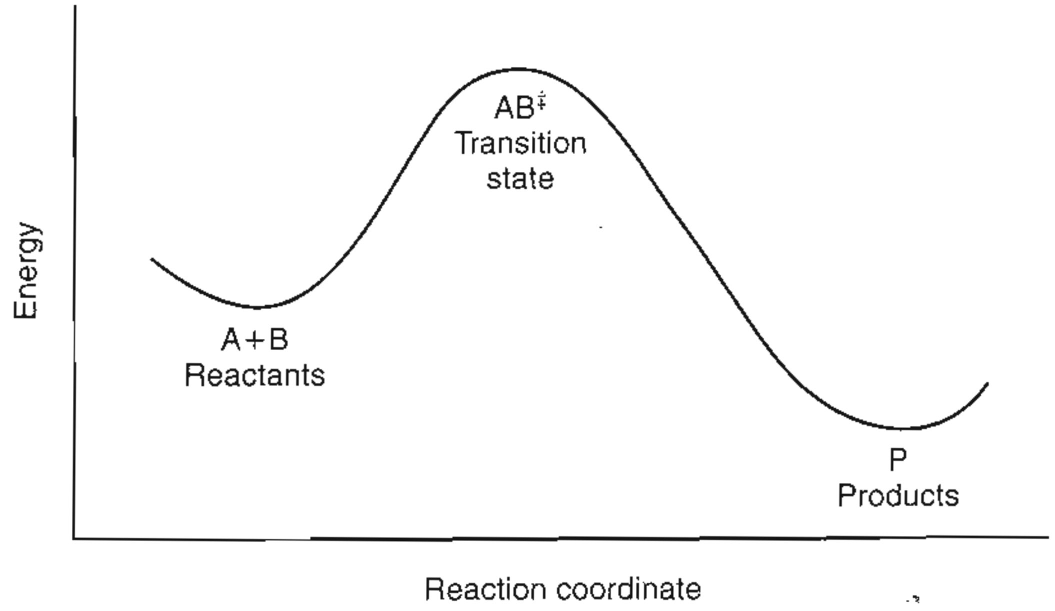


FIGURE 35.21
Illustration of transition state theory. Similar to reaction coordinates depicted previously, the reactants (A and B) and products (P) are separated by an energy barrier. The transition state is an activated reactant complex envisioned to exist at the free-energy maximum along the reaction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

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

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

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 $K_c^\ddagger$:

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

k_1, k_{-1} : equilibrium between reactants and TS

k_2 : decay of TS into products P

equilibrium : $\left.\frac{d(A)}{dt}\right|_{eq} = 0$

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

$$\Rightarrow \quad [AB^{\ddagger}] = \frac{k_1}{k_{-1}} [A][B] = \frac{K_c^{\ddagger}}{c_0} [A][B]$$

c^0 = standard ~~stante~~ state concentration, = 1 M

$K^{\ddagger}$ equilibrium constant for the TS

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

reaction rate R = rate of product formation :

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

$$\rightarrow \quad R = \frac{d[P]}{dt} = \frac{k_2 K_c^{\ddagger}}{c^0} [A][B]$$

k_2 rate of TS decay

P formation can require the breaking of a weak bond in TS

TS not stable → dissociation along the corresponding bond stretching vibration

→ k_2 must be related to the frequency ν of that bond stretching vibration

$k_2 = \nu$ if always when TS is formed, it dissociates with P formation

However because of equilibrium with reactants, TS can can also react back to the reactants

⇒ only a fraction of TS formed lead to P formation

⇒ ~~bro~~ a transmission coefficient κ is needed:

$$k_2 = \kappa\nu$$

$$R = \frac{\kappa\nu K_c^{\ddagger}}{c^{\circ}}(A)(B)$$

$$K_c^{\ddagger} = \underset{\uparrow}{q_{rc}}\,\overline{K_c^{\ddagger}} = \frac{k_BT}{h\nu}\bar{K}_c^{\ddagger}$$

reaction coordinate

q_{rc} so-called partition function for the decay vibration (sum over all states relative to $kT)^{-1}$

here only 1 stretch → $q_{rc} = \frac{k_BT}{h\nu} = \cancel{\sum e^{-\varepsilon_i/k_BT}}\ \frac{1}{1-e^{-hc\tilde{\nu}/k_BT}}$

$\overline{K_c^{\ddagger}}$ equilibrium constant without the factor q_{rc}

k_B: Boltzmann's constant

weak bond: $h\nu \ll kT$

$$\rightarrow k = \kappa\frac{k_BT}{hc^{\circ}}\overline{K_c^{\ddagger}}$$

ν cancels because $R = \frac{\kappa\nu \overline{K_c^{\ddagger}}}{c^{\circ}}(A)(B)$

<u>and</u> $\overline{K_C^{\ddagger}} = \frac{k_BT}{h\nu}\bar{K}_c^{\ddagger}$

→ determination of $\bar{K}_c^{\ddagger}$ is necessary

q_{rc} partition function, sum of states

$$q_{rc} = \sum_{n=0}^{\infty} e^{-\frac{h\nu(n+\frac{1}{2})}{k_B T}}$$

E_n relative to E_0: $E_n' = h\nu(n+\frac{1}{2}) - \frac{h\nu}{2}$
$= h\nu n$

$$q_{rc} = \sum_{n=0}^{\infty} e^{-\frac{h\nu n}{k_B T}}$$

$$= \frac{1}{1 - e^{-\frac{h\nu}{k_B T}}}$$

weak bond: $h\nu \ll k_B T$

& $e^{-x} \approx 1 - x$ when x small

→ high T approx:

$$q_{rc} \approx \frac{1}{1 - 1 + \frac{h\nu}{k_B T}} = \frac{k_B T}{h\nu}$$

㉕ -7

Obj. - to finish activated complex theory
to relate Arrhenius law to theory (sorry you
- Diffusion controlled reactions   not mentioned)

activated complex theory: connection of kinetic results to thermodynamic description of chemical reactions!

equilibrium constant $K_c^{\ddagger}$ is related to the corresponding change in Gibbs energy:

$$\Delta G^{\ddagger} = -RT \ln K_c^{\ddagger} \quad \text{for } A+B \rightleftharpoons AB^{\ddagger}$$

$$\Rightarrow k = \frac{k_B T}{h c^\circ} e^{-\Delta G^{\ddagger}/RT} \quad (K=1 \text{ assumed})$$

$c^\circ = 1M$

further from thermodynamics:

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

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

T-dependence different from Arrhenius equation

there: A T independent

here: pre-exponential factor ~ T

both describe $k = f(T)$

$\Rightarrow$ parameters here ($\Delta H^{\ddagger}, \Delta S^{\ddagger}$) should be connected to parameters there (A, E_a)

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

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

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

$$k = \frac{k_B T}{hc^\circ}\,\bar{K}_c^\ddagger \quad (\kappa = 1)$$

$$E_a = RT^2 \frac{d}{dT} \ln\left(\frac{k_B T}{hc^\circ}\,\bar{K}^\ddagger\right)$$

$$= RT^2 \left[\frac{d}{dT}\left(\ln \frac{k_B T}{hc^\circ}\right) + \frac{d}{dT} \ln\left(\bar{K}_c^\ddagger\right)\right]$$

$$= RT^2 \left[\frac{hc^\circ}{k_B T}\left(\frac{k_B}{hc^\circ}\right) + \frac{d}{dT} \ln \bar{K}_c^\ddagger\right]$$

$\frac{d}{dx} \ln x = \frac{1}{x}$, $\frac{1}{x}$ here $= \frac{hc^\circ}{k_B T}$

$\frac{d\,\frac{k_B T}{hc^\circ}}{dT} = \frac{k_B}{hc^\circ}$ $\qquad \frac{hc^\circ}{k_B T}\,\frac{k_B}{hc^\circ} = \frac{1}{T}$

$$\Rightarrow E_a = RT^2 \cdot \frac{1}{T} + RT^2 \frac{d}{dT} \ln \bar{K}_c^\ddagger$$

$$= RT + RT^2 \frac{d \ln \bar{K}_c^\ddagger}{dT}$$

thermodynamics: $\frac{d}{dT} \ln K_c = \frac{\Delta U}{RT^2}$ $(\cdot RT^2)$

$\Rightarrow$ $E_a = RT + \Delta U^\ddagger$ since $H = U + PV$

$\Delta U^\ddagger = \Delta H^\ddagger - \Delta(PV)^\ddagger$

$\Delta(PV)^\ddagger = PV(AB^\ddagger) - (PV)(A+B)$ (reactants)

reactions in solutions (no gases involved)

liquids like H_2O rather incompressible

→ no change in volume without gases involved

$\Rightarrow$ $\Delta U^\ddagger = \Delta H^\ddagger$ for reactions in solutions
(no gases)

$E_a = \Delta H^\ddagger + RT$ for solution reactions
(without gases)

→ (by comparison) Arrhenius pre-ex~~ponti~~onential factor:

$$A = e\,\frac{k_B T}{h c^\circ}\, e^{\Delta S^{\ddagger}/R}$$ for bimolecular reactions in solution (no gases)

unimolecular reactions in solution: $E_a = \Delta H^{\ddagger} + RT$

but <u>without</u> c° which came from:

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

but now we have (unimolecular): $A \rightleftharpoons A\cancel{B}^{\ddagger}$

$$\rightarrow K_c^{\ddagger} = \frac{[A\cancel{B}^{\ddagger}]/c^\circ}{[A]/c^\circ} = \frac{[A\cancel{B}^{\ddagger}]}{[A]}$$

$$\Rightarrow A = e\,\frac{k_B T}{h}\, e^{\Delta S^{\ddagger}/R}$$ unimolecular solution-reactions without gases

remember Eyring equation (bimolecular)

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

$E_a = \Delta H^{\ddagger} + RT$ bimolecular in solutions

$\Delta H^{\ddagger} = E_a - RT$

$$k = \frac{k_B T}{h c^\circ}\, e^{\Delta S^{\ddagger}/R}\, e^{-\frac{E_a - RT}{RT}} = e\,\frac{k_B T}{h c^\circ}\, e^{\Delta S^{\ddagger}/R}\, e^{-E_a/RT}$$

$\Rightarrow$ A as above!

<u>gas-phase reactions</u>

$$\Delta (PV)^{\ddagger} = \Delta (n_g^{\ddagger} RT) = \Delta n_g^{\ddagger} RT$$

$\Delta n_g^{\ddagger}$ = no of <u>gas</u> moles in transition state (TS)
- no. of <u>gas</u> moles in reactants

unimolecular gas-phase reactions: $\Delta n_g^{\ddagger} = 0$ ㉕-4

$A(g) \rightarrow A^{\ddagger}(g)$

bimolecular gas-phase reactions: $\Delta n_g^{\ddagger} = -1$

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

→ unimolecular gas phase reactions

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

bimolecular gas phase reactions

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

ooth, E_a and A should depend in principle on T

if $\Delta H^{\ddagger} \gg RT$: only small T-dependence of E_a

if $H(AB^{\ddagger}) < H(\text{reactants}) \Rightarrow \Delta H^{\ddagger}$ negative
and the reaction can get faster $e^{-\Delta H^{\ddagger}/RT}$
on T-decrease

if $\Delta S^{\ddagger} > 0$ and E_a very small
$\Rightarrow$ reaction is entropy-controlled

important in the higher atmosphere is the thermal decomposition of nitrosyl halides like NOCl e.g.

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

for this reaction $A = 1.00 \cdot 10^{13}\,\frac{1}{Ms}$ (bimolecular)

$E_a = 104.0\,\frac{kJ}{mol}$

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

bimolecular gas-phase reaction $\Rightarrow$

$\Delta H^{\ddagger} = E_a - 2RT = 104.0\,\frac{kJ}{mol} - 2\cdot10^{-3}\cdot 8.314\,\frac{kJ}{K\,mol}\cdot 300\,K$

$= 104.0\,\frac{kJ}{mol} - 4.99\,\frac{kJ}{mol} = 99.0\,\frac{kJ}{mol}$

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

$$= 8.314 \frac{J}{K\,mol} \cdot \ln \left[\frac{1 \cdot 10^{13} \frac{1}{M\,s} \cdot 6.626 \cdot 10^{-34} Js \cdot \overset{c^{\circ}}{1M}}{e^2 \cdot (1.38 \cdot 10^{-23}\ J/K) \cdot 300K} \right]$$

$$= -12.7 \frac{J}{K\,mol}$$

$\Delta S^{\neq} < 0$ → activated complex has smaller entropy (is more ordered) than the reactants

consistent with: 2 NOCl form a complex (more ordered than 2 free gas molecules) which decays to NO and Cl_2

Diffusion controlled reactions

Transp. A+B in gas-phase and in solution

The average translational energy of A and B is the same in gas-phase and solution: $\frac{3}{2}RT$ ($\frac{1}{2}RT$ for each degree of freedom: x, y, z)

but due to the solvent molecules, many solvent-solute collisions happen before A and B can collide in solution: reactants must diffuse before a reactive collision

in gas-phase: direct approach of A to B

⇒ the reaction rate in solution can be determined by the diffusion rate constant k_d

$A + B \xrightarrow{k_d} AB$ (close) diffusion

$(AB) \xrightarrow{k_r} A + B$ reverse process

$(AB) \xrightarrow{k_p} P$ reaction

$$= 104.0\ \mathrm{kJ\ mol^{-1}} - (4.99 \times 10$$

$$\Delta S^{\ddagger} = R \ln\left(\frac{Ahc^{\circ}}{e^{2}kT}\right)$$

$$= (8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}) \ln\left(\frac{(1.00 \times 10^{13}}{e^{2}(1.3}\right.$$

$$= -12.7\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

One of the utilities of this calculation is that the si information on the structure of the activated comp reactants. The negative value in this example illus lower entropy (or is more ordered) than the reacta a mechanism in which the two NOCl reactants fo to produce NO and Cl.

35.15 Diffusion Contr

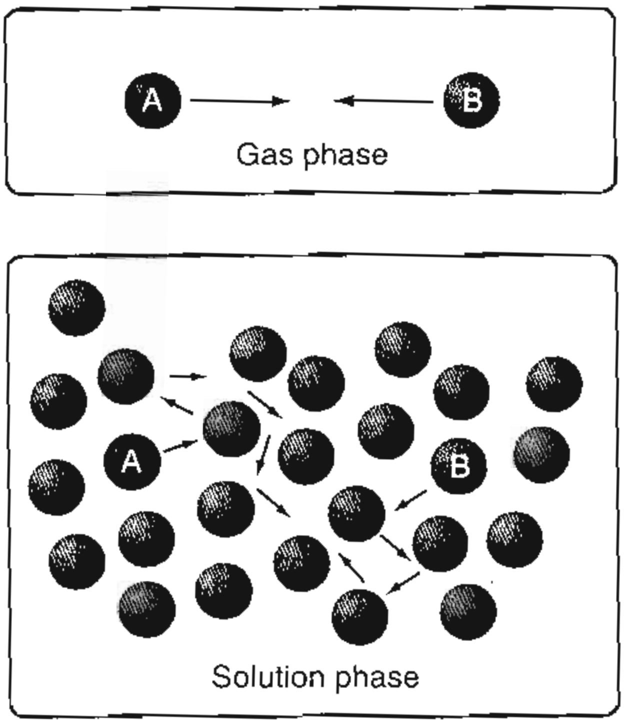


FIGURE 35.22
Top: Reactants A and B approach each other and collide in the gas phase. Bottom: In solution, the reactants undergo a series of collisions with the solvent. In this case, the approach of the reactants is dependent on the rate of reactant diffusion in solution.

For bimolecular chemical reactions in solution, result in reaction dynamics that differ significantl ple, the activation energy and relative orientatio being key factors in defining the rate constant Imagine a reaction occurring in solution as illus kinetic energy of the reactants is $3/2\ RT$, the ave in the gas phase. However, in solution the prese number of solvent–solute collisions before the r terrupted approach of the reactants characteristi the reactants undergoing diffusion in solution un the rate of diffusion can determine the rate of re

The role of diffusion in solution-phase che ing kinetic scheme:

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_d}$$

$$\mathrm{AB} \xrightarrow{k_r}$$

$$\mathrm{AB} \xrightarrow{k_p}$$

In this scheme, reactants A and B diffuse wit and form the intermediate complex AB. Once rate: $R = k_p[AB]$

AB is an intermediate $\Rightarrow$ <u>SSA</u> for AB

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

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

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

if $k_p \gg k_r$ faster product formation than reactant re-formation

k_r neglected, k_p cancels

$$\rightarrow R = k_d[A][B]$$

diffusion controlled limit

= diffusion of A and B limit the rate of product formation

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

r_A, r_B radius of A and B

D_{AB} diffusion coefficient for the reactants:

$D_{AB} = D_A + D_B$ Fick's law: $J = \frac{dn}{dt} = -DA\frac{\partial c}{\partial x}$

flux along diffusion dir

spherical particle in solution: Stokes-Einstein equ.:

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

η: solvent viscosity, r radius of the diffusing particle

$\Rightarrow$ reaction rate constant $\sim \frac{1}{\eta}$