should be Quiz, Chapter 36 (now: Lec. 29)

Mechanisms and Rate Laws

correct reaction mechanism

= collection of elementary (one-step) reactions leading from reactants R to products P:

$$R \rightarrow P$$

Rate laws and orders of reactions follow from the mechanism, not from the overall stoichiometry

a mechanism is valid (maybe true) if the predicted rate law agrees with experiment

Valid ≠ sure correct

Valid = useful, because not in contradiction to experiment

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

simplest possible mechanism:

single step, elementary, bimolecular reaction:

collision of 2 N_2O_5 molecules → reaction

single, elementary step = simple reaction

but experiment → rate law from single step assumption:
2. order in N_2O_5

but experiment: 1. order in N_2O_5

possible explanation: pre-equilibrium:

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

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

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

this is called a complex reaction,

because there are 2 or more elementary steps in the mechanism

1. step: equilibrium between N_2O_5, NO_2, and NO_3

2. step: bimolecular reaction between NO_2 and NO_3 which ~~fot~~ forms NO_2, O_2, and NO

dissociation of NO_3 after bimolecular collision $NO_2 + NO_3$

3. step: bimolecular reaction between NO and NO_3 forming $2NO_2$ molecules

In the mechanism there are 2 molecules, NO and NO_3 which are not in the overall equation

→ NO and NO_3 are reaction intermediates

they are stable molecules, no transition states

intermediates that form in 1 mechanism step must be consumed in a following one

⇒ the pre-equilibrium must occur twice

2 times to balance the $2NO_3$ which are consumed in steps 2 and 3

⇒ step 1 must be multiplied by 2

= step 1 must occur 2× before step 2 and 3 can happen

the number of times a step must occur in a mechanism is called stoichiometric number of that step.

here step 1 has stoichiometric number 2
steps 2 and 3 have each the stoichiometric number 1

correct stoichiometric number ⇒ adding up the elementary steps yields the overall reaction equation of the process

a valid reaction mechanism must be consistent (must predict it) with the experimental rate law

this mechanism → rate of reaction for equilibrium

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

↑ consumption of N_2O_5 ⊖ at the derivative

↓ formation of N_2O_5 must have ⊖ because of the ⊖ at the derivative

stoichiometric number not included (only as $\frac{1}{2}$)

≙ loss of N_2O_5 by unimolecular decay
and formation of N_2O_5 by bimolecular back-reaction of $NO_2 + NO_3$

NO_2 and NO_3 are the reaction intermediates

⇒ rate equation for them + SSA yields:

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

formation of NO consumption of NO

$$\frac{d[NO_3]}{dt} = 0 = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO_2][NO_3] - k_3[NO][NO_3]$$

$$\text{from } \frac{d[NO]}{dt} = 0 \Rightarrow [NO] = \frac{k_2[NO_2][NO_3]}{k_3[NO_3]} = \frac{k_2[NO_2]}{k_3}$$

intermediates must be eliminated in a valid rate-law !

$$-\frac{d[N_2O_5]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO_3]$$

because of stoichiometric number 2

(no squares of concentrations)

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

from $\frac{d[NO_3]}{dt} = 0$:

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO_2][NO_3] - k_3[NO][NO_3]$$

$$[NO] = \frac{k_2}{k_3}[NO_2]$$

$$0 = k_1[N_2O_5] - (k_{-1} + k_2)[NO_2][NO_3] - k_3\frac{k_2}{k_3}[NO_2][NO_3]$$

$$0 = k_1[N_2O_5] - (k_{-1} + 2k_2)[NO_2][NO_3]$$

$$[NO_2][NO_3] = \frac{k_1}{k_{-1}+2k_2}[N_2O_5]$$

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

$$= \frac{1}{2}\left(k_1 - \frac{k_1 k_{-1}}{k_{-1}+2k_2}\right)[N_2O_5] = k_{eff}[N_2O_5]$$

$$k_{eff} = \frac{1}{2}\frac{k_1(k_{-1}+2k_2) - k_1k_{-1}}{k_{-1}+2k_2}$$

$$= \frac{1}{2}\frac{k_1k_{-1} + 2k_1k_2 - k_1k_{-1}}{k_{-1}+2k_2}$$

$$= \frac{k_1k_2}{k_{-1}+2k_2}$$

consistent with experimental 1. order rate in N_2O_5

<u>remember</u> this means it is a valid mechanism, but it is <u>no</u> proof that the mechanism is absolutely correct

propene (P) + HCl ⟶ propane chloride (PCl)

<u>experimentally found:</u>

PCl formation is 3. order in HCl, 1. order in propene, thus 4. order overall

explanation?

it is known, that HCl forms a dimer:

$$2\,HCl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (HCl)_2 \quad K_1 \text{ known from HCl solutions!}$$

fast

and that propene and HCl form a complex (spectroscopically):

$$HCl + P \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HCl \cdot P \quad K_2$$

fast

<u>only</u> the dimer can react with the complex to form the product:

$$(HCl)_2 + HCl \cdot P \xrightarrow{k_3} PCl + 2\,HCl \quad \text{slow}$$

$\Rightarrow k_1, k_{-1}, k_2, k_{-2} \gg k_3$

$$R = \frac{d[PCl]}{dt} = k_3[(HCl)_2][(HCl \cdot P)]$$

$(HUU)_2$ and $HUU \cdot P$ are both intermediates and must be eliminitated in the final rate equation

overall equilibrium constant $K = K_1 \cdot K_2$

fast equilibria ⇒ in most of reaction time (as long as there are enough chemicals) the concentration will adjust such that $K = \text{const.}$

$$K_1 = \frac{[(HUU)_2]}{[HUU]^2} \qquad K_2 = \frac{[HUU \cdot P]}{[HUU] \cdot [P]}$$

$$K = \frac{[(HUU)_2][HUU \cdot P]}{[HUU]^3 [P]} = \text{const.}$$

$$\rightarrow [(HUU)_2] \cdot [HUU \cdot P] = K_1 K_2 [HUU]^3 [P]$$

$$\Rightarrow \frac{d[PUU]}{dt} = k_3 K_1 K_2 [HUU]^3 [P]$$

3. order in HUU, 1. order in P

as experimentally found.

With SSA for $(HUU)_2$ and $HUU \cdot P$ the same result is obtained

<u>but</u> in an additional step the small k_3 must be neglected against the large $k_{\pm 1}, k_{\pm 2}$ with fast equilibria simpler!

1 step saved!

Σ mechanism steps

= overall reaction equation

overall here: $2N_2O_5 \rightarrow 4NO_2 + O_2$

mech.

maybe wrong written

I wrote $2NO_2$

$2N_2O_5 \rightleftharpoons 2NO_2 + 2NO_3$ not $4NO_2$

$NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$ as is correct

$NO + NO_3 \rightarrow 2NO_2$

$2N_2O_5 \rightarrow 4NO_2 + O_2$

- Pre-Equilibrium Approximation:
  General, Example
- Lindemann Mechanism

The pre-equilibrium Approximation is useful, when fast equilibrium occurs between some molecules in a mechanism, before the final product formation occurs.

Thus in case of fast equilibria (so fast, that K = const. can be maintained - enough chemicals)

General: $A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} I$

$I \xrightarrow{k_p} P$

here the equilibrium links the reactants A & B with an intermediate I

and decay of I → product P

If the forward (k_f) and backward (k_r) reactions are faster than the product formation

then: 2 distinct step

1) equilibrium between reactants and intermediate is maintained (established) through all reaction time

2) I decays ~~fast~~ to form product P

= pre-equilibrium approximation

rate of product formation: $\frac{d[P]}{dt} = k_p[I]$

no final rate equation, because the intermediate must be eliminated (expressed in terms of reactants)

I is always in equilibrium with reactants

$$\Rightarrow K_c = \frac{k_f}{k_r} = \frac{[I]}{[A][B]} = \text{const.}$$

$$\Rightarrow [I] = K_c[A][B]$$

$\Rightarrow$ final rate equation for product formation:

$$\frac{d[P]}{dt} = k_p[I] = k_p K_c [A][B]$$
$$= k_{eff}[A][B]$$

$$k_{eff} = k_p K_c$$

the rate law is 2. order, 1. order with respect to both reactants

further: $K_c = \frac{k_f}{k_r}$, $k_{eff} = k_p \frac{k_f}{k_r}$

Example

Reaction of $NO + O_2$ which forms NO_2

overall: $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

possible mechanisms:

single elementary one-step reaction

= trimolecular reaction of $2NO$ with $1\ O_2$

experiment: 2. order in NO, 1. order in O_2

agrees with a trimolecular reaction

but further the T-dependence of the rate was determined

if mechanism correct: increasing T would increase the number of collisions, and thus increase the rate.

but found rate decrease when T increases

$\rightarrow$ trimolecular 1 step mechanism is incorrect!

later proposed:

$$2NO \underset{k_r}{\overset{k_f}{\rightleftharpoons}} N_2O_2$$

$$N_2O_2 + O_2 \xrightarrow{k_p} 2NO_2$$

in step 1 an equilibrium between NO and N_2O_2 is established faster than the rate of product formation

in step 2 a bimolecular reaction of N_2O_2 with O_2 happens to form $2NO_2$

stoichiometric number of each step: 1

<u>step 1</u> pre-equilibrium approximation:

$$K_c = \frac{k_f}{k_r} = \frac{[N_2O_2]}{[NO]^2}$$

$$[N_2O_2] = \frac{k_f}{k_r}[NO]^2 = K_c[NO]^2$$

<u>step 2</u>:

$$R = \frac{1}{2}\frac{d[NO_2]}{dt} = k_p[N_2O_2][O_2]$$

↑ factor 2 at NO_2

pre-equilibrium approx. used to eliminate $[N_2O_2]$ from the rate equation

$$R = k_p[N_2O_2][O_2] = k_p K_c [NO]^2 [O_2] = k_{eff}[NO]^2[O_2]$$

$$k_{eff} = k_p K_c$$

2. order in NO, 1. order in O_2 as in experiment

T-dependence: formation of N_2O_2 is exothermic

exothermic N_2O_2 formation ⇒ a T increase will shift the equilibrium towards NO (k_f decreases)

→ less N_2O_2 to react with O_2 → rate of NO_2 formation

will decrease when T increases

Lindemann mechanism for unimolecular reactions

unimolecular dissociation:

$$A \rightarrow \text{fragments}$$

A decomposes when one (1) or more vibrations get enough energy for decomposition

from where comes the energy?

possible: bimolecular collision with another A

Experiment at high [A] only 1. order, not 2. order as expected for a 1-step bimolecular mechanism

another mechanism was proposed by Frederick Lindemann. here: 2 steps

1. bimolecular collision for A to get energy:

$$2A \xrightarrow{k_1} A^* + A$$

A^*: activated reactant with enough energy to decompose

A: less energy than needed for decomposition

2. step: A^* can either be deactivated again by another collision or it can decompose

$$A^* + A \xrightarrow{k_{-1}} 2A$$

or

$$A^* \xrightarrow{k_2} P$$

the mechanism implies different time-scales between activation & deactivation or product formation

P only formed by A^* decomposition:

$$\rightarrow \frac{d[P]}{dt} = k_2[A^*]$$

$[A^*]$ must be replaced (intermediate):

$\rightarrow$ $\frac{d[A^*]}{dt}$ equation + SSA

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A][A^*] - k_2[A^*] = 0$$

(When) react: decay rate of intermediate A^* > A^* production rate, sothat $[A^*]$ would be small and constant

$$\rightarrow [A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2}$$

$$\Rightarrow \frac{d[P]}{dt} = \frac{k_1 k_2 [A]^2}{k_{-1}[A] + k_2}$$

large $[A]$ $\Rightarrow k_{-1}[A] > k_2 \Rightarrow \frac{d[P]}{dt} = \frac{k_1 k_2 [A]^2}{k_{-1}[A]} = \frac{k_1 k_2}{k_{-1}}[A]$

at high $[A]$ or partical presure P_A : $\left(P_A/RT = \frac{n_A}{V} = [A] \right)$

rate of product formation: 1. order in $[A]$

as in experiment: high P_A : A^* produced faster than product formation (A^* decomposition)

$\Rightarrow$ rate of decomposition (slow) is rate limiting (or determining) in P formation

low [A] or P_A $\quad k_2 > k_{-1}[A]$

$$\Rightarrow \frac{d[P]}{dt} = \frac{k_1 k_2 [A]^2}{k_2} = k_1 [A]^2$$

→ 2. order in [A]

more general (Lindemann) formulation:

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M$$

M is the partner in collisions with A and can be another A or also some added buffer gas

$$\rightarrow \frac{d[P]}{dt} = \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_2} = k_{uni}[A]$$

$$k_{uni} = \frac{k_1 k_2 [M]}{k_{-1}[M] + k_2}$$

high [M]: $k_{-1}[M] \gg k_2 \Rightarrow k_{uni} = \frac{k_1 k_2}{k_{-1}}$

decrease of [M] ⇒ k_{uni} decreases until $k_2 \gg k_{-1}[M]$

then $k_{uni} = k_1[M]$ rate of 1. order in [M]

Transp. $CH_3 - NC \rightarrow CH_3 - CN$ isomerisation of methyl isocyanide

experimental plot of k_{uni} vs P

shows: k_{uni} linear with P at low P

and k_{uni} = const. at high P

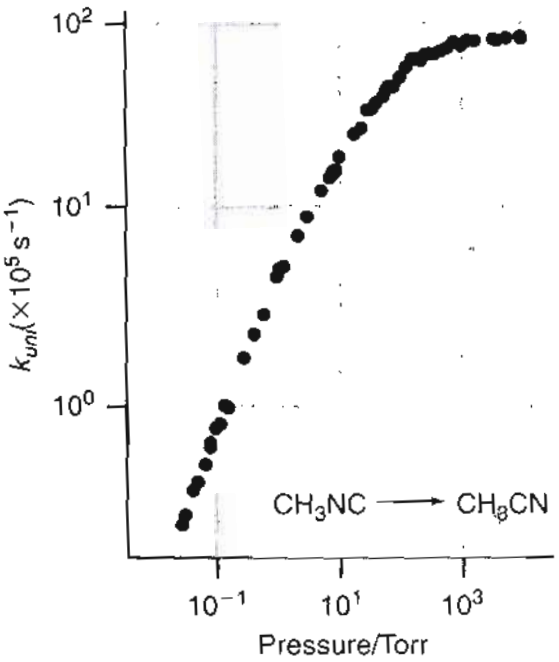
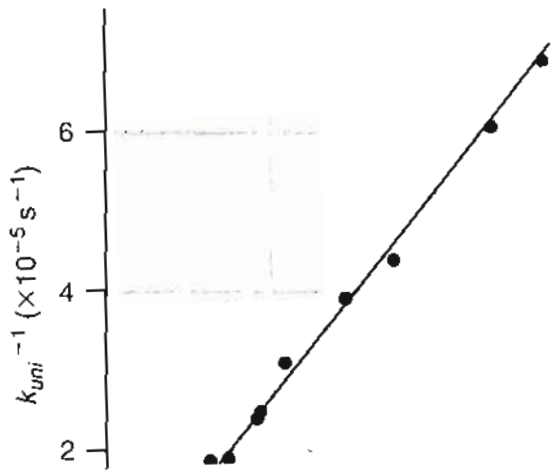


FIGURE 36.1
Pressure dependence of the observed rate constant for the unimolecular isomerization of methyl isocyanide.
[Data from Schneider and Rabinovitch, "Thermal Unimolecular Isomerization of Methyl Isocyanide - Fall-Off Behavior," *J. American Chemical Society* 84 (1962): 4225.]



Substituting Equation (36.27) into Equa
expression for [P]:

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

Equation (36.28) is the central result of
observed order dependence on [A] depen
k_2. At high reactant concentrations, $k_{-1}[$

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

Equation (36.29) demonstrates that at hig
that $P_A/RT = n_A/V = [A]$) the rate of
consistent with experiment. Mechanistica
be produced faster than decomposition oc
rate-limiting step in product formation.
and Equation (36.28) becomes

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

Equation (36.30) demonstrates that at low
becomes the rate-limiting step in the reactic
order in [A].

The Lindemann mechanism can be gen
lar reactions through the following generic

$$A + M \underset{k_-}{\overset{k_1}{\rightleftharpoons}}$$

$$A^* \longrightarrow$$

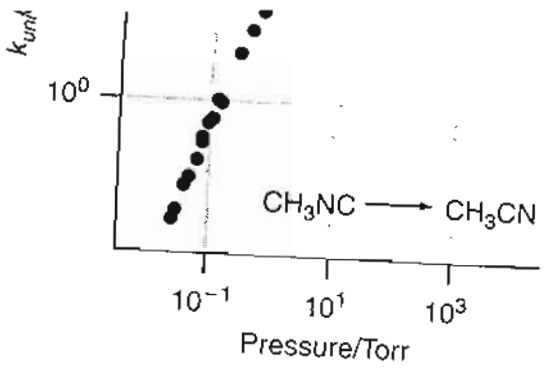
In this mechanism, M is a collisional partne
other species such as a nonreactive buffer ga
formation can be written as follows:

$$\frac{d[P]}{dt} = \frac{k_1 k_2[A]}{k_{-1}[M]}$$

In Equation (36.33), k_{uni} is the apparent rate

$$k_{uni} = \frac{k_1}{k_{-1}[}$$

In the limit of high M concentrations, $k_{-1}[M$
an apparent rate constant that is independe
decrease until $k_2 > k_{-1}[M]$, at which poi
demonstrates first-order dependence on M. F
rate constant f



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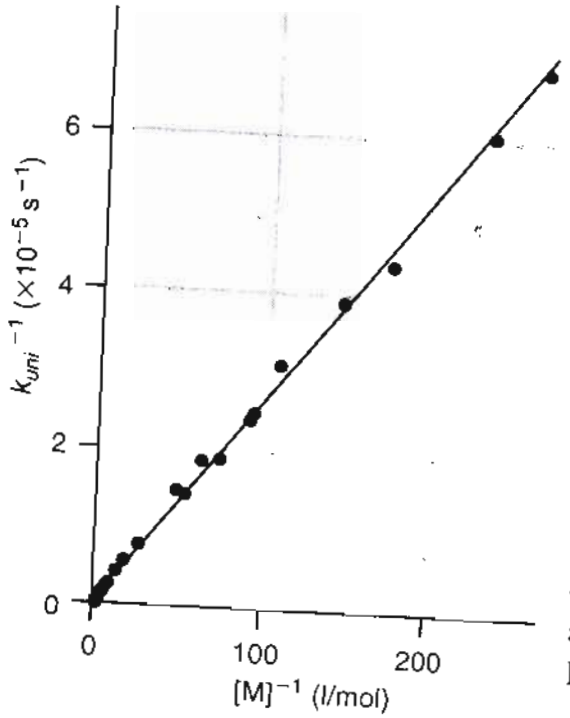


FIGURE 36.2
Plot of k_{uni}^{-1} versus $[M]^{-1}$ for the unimolecular isomerization of methyl isocyanide at 230.4°C. The solid line is the best fit to the data.

Equation (36.30) demonstrates that at becomes the rate-limiting step in the re order in [A].

The Lindemann mechanism can be lar reactions through the following gen

$$A + M$$

$$A$$

In this mechanism, M is a collisional pa other species such as a nonreactive buff formation can be written as follows:

$$\frac{d[P]}{dt} = \frac{k_1 k_2}{k_{-1}[$$

In Equation (36.33), k_{uni} is the apparent

$$k_{uni} =$$

In the limit of high M concentrations, k_{-} an apparent rate constant that is indep decrease until $k_2 > k_{-1}[M]$, at which demonstrates first-order dependence on M rate constant for the isomerization of me 230.4°C by Schneider and Rabinovitch. T ear relationship between k_{uni} and pressure corresponding limiting behavior of Equat addition, at high pressure k_{uni} reaches a co limiting behavior of Equation (36.34).

The Lindemann mechanism provides a for a unimolecular reaction will vary Equation (36.34), the relationship between

$$\frac{1}{k_{uni}} = \frac{k_{-1}}{k_1 k_2}$$

inversion of k_{uni}

$$\rightarrow \quad \frac{1}{k_{uni}} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1}\frac{1}{(M)}$$

from $k_{uni} = \dfrac{k_1 k_2 (M)}{k_{-1}(M) + k_2}$

$\rightarrow$ <u>Transp.</u> k_{uni}^{-1} vs $\dfrac{1}{(M)}$ linear plot

k_{uni}^{-1} vs $\frac{1}{(M)}$: straight line:

slope $= \frac{1}{k_1}$, intercept $\frac{k_{-1}}{k_1 k_2}$

<u>again</u> as example $CH_3-NC \rightarrow CH_3-CN$ isomerization

$\rightarrow$ (slope)$^{-1}$ $\rightarrow$ $k_1 = 4.16 \cdot 10^6 \frac{1}{Ms}$

k_1 + intercept: $\frac{k_{-1}}{k_2}$ = intercept $\cdot k_1$

$$\rightarrow \frac{k_{-1}}{k_2} = 1.76 \cdot 10^5 \frac{1}{M}$$

k_{-1} bimolecular $\Rightarrow$ $[k_{-1}] = \frac{1}{Ms}$

k_2 unimolecular $\Rightarrow$ $[k_2] = 1/s^{-1}$

$\rightarrow$ $\left[\frac{k_{-1}}{k_2}\right] = \frac{1/Ms}{1/s} = \frac{1}{M}$

next class is Quiz #3, chap. 35
- Catalysis, general remarks
- case of low catalyst concentration
- " " high " "
- Enzyme catalysis

A catalyst is a chemical that takes part in a reaction and increases its' rate, but its concentration is not changed in the reaction

→ A catalyst provides a new mechnism for the reaction

E_a along the new reaction path is lower than without the catalyst ⇒ k larger

R_0: uncatalyzed rate, R_c catalyzed rate:

$$R_c > R_0$$

now $R = R_0 + R_c$ Transp.

The catalyst must bind to a reactant or to an intermediate, and when the reaction is complete, the catalyst is set free again unchanged and can react again

the catalyst is not consumed ⇒ small amount is enough to speed up a reaction

SC: substrate (reactant) - catalyst complex

S: reactant, also called substrate, C = catalyst:

$$S + C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SC \qquad SC \xrightarrow{k_2} P + C$$

$$\frac{d[P]}{dt} = k_2[SC]$$ SC is intermediate

to remove [SC): SSA to obtain [SC]:

$$\frac{d[SC]}{dt} = k_1[S][C] - k_{-1}[SC] - k_2[SC] \overset{SSA}{=} 0$$

$$\Rightarrow [SC] = \frac{k_1[S][C]}{k_{-1} + k_2} = \frac{[S][C]}{K_m}$$ K_m: composite or Michaelis constant

l mechanism by which reactants are converted to
nechanism involving the catalyst results in a sec-
:tants and products. The activation energy along
wer in comparison to the uncatalyzed reaction;
ncrease. For example, consider Figure 36.3 in
ı of reactant A to product B with and without a
ıtalyst, the rate of product formation is given by
:, a second pathway is created, and the reaction
ıs the rate for the catalyzed reaction, or $r_0 + r_c$.
ın is found in the electrical circuits depicted
:trical circuit, a second, parallel pathway for
ır increased total current when compared to the
addition of the second, parallel pathway is
chanism involving the catalyst.
bine with one or more of the reactants or with
eaction. After the reaction has taken place, the
nc er reactant or intermediate in a subsequent
during the reaction, so a small amount of cata-
ns. The simplest mechanism describing a cat-

$$\text{C} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{SC} \qquad \textbf{(36.36)}$$

$$\xrightarrow{k_2} \text{P} + \text{C} \qquad \textbf{(36.37)}$$

rate, C is the catalyst, and P is the product. The
ıted by SC and is an intermediate species in this
sion for product formation is

$$\frac{]}{} = k_2[\text{SC}] \qquad \textbf{(36.38)}$$

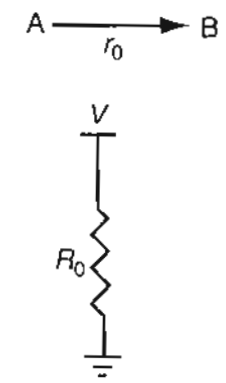
write the differential rate expression for this
ximation:

$$- k_{-1}[\text{SC}] - k_2[\text{SC}] = 0$$

$$= \frac{[\text{S}][\text{C}]}{K_m} \qquad \textbf{(36.39)}$$

s the **composite constant** and is defined as

$$= \frac{k_{-1} + k_2}{k_1} \qquad \textbf{(36.40)}$$



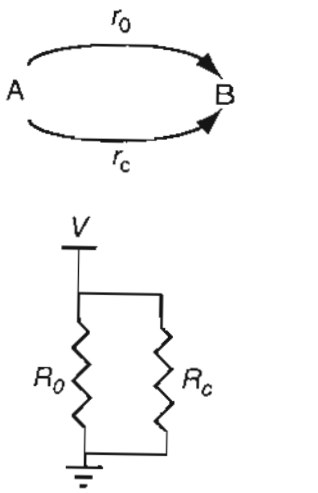


FIGURE 36.3
Illustration of catalysis. In the uncatalyzed reaction, the rate of reaction is given by r_0. In the catalyzed case, a new pathway is created by the presence of the catalyst with corresponding rate r_c. The total rate of reaction for the catalyzed case is $r_0 + r_c$. The analogous electrical circuits are also presented for comparison.

Michaelis constant in enzyme catalysis

$$K_m = \frac{k_{-1} + k_2}{k_1}$$

$$\rightarrow \frac{d[P]}{dt} = k_2[SC] = \frac{k_2[S][C]}{K_m}$$

rate of product formation $\sim [S][C]$

difficult to measure:

since $[S]$, $[C]$ are for free molecules which are not in the complex

$[S]_0$, $[C]_0$ initial substrate and catalyst concentration at $t=0$ (beginning)

all SC, P and S molecules in the reaction mixture are formed from $[S]_0$

$$[S]_0 = [S] + [SC] + [P]$$

$$\rightarrow [S] = [S]_0 - [SC] - [P]$$

$$[C]_0 = [C] + [SC], \quad [C] = [C]_0 - [SC]$$

SSA $\quad [SC] = \frac{[S][C]}{K_m} \rightarrow K_m[SC] = [S][C]$

$$K_m[SC] = [S][C] = ([S]_0 - [SC] - [P])([C]_0 - [SC])$$

$$0 = [S][C] - K_m[SC]$$

$$= ([S]_0 - [SC] - [P])([C]_0 - [SC]) - K_m[SC]$$

$$= [C]_0([S]_0 - [P]) - [SC]([S]_0 + [C]_0 - [P] + K_m) + [SC]^2$$

can be solved as quadratic equation in $[SC]$

but usually two assumptions are made to make it simpler

$[S]_0$, $[C]_0$ are controlled such that $[SC]$ is small

$[SC]$ small $\rightarrow [SC]^2$ can be neglected

early in the reaction (small t): little P is formed

$\Rightarrow [P]$ can also be neglected

$$\rightarrow [C]_0[S]_0 - [SC]([S]_0 + [C]_0 + K_m) = 0$$

$$\rightarrow [SC] = \frac{[C]_0[S]_0}{[S]_0 + [C]_0 + K_m}$$

R_0: rate at early times (near $t=0$)

$$R_0 = \frac{d[P]}{dt} = k_2[SC] = \frac{k_2[S]_0[C]_0}{[S]_0 + [C]_0 + K_m}$$

limiting case 1 : $[C]_0 \ll [S]_0$

most common case

much substrate with little catalyst at $t=0$

$$\rightarrow R_0 = \frac{k_2[S]_0[C]_0}{[S]_0 + K_m}$$

$\rightarrow$ when $[S]_0 \ll K_m$ $\rightarrow$ R_0 should be linear with $[S]_0$ with slope $k_2[C]_0/K_m$ $\qquad R_0 = \frac{k_2[S]_0[C]_0}{K_m}$

inversion

$$\frac{1}{R_0} = \frac{K_m}{k_2[C]_0}\frac{1}{[S]_0} + \frac{1}{k_2[C]_0}$$

$\rightarrow$ plot of $\frac{1}{R_0}$ (inverse initial rate) vs $\frac{1}{[S]_0}$

(make kinetic experiments with different $[S]_0 \gg [C]_0$ and measure initial rates)

$\rightarrow$ straight line with slope $= \frac{K_m}{k_2[C]_0}$ and

$$\text{intercept} = \frac{1}{k_2[C]_0}$$

$\rightarrow K_m, k_2$, since $[C]_0$ is known

when $[S]_0 \gg K_m$ only $[S]_0$ in denom; cancels

$\rightarrow R_0 = k_2[C]_0 = R_{max}$

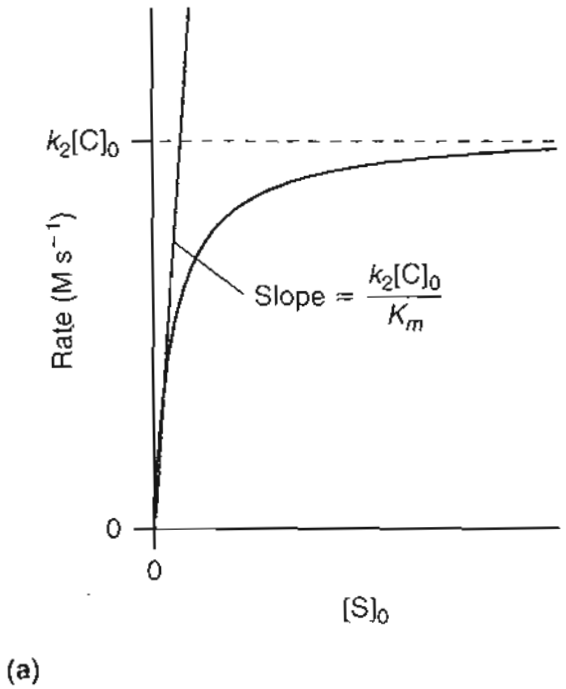
K_m, the reaction rate should increase
slope equal to $k_2[C]_0/K_m$. Parameters
mparing experimental reaction rates to
to determining these parameters is to
g relationship between the reaction rate

$$\frac{1}{S]_0} + \frac{1}{k_2[C]_0} \qquad \textbf{(36.50)}$$

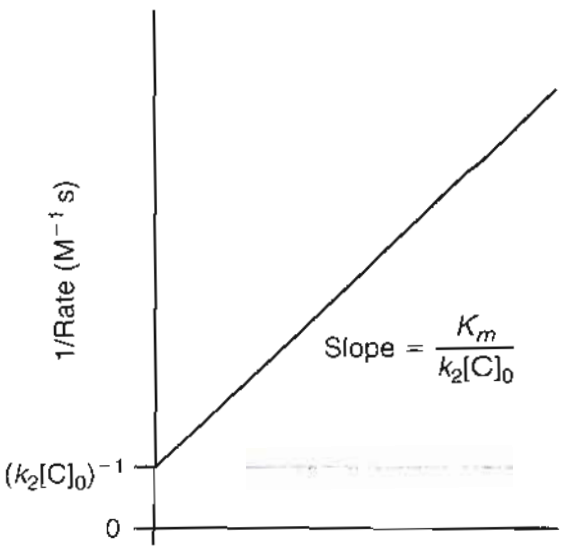
ıe inverse of the initial reaction rate ver-
ould yield a straight line. The y intercept
and k_2, assuming $[C]_0$ is known.
/here $[S]_0 \gg K_m$, the denominator in
resulting in the following expression for

$$= R_{max} \qquad \textbf{(36.51)}$$

a limiting value where the rate becomes
s limit, the reaction rate can only be
t. An illustration of the variation in the
ation predicted by Equations (36.49)



(a)



$$\frac{[C]_0}{K_m} \qquad \textbf{(36.52)}$$

irst order in $[S]_0$ but can be first or zero
$C]_0$ relative to K_m. In catalysis studies,
ght to be gained regarding the rate con-
easily evaluated for the previously dis-
ın be expensive; therefore, employing

$[S]_0$, resulting in the following expression for

$$[C]_0 = R_{max} \tag{36.51}$$

each a limiting value where the rate becomes In this limit, the reaction rate can only be atalyst. An illustration of the variation in the ıcentration predicted by Equations (36.49)

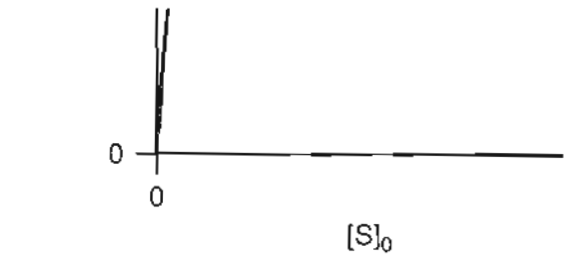
$$\frac{k_2[S]_0[C]_0}{[C]_0 + K_m} \tag{36.52}$$

ate is first order in $[S]_0$ but can be first or zero de of $[C]_0$ relative to K_m. In catalysis studies, ıe insight to be gained regarding the rate con- more easily evaluated for the previously dis- ysts can be expensive; therefore, employing ffective.

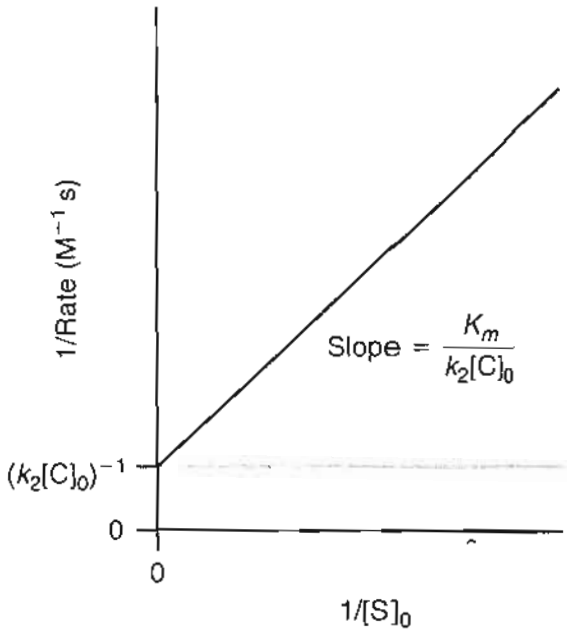
zyme Kinetics

rve as catalysts in a wide variety of chemical reaction specificity, with nature having devel- ıst majority of biological reactions required for ·n.. with associated substrate is presented in :-filling model derived from a crystal structure a bound substrate analogue (red). This enzyme ɔspholipids. The substrate analogue contains a e enzyme-susceptible ester. The substrate ana- s so that it does not suffer chemical breakdown :ess. With reactive substrate, ester hydrolysis n are released from the enzyme, resulting in

lipase A_2 catalysis can be described using the /me activity illustrated in Figure 36.6. The fig- or enzyme reactivity in which the substrate is here the reaction is catalyzed. The enzyme and :omplex, which dissociates into product and involved in creation of the enzyme–substrate



(a)



(b)

FIGURE 36.4
Illustration of the variation in the reaction rate with substrate concentration under Case 1 conditions as described in the text. **(a)** Plot of the initial reaction rate with respect to substrate concentration [Equation (36.49)]. At low substrate concentrations, the reaction rate increases linearly with substrate concentration. At high substrate concentrations, a maximum reaction rate of $k_2[C]_0$ is reached. **(b)** Reciprocal plot where the inverse of the reaction rate is plotted with respect to the inverse of substrate concentration [Equation (36.50)]. The y intercept of this line is equal to the inverse of the maximum reaction rate, or $(k_2[C]_0)^{-1}$. The slope of the line is equal to $K_m(k_2[C]_0)^{-1}$; therefore, with the slope and y intercept, K_m can be determined.

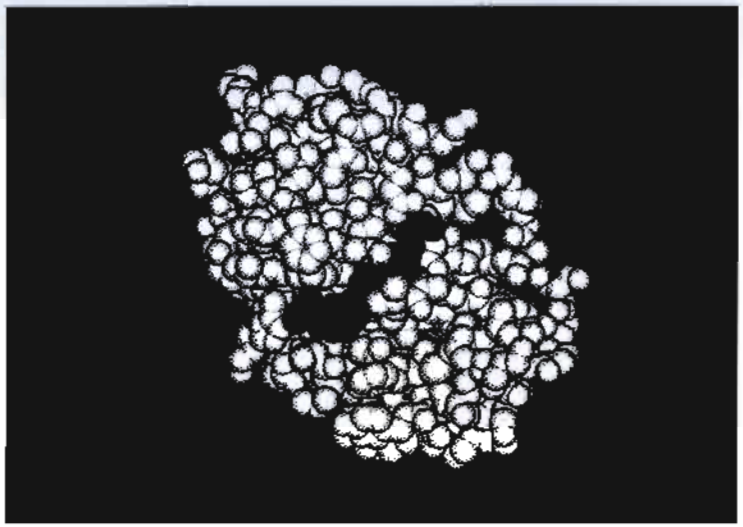


FIGURE 36.5
Space-filling model of the enzyme phospholipase A_2 (white) containing a bound substrate analogue (red). The substrate analogue contains a stable phosphonate group in place of the enzyme-susceptible ester; therefore, the substrate analogue is resistant to enzymatic hydrolysis and the enzyme–substrate complex remains stable in the complex during the X-ray diffraction structure determination process. [Structural data from Scott, White, Browning, Rosa, Gelb, and Sigler. "Structures of Free Inhibited Human Secretory Phospholipase A_2 from Inflammatory Exudate." *Science* 5034 (1991): 1007.]

complex are enzyme specific. For example, the active site may bind the substrate in more than one location, thereby creating geometric strain that promotes product formation. The enzyme may orient the substrate so that the reaction geometry is optimized. In summary, the details of enzyme-mediated chemistry are highly dependent on the reaction of interest. Rather than an exhaustive presentation of enzyme kinetics, our motivation here is to describe enzyme kinetics within the general framework of catalyzed reactions.

A schematic description of the mechanism illustrated in Figure 36.6 is as follows:

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES} \xrightarrow{k_2} \mathrm{E} + \mathrm{P} \tag{36.53}$$

In this mechanism, E is enzyme, S is substrate, ES is the complex, and P is product. Comparison of the mechanism of Equation (36.53) to the general catalytic mechanism described earlier in Equations (36.36) and (36.37) demonstrates that this mechanism is identical to the general catalysis mechanism except that the catalyst C is now the

→ for large $[S]_0$ the limiting rate is reached which is 0 order in $[S]_0$, then the rate can be increased only by increase in $[C]_0$

Transp. R vs $[S]_0$ and $\frac{1}{R}$ vs $\frac{1}{[S]_0}$

↓ straight near ~~t=0~~ small $[S]_0$

Limiting case 2: $[C]_0 \gg [S]_0$

usually avoided, since informations can be obtained from case 1 and $[C]_0 \gg [S]_0$ can be expensive.

here $R_0 = \frac{k_2 [S]_0 [C]_0}{[C]_0 + K_m}$ 1. order in $[S]_0$

in dinominator $[S]_0$ neglected

but 1. order in $[C]_0$ if $K_m \gg [C]_0$

or 0. order in $[C]_0$ if $[C]_0 \gg K_m$

Enzyme Kinetics (Michaelis-Menten mechanism)

Enzyme E = protein

specical enzymes developed by nature for almost all reactions needed in a cell

protein: poly-amino acids (different ones)

Transp. enzyme + substrate:

crystal structure of phospholipase A_2 with a substrate bound to it (substrate analogue)

substrate analogue: stable phosphonate group which is resistant to enzyme activity → X-Ray analysis possible before substrate decay

an ester group would be hydrolized ~~stell~~ setting P and E free

motivation here is to describe enzyme kinet
catalyzed reactions.

A schematic description of the mechanism il

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES -$$

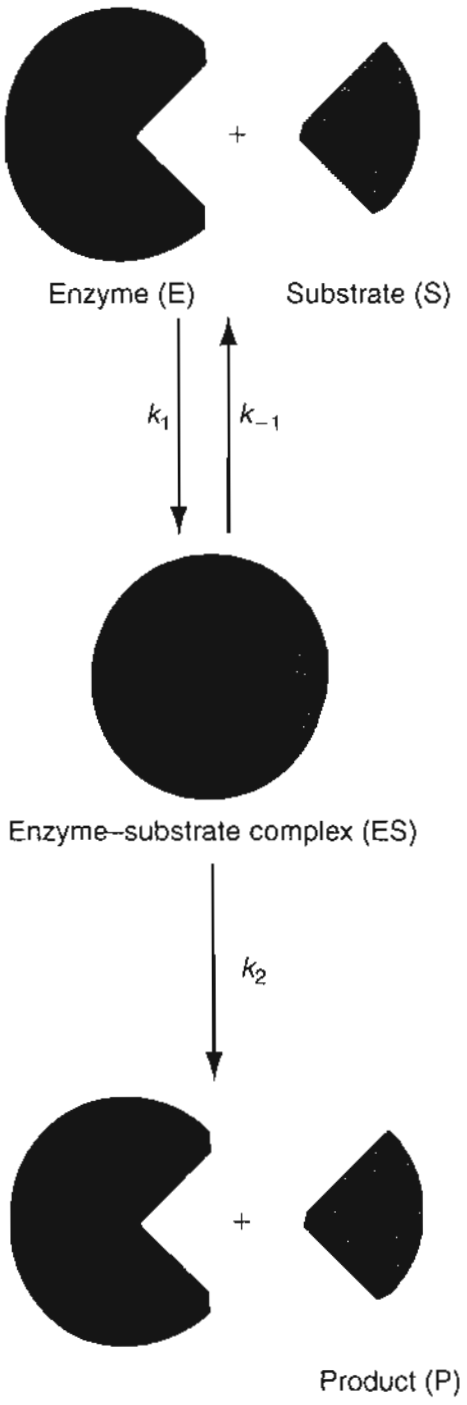


FIGURE 36.6
Schematic of enzyme catalysis.

In this mechanism, E is enzyme, S is substrate
Comparison of the mechanism of Equation (36.
described earlier in Equations (36.36) and (36.3
identical to the general catalysis mechanism
enzyme E. In the limit where the initial substrat
than that of the enzyme ($[S]_0 \gg [E]_0$ or Case
the rate of product formation is given by

$$R_0 = \frac{k_2[S]_0}{[S]_0 +}$$

In enzyme kinetics the composite constant K_m i
Michaelis constant in enzyme kinetics, and
Michaelis–Menten rate law. When $[S]_0 \gg K$
lected, resulting in the following expression for

$$R_0 = k_2[E]_0 =$$

Equation (36.55) demonstrates that the rate of
maximum value equal to the product of initial
constant for product formation, consistent with
A reciprocal plot of the reaction rate ca
Equation (36.54), which results in the **Linewea**

$$\frac{1}{R_0} = \frac{1}{R_{max}} + \frac{}{R}$$

For the Michaelis–Menten mechanism to be cc
inverse of the initial rate with respect to $[S]_0^{-1}$.
the y intercept and slope can be used to determ
Michaelis constant. This reciprocal plot is refe
In addition, because $[E]_0$ is readily determin
can be used to determine k_2, referred to as
[Equation (36.55)]. The turnover number can be

Transp. Lock-Key model

E as a lock, S as the key

the active site can bind S, however in more than 1 specific places

leads to a geometric strain which promotes product formation

also the reaction geometry can be optimized by substrate reorientation

mechanism:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \qquad ES \xrightarrow{k_2} E + P$$

same as the general catalysis mechanism before, only now C = E

E enzyme, S substrate,

ES enzyme-substrate complex

⇒ when $[S]_0 \gg [E]_0$ (case 1) then:

initial rate $R_0 = \dfrac{k_2 [S]_0 [E]_0}{[S]_0 + K_m}$

K_m: Michaelis constant, Michaelis-Menten rate law

$[S]_0 \gg K_m \Rightarrow R_0 = k_2 [E]_0 = R_{max}$

reciprocal form: ✓ Lineweaver-Burk equation:

$$\frac{1}{R_0} = \frac{1}{R_{max}} + \frac{K_m}{R_{max}} \frac{1}{[S]_0} \quad \text{with } R_{max} = k_2 [E]_0$$

plot $\frac{1}{R_0}$ vs $\frac{1}{[S]_0}$ → straight line

with slope = $\frac{K_m}{R_{max}}$, intercept = $\frac{1}{R_{max}}$

Line weaver-Burk plot

→ R_{max} easier than from R_0 vs $[S]_0$ plot! difficult to make sure that R_{max} is reached

$$k_2 = \frac{R_{max}}{[E]_0}$$

turnover number: maximum number of S molecules that can be converted to P

mostly: $k_2 \approx 1 - 10^5\ s^{-1}$

<u>experiment</u>: CO_2 hydration with carbonic anhydrase

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

the bicarbonate ion HCO_3^- can be transported in the blood and converted back to CO_2 in the lung with the same enzyme

$[E]_0 = 2.3\ nM$, 0.5°C:

R_0 ($10^{-5}\ M/s$)	2.78	5.00	8.33	16.7
$[CO_2]$ (mM)	1.25	2.5	5.0	20.0

K_m, k_2 = ?

<u>Transp.</u> Lineweaver-Burk plot for this: R_0^{-1} vs $[CO_2]^{-1}$

→ intercept = $4000\ M^{-1}s$, $R_{max} = \frac{1}{\text{intercept}} = 2.5 \cdot 10^{-4}\ M/s$

with $[E]_0 = 2.3\ nM$

→ $k_2 = \frac{R_{max}}{[E]_0} = \frac{2.5 \cdot 10^{-4}\ M/s}{2.3 \cdot 10^{-9}\ M} = 1.1 \cdot 10^5\ s^{-1}$

1. order rate constant as in the mechanism

slope = 40 s → K_m = slope · R_{max} = $40s \cdot 2.5 \cdot 10^{-4}\ \frac{M}{s}$

= 10 mM

$[S]_0$ chosen such that $R_0 = \frac{1}{2} R_{max}$:

$$R_0 = \frac{R_{max}[S]_0}{[S]_0 + K_m} \Rightarrow \frac{1}{2} R_{max} = \frac{R_{max}[S]_0}{[S]_0 + K_m}$$

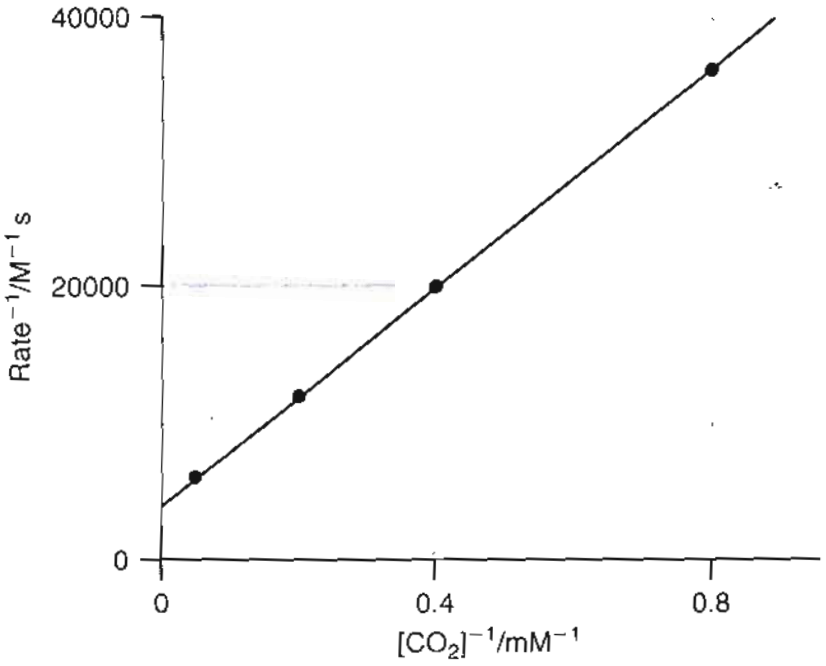
$\frac{1}{2}([S]_0 + K_m) = [S]_0$, $[S]_0 + K_m = 2[S]_0 \Rightarrow K_m = [S]_0$

Rate ($M\ s^{-1}$)	$[CO_2]$ (mM)
2.78×10^{-5}	1.25
5.00×10^{-5}	2.5
8.33×10^{-5}	5.0
1.67×10^{-4}	20.0

Determine K_m and k_2 for the enzyme at this temperature.

Solution

The Lineweaver–Burk plot of the rate^{-1} versus $[CO_2]^{-1}$ is shown here:



The y intercept for the best fit line to the data is 4000 M^{-1} s corresponding to $R_{max} = 2.5 \times 10^{-4}\ M\ s^{-1}$. Using this value and $[E]_0 = 2.3$ nM, k_2 is

$\Rightarrow$ when $R_0 = \frac{1}{2} R_{max}$, then $K_m = [S]_0$

Transp. R vs $[CO_2]$

R_{max} from Lineweaver-Burk plot

$$R_0 = \frac{R_{max}}{2} \Rightarrow K_m = 10\,mM$$

R_{max} from R_0 vs $[S]_0$ must be carefully checked to make sure that $[S]_0$ is large enough that $R_0 = R_{max}$

next, (29) is Quiz chap. 35

r e A_2 in Figure 36.5 is an example c a competitive inhibitor. Competitive inhibition can be described using the following mechanism:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \tag{36.58}$$

$$ES \xrightarrow{k_2} E + P \tag{36.59}$$

$$E + I \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} EI \tag{36.60}$$

In this mechanism, I is the inhibitor, EI is the enzyme–inhibitor complex, and the other species are identical to those employed in the standard enzyme kinetic scheme of Equation (36.53). How does the rate of reaction differ from the noninhibited case discussed earlier? To answer this question, we first define the initial enzyme concentration:

$$[E]_0 = [E] + [EI] + [ES] \tag{36.61}$$

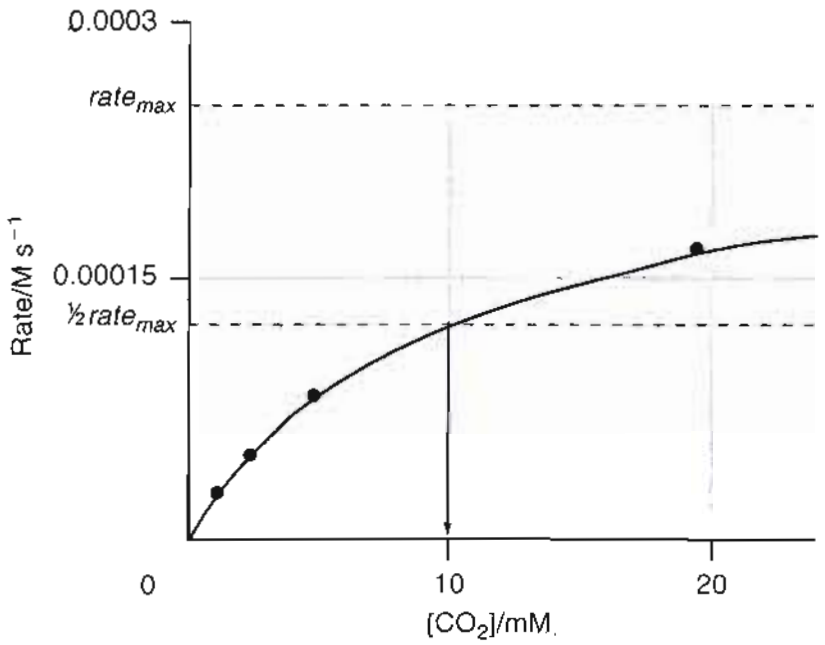


FIGURE 36.7
Determination of K_m for the carbonic-anhydrase catalyzed hydration of CO_2. The substrate concentration at which the rate of reaction is equal to half that of the maximum rate is equal to K_m.

- Competitive Inhibition Quiz # 3 (29)
- Homogeneous and Heterogeneous catalysis (30)-1

The activity of an enzyme can be <u>decreased</u> by adding a substance with a structure similar to the substrate, that can occupy the active site without leading to reaction

= blocking of active site

= competitive inhibition like the phosphonated chemical (competitive inhibitor) from last class

description: I = inhibitor, S = substrate

E = enzyme

K_1 $E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$ $ES \xrightarrow{k_2} P$ (product)

K_2 $E + I \underset{k_{-1}}{\overset{k_3}{\rightleftharpoons}} EI$

EI = enzyme-inhibitor complex

$[E]_0 = [E] + [EI] + [ES]$ at all time

last class: without inhibitor: $K_m[SC] = [S][C]$

for general catalysis

$K_S = \frac{k_{-1}}{k_1} = \frac{[E][S]}{[ES]} \approx K_m$ $K_I = \frac{k_{-3}}{k_3} = \frac{[E][I]}{[EI]}$ $K_I = K_2^{-1}$

$K_1 = K_1^{-1}$

$k_{-1} \gg k_2$: fast equilibrium $\Rightarrow K_m = \frac{k_{-1} + k_2}{k_1} \approx \frac{k_{-1}}{k_1} = K_S$

$[E]_0 = \frac{K_m[ES]}{[S]} + \frac{[E][I]}{K_I} + [ES]$

$= [E]$ $= [EI]$

$[E] = K_m \frac{[E]}{[E]}$

$[EI] = \frac{[E][I]}{K_I}$

pre-equilibrium

with $[E] = \frac{K_m [ES]}{[S]}$ from K_S:

$$[E]_0 = \frac{K_m [ES]}{[S]} + \frac{K_m [ES]}{[S]} \frac{[I]}{K_I} + [ES]$$

~~$[ES] = \frac{[E]_0}{\quad}$~~

$$= [ES] \left[\frac{K_m}{[S]} + \frac{K_m [I]}{[S] K_I} + 1 \right]$$

$$[ES] = \frac{[E]_0}{1 + \frac{K_m}{[S]} + \frac{K_m [I]}{[S] K_I}}$$

$$\Rightarrow R = \frac{d[P]}{dt} = k_2 [ES]$$

$$= \frac{k_2 [E]_0}{1 + \frac{K_m}{[S]} + \frac{K_m [I]}{[S] K_I}} = \frac{k_2 [E]_0}{\frac{1}{[S]} \left[[S] + K_m + \frac{K_m [I]}{K_I} \right]}$$

$$= \frac{k_2 [E]_0 [S]}{[S] + K_m \left(1 + \frac{[I]}{K_I} \right)}$$

if $[S] = [S]_0 \Rightarrow R_0 = \frac{k_2 [E]_0 [S]_0}{[S]_0 + K_m \left(1 + \frac{[I]}{K_I} \right)}$

here it was used that ~~$[S] \ll$~~ $[ES] \ll [S]$, $[P] \ll [S]$

then $[S] \approx [S]_0$ as before for uninhibited catalysis:

there $R_0 = \frac{k_2 [S]_0 [E]_0}{[S]_0 + K_m}$

$\Rightarrow$ a new apparent Michaelis constant K^* can be introduced: $K_m^* = K_m \left(1 + \frac{[I]}{K_I} \right)$

if there is no inhibitor, then $K_m^* \rightarrow K_m$

before: $R_{max} = k_2 [E]_0 = R_0$, when $[S]_0 \gg K_m$

here with K_m^*:

$$R_0 = \frac{R_{max}[S]_0}{[S]_0 + K_m^*}$$

with inhibitor $K_m^* > K_m$

and more S is needed to reach $\frac{1}{2}R_{max}$ than in the ~~inhibi~~ uninhibited case (when we reach $\frac{1}{2}R_{max}$ then $K_m = [S]_0$, here $K_m^* = [S]_0$ for $\frac{1}{2}R_{max}$)

Line weaver-Burk plot:

$$\frac{1}{R_0} = \frac{1}{R_{max}} + \frac{K_m^*}{R_{max}} \frac{1}{[S]_0}$$

larger slope in the $\frac{1}{R_0}$ vs $\frac{1}{[S]_0}$ plot than in the uninhibited case, since $K_m^* > K_m$

Transp. R vs $[S]_0$ and $\frac{1}{R}$ vs $\frac{1}{[S]_0}$

R_{max} is the same with or without I ($R_{max} = k_2[E]_0$)

good for drug design: example sulfanilamide is similar to amino benzoic acid which bacteria use to create folate → no folate, bacteria die

people use other folate sources ⇒ sulfanilamide is not toxic for people, but for bacteria (Transp.)

Homogeneous and Heterogeneous Catalysis

a homogeneous catalyst is in the same phase as reactants or products (l & g)

a heterogeneous catalyst (s) is in another phase than reactants or products (l, g)

homogeneous example: gas-phase catalytic depletion of O_3 in stratosphere by Cl_2 atoms

$$\left(\frac{K_m[\mathrm{I}]}{[\mathrm{S}]}\right)\frac{[\mathrm{I}]}{K_i} + [\mathrm{ES}]$$

$$+ \frac{K_m[\mathrm{I}]}{[\mathrm{S}]K_i} + 1\Bigg) \qquad \textbf{(36.64)}$$

$$\frac{[\mathrm{E}]_0}{} \qquad \textbf{(36.65)}$$

$$+ \frac{K_m}{[\mathrm{S}]} + \frac{K_m[\mathrm{I}]}{[\mathrm{S}]K_i}$$

given by

$$\frac{k_2[\mathrm{E}]_0}{\frac{K_m}{[\mathrm{S}]} + \frac{K_m[\mathrm{I}]}{[\mathrm{S}]K_i}} = \frac{k_2[\mathrm{S}][\mathrm{E}]_0}{[\mathrm{S}] + K_m\left(1 + \frac{[\mathrm{I}]}{K_i}\right)}$$

$$\frac{k_2[\mathrm{S}]_0[\mathrm{E}]_0}{} \qquad \textbf{(36.66)}$$

$$+ K_m\left(1 + \frac{[\mathrm{I}]}{K_i}\right)$$

it [ES] and [P] $\ll$ [S] has been employed so previous treatment of uninhibited catalysis. corresponding expression for the uninhibited t with competitive inhibition, a new apparent

$$K_m\left(1 + \frac{[\mathrm{I}]}{K_i}\right) \qquad \textbf{(36.67)}$$

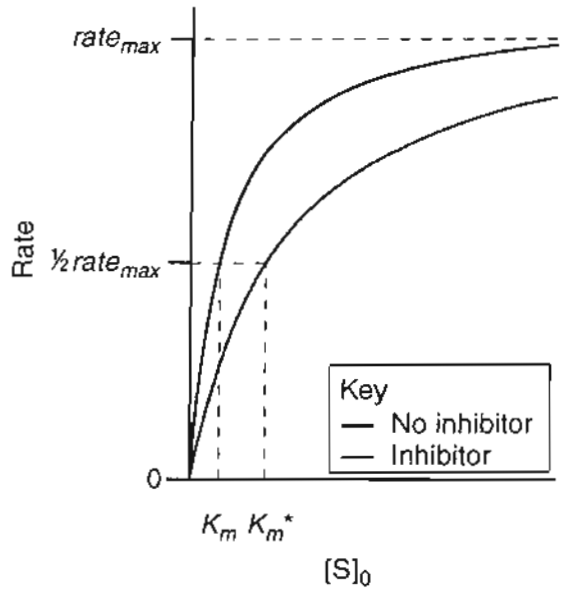
ose ce of inhibitor ([I] = 0). Next, using the fined earlier in Equation (36.55), the reaction can be written as

$$\frac{R_{max}[\mathrm{S}]_0}{[\mathrm{S}]_0 + K_m^*} \qquad \textbf{(36.68)}$$

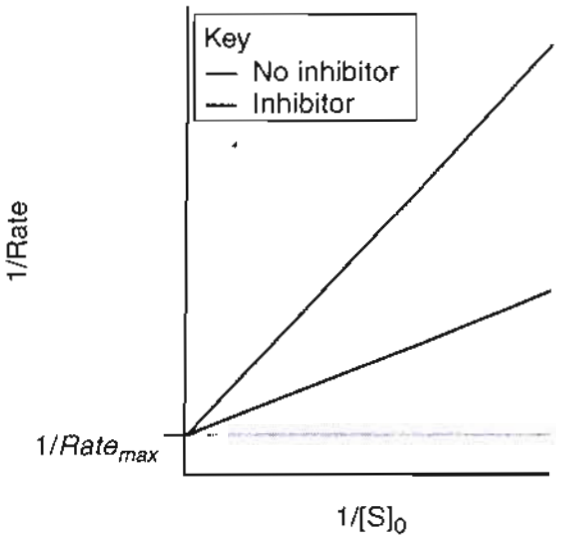
and more substrate is required to reach half the nhibited case. The effect of inhibition can also of the following form:

$$\frac{}{ax} + \frac{K_m^*}{R_{max}}\frac{1}{[\mathrm{S}]_0} \qquad \textbf{(36.69)}$$

eweaver–Burk plot will be greater with inhibitor igure 36.8 presents an illustration of this effect.

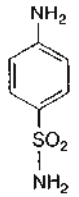


(a)

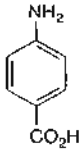


(b)

FIGURE 36.8
Comparison of enzymatic reaction rates in the presence and absence of a competitive inhibitor. (**a**) Plot of rate versus initial substrate concentration. The location of K_m and K_m^* is indicated. (**b**) Reciprocal plots ($1/R$ versus $1/[\mathrm{S}]_0$). Notice that $1/R_{max}$ is identical in the presence and absence of a competitive inhibitor.



Sulfanilamide



p-Aminobenzoic acid

FIGURE 36.9
Structural comparison of the antibacterial drug sulfanilamide, a competitive inhibitor of the enzyme dihydropteroate synthetase, and the active substrate, *p*-aminobenzoic acid. The change in functional group from $-CO_2H$ to $-SO_2NH_2$ is such that sulfanilamide cannot be used by bacteria to synthesize folate, and the bacterium starves.

Competitive inhibition has been used in drug design for antiviral, antibacterial, and antitumor applications. Many drugs are molecules that serve as competitive inhibitors for enzymes required for viral, bacterial, or cellular replication. For example sulfanilamide (Figure 36.9) is a powerful antibacterial drug. This compound is similar to *p*-aminobenzoic acid, the substrate for the enzyme dihydropteroate synthetase that participates in the production of folate. When present, the enzyme in bacteria cannot produce folate, and the bacteria die. However, humans do not possess this enzyme; they obtain folate from other sources. Therefore, sulfanilamide is not toxic.

36.4.5 Homogeneous and Heterogeneous Catalysis

A **homogeneous catalyst** is a catalyst that exists in the same phase as the species involved in the reaction, and a **heterogeneous catalyst** exists in a different phase. Enzymes serve as an example of a homogeneous catalyst; they exist in solution and catalyze reactions that occur in solution. A famous example of gas-phase catalysis is the catalytic depletion of stratospheric ozone by atomic chlorine. In the mid-1970s, F. Sherwood Rowland and Mario Molina proposed that Cl atoms catalyze the decomposition of stratospheric ozone by the following mechanism:

$$Cl + O_3 \xrightarrow{k_1} ClO + O_2 \qquad (36.70)$$

$$ClO + O \xrightarrow{k_2} Cl + O_2 \qquad (36.71)$$

$$O_3 + O \rightarrow 2\,O_2 \qquad (36.72)$$

In this mechanism, Cl reacts with ozone to produce chlorine monoxide (ClO) and molecular oxygen. The ClO undergoes a second reaction with atomic oxygen, largely formed by O_3 photolysis, resulting in the reformation of Cl and the product of O_2. The sum of these reactions leads to the net conversion of O_3 and O to 2 O_2. Notice that the Cl is not consumed in the net reaction.

The catalytic efficiency of Cl can be determined using standard techniques in kinetics. The experimentally determined rate law expression for the uncatalyzed reaction of Equation (36.72) is

$$R_{nc} = k_{nc}[O][O_3] \qquad (36.73)$$

The stratospheric temperature where this reaction occurs is roughly 220 K, at which temperature k_{nc} has a value of $3.30 \times 10^5\ M^{-1}\ s^{-1}$. For the Cl catalyzed decomposition of ozone, the rate constants at this temperature are $k_1 = 1.56 \times 10^{10}\ M^{-1}\ s^{-1}$ and $k_2 = 2.44 \times 10^{10}\ M^{-1}\ s^{-1}$. To employ these rates in determining the overall rate of reaction, the rate law expression for the catalytic mechanism must be d mined. Notice that both Cl and ClO are intermedi in this mechanism. Applying the steady-state approximation, the concentrat of intermediates is taken to be a constant such that

Substituting Equation (36.75) into Equation (36.74) yields for [Cl]:

$$[Cl] = \frac{k_2[Cl]_{total}[O]}{k_1[O_3] + k_2[O]}$$

Using Equation (36.76), the rate law expression for the cat mined as follows:

$$R_{cat} = -\frac{d[O_3]}{dt} = k_1[Cl][O_3] = \frac{k_1k_2[Cl]_{t}}{k_1[O_3]}$$

The composition of the stratosphere is such that $[O_3] \gg [$ with the numerical values for k_1 and k_2 presented earli denominator of Equation (36.77) can be neglected, and t the catalyzed reaction becomes

$$R_{cat} = k_2[Cl]_{total}[O]$$

The ratio of catalyzed to uncatalyzed reaction rates is

$$\frac{R_{cat}}{R_{uc}} = \frac{k_2[Cl]_{total}}{k_{nc}[O_3]}$$

In the stratosphere $[O_3]$ is roughly 10^3 greater than $[Cl]_{total}$, an

$$\frac{R_{cat}}{R_{uc}} = \frac{k_2}{k_{nc}} \times 10^{-3} = \frac{2.44 \times 10^{10}\ M^{-1}s^{-1}}{3.30 \times 10^5\ M^{-1}s^{-1}} >$$

Therefore, through Cl-mediated catalysis, the rate of O_3 los magnitude greater than the loss through the bimolecular reac

Where does stratospheric Cl come from? Rowland and M source of Cl was from the photolysis of chlorofluorocarbons anthropogenic compounds that were common refrigerants at are extremely robust, and when released into the atmosphere, port through the troposphere and into the stratosphere. Onc molecules can absorb a photon of light with sufficient energ bond, and Cl is produced. This proposal served as the impet of stratospheric ozone depletion, and it led to the Montreal majority of nations agreed to phase out the industrial use of c

Heterogeneous catalysts are extremely important in indus ity of industrial catalysts are solids. For example, the synthesi and H_2 is catalyzed using Fe. This is an example of heteroge reactants and product are in the gas phase, but the catalyst is in reactions involving solid catalysis is the adsorption of one the solid surface. First, we assume that the particles adsorb to ing their internal bonding, a process referred to as **physisor**

direct 1. step reaction: $O_3 + O \rightarrow 2O_2$

catalyzed: $M + O_3 \xrightarrow{k_1} MO + O_2$

$MO + O \xrightarrow{k_2} M + O_2$

overall: $O_3 + O \rightarrow 2O_2$ same as uncatalyzed

atmospheric O by photolysis of O_3

M is not consumed (catalyst)

non-catalyzed: $R_{nc} = k_{nc}[O][O_3]$

exp. at 220K in stratosphere: $k_{nc} = 3.30 \cdot 10^{-5} \frac{1}{ms}$

f catalyzed reaction there:

$k_1 = 1.56 \cdot 10^{10} \frac{1}{ms}$, $k_2 = 2.44 \cdot 10^{10} \frac{1}{ms}$

to use these constants, rate law for catalyzed reaction is needed

M, MO are intermediates → SSA

$[M]_{total} = [M]_t = [M] + [MO]$

$\frac{d[M]}{dt} = 0 = -k_1[M][O_3] + k_2[MO][O]$

$k_1[M][O_3] = k_2[MO][O]$, $[MO] = \frac{k_1[M][O_3]}{k_2[O]}$

$[M] = [M]_t - [MO]$

$= [M]_t - \frac{k_1[O_3][M]}{k_2[O]}$

$[M]_t = [M]\left(1 + \frac{k_1[O_3]}{k_2[O]}\right) = [M]\frac{k_2[O] + k_1[O_3]}{k_2[O]}$

$[M] = \frac{k_2[O][M]_t}{k_1[O_3] + k_2[O]}$ ⇒ for catalyzed reaction:

$R_{cat} = -\frac{d[O_3]}{dt} = k_1[M][O_3] = \frac{k_1 k_2 [M]_t [O][O_3]}{k_1[O_3] + k_2[O]}$

stratosphere: $[O_3] \gg [O_p]$

together with k_1, k_2 values: $k_2(O)$ can be neglected

$$\rightarrow R_{cat} = k_2 [Cl]_t [O] \rightarrow \frac{R_{cat}}{R_{nc}} = \frac{k_2 (Cl)_t}{k_{nc} [O_3]}$$

stratosphere: $[O_3] \approx 10^3 [Cl]_t$

$$\frac{R_{cat}}{R_{nc}} = \frac{k_2}{k_{nc}} \cdot 10^{-3} = \frac{2.44 \cdot 10^{10} \frac{l}{ms}}{3.3 \cdot 10^{5} \frac{l}{ms}} \cdot 10^{-3} \approx 74$$

with Cl catalysis R_{cat} for O_3 depletion ~ 2 orders larger than R_{nc}

Cl: from photolysis of $CFCl_3$ and CF_2Cl_2 which were common refrigerents before. They are very stable and come up into the stratosphere, where they are photolyzed and yield Cl atoms

- Adsorption
- example
- radical reaction

→ forbidden now as refrigerents (O_3 depletion)

in industry: mostly solid catalysts (heterogeneous), like Fe for NH_3 synthesis from $N_2 + H_2$

important step: adsorption of 1 or more reactants (can be) on solid surface: adsorption without chemical changes (adsorbens) = Physisorption (weak intermolecular bonding) equilibrium between adsorbed (adsorbate) and free molecules

fractional coverage $\theta = \frac{\#\text{ of occupied sites}}{\#\text{ of all adsorption sites}}$

θ = fraction of occupied surface sites

also: $\theta = \frac{V_{ads}}{V_m}$ V_{ads}: adsorbed volume

V_m ~~need~~ volume (needed) to cover 1 monolayer fully

Transp.

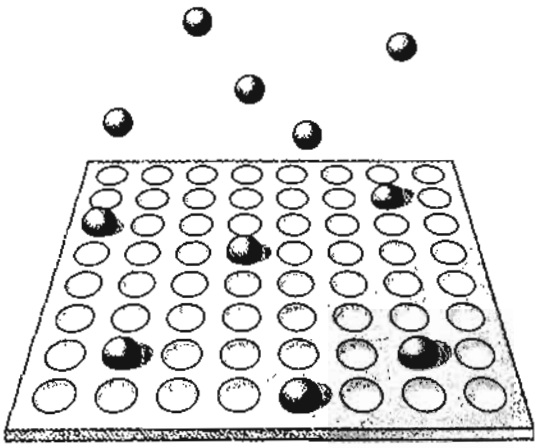


FIGURE 36.10
Illustration of fractional coverage θ. The surface (orange parallelogram) contains a series of adsorption sites (white circles). The reactant (blue spheres) exists in an equilibrium between free reactants and adsorbates. The fractional coverage is the number of occupied adsorption sites divided by the total number of sites on the surface.

Studies of adsorption involve measuring t
of reactant-gas pressure at a specific tempera
fixed temperature is called an **adsorption**
describing the adsorption process is known as
is described by the following mechanism:

$$R(g) + M(surface) \rightleftharpoons$$

In Equation (36.80), R is reagent, M (surface)
surface of the catalyst, RM (surface) is an occ
stant for adsorption, and k_d is the rate consta
are employed in the Langmuir model:

1. Adsorption is complete once monolayer cc
2. All adsorption sites are equivalent, and the
3. Adsorption and desorption are uncoopera
the adsorption site will not affect the pro
adjacent sites.

With these approximations, the rate of change
adsorption k_a, reagent pressure P, and the nu
$N(1 - \theta)$ or the total number of adsorption s
open $(1 - \theta)$:

$$\left(\frac{d\theta}{dt}\right)_{abs} = k_a P$$

The corresponding change in θ due to deso
desorption k_d and the number of occupied adsc

$$\left(\frac{d\theta}{dt}\right)_{des} =$$

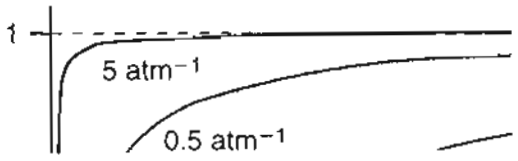
At equilibrium, the change in fractional coverage

$$\frac{d\theta}{dt} = 0 = k_a PN(1$$

$$(k_a PN + k_d N)\theta =$$

$$\theta = \frac{k_a P}{k_a P + k_d}$$

$$\theta = \frac{K}{KP}$$



where K is the equilibrium constant defined as
for the **Langmuir isotherm**. Figure 36.11 ...

$\theta = f(p)$ at $T = \text{const.}$:

adsorption isotherm

Langmuir model: $R(g) + M(\text{surface}) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} RM(\text{surface})$

$R(g)$: gas-phase reactant, $M(\text{surface})$ free surface site

$RM(\text{surface})$ occupied surface site

Approximations in Langmuir model:

1. Adsorption only in 1 Layer (monolayer)
2. Uniform surface (all sites equal)
   No interactions between occupied sites

rate of adsorption $\sim k_a$ ~~fractio~~ ~~no~~ No. of free sites $N(1-\theta)$
$\sim P$

N: total # of surface sites

$$\left(\frac{d\theta}{dt}\right)_{ads} = k_a P N (1-\theta)$$

desorption: $\left(\frac{d\theta}{dt}\right)_{des} = -k_d \theta N$

equilibrium: $\frac{d\theta}{dt} = 0 = k_a P N(1-\theta) - k_d N\theta = 0$

$(k_a P N + k_d N)\theta = k_a P N$ all with θ added to the left

$$\rightarrow \quad \theta = \frac{k_a P}{k_a P + k_d} = \frac{(k_a/k_d)P}{(k_a/k_d)P + 1} = \frac{KP}{1+KP} \qquad K = \frac{k_a}{k_d}$$

K equilibrium constant for adsorption

Transp: Langmuir isotherms

if k_d increases $\Rightarrow$ K decreases $\Rightarrow$ P must be larger for $\theta = 1$ (full monolayer coverage)

$$\left(\frac{d\theta}{dt}\right)_c$$

At equilibrium, the change in fractional co

$$\frac{d\theta}{dt} = 0 = k_a I$$

$$(k_a PN + k_d N$$

$$\theta = \frac{k_a P}{k_a P + k_d}$$

$$\theta =$$

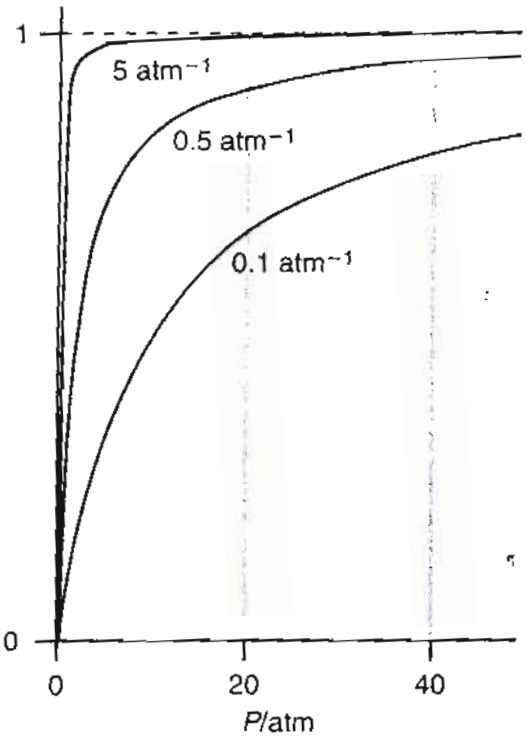


FIGURE 36.11
Langmuir isotherms for a range of k_a/k_d.

where K is the equilibrium constant define for the **Langmuir isotherm.** Figure 36.1 values of k_a/k_d. Notice that as the rate c adsorption, higher pressures must be empl be understood based on the competition b orption. Correspondingly, if the rate cons becomes independent of pressure for lower

In many instances adsorption is accom process that is referred to as **chemisorption** a

$$R_2(g) + 2M\,(surface)$$

Kinetic analysis of this mechanism (see the e ing expression for θ:

$$\theta = \frac{(K}{1 + (}$$

Inspection of Equation (36.84) reveals that the strate weaker pressure dependence compared

competition between adsorption and desorption if k_d is large (more R escapes surface)

after adsorption dissociation can happen (chemisorption,

$$R_2(g) + 2M(\text{surface}) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} 2\,RM(\text{surface})$$

then $\theta = \frac{\sqrt{KP}}{1+\sqrt{KP}}$ $\quad \frac{1}{\theta}$ vs $\frac{1}{\sqrt{P}}$ straight line

$$\text{slope} = \frac{1}{\sqrt{K}}$$

$$\frac{1}{\theta} = \frac{1}{\sqrt{KP}} + 1$$

→ weaker P dependence

Transp.

different isotherms → $K = f(T)$

→ van't Hoff plot $\ln K$ vs $\frac{1}{T}$ straight line

$$\text{slope} = -\frac{\Delta H_{ads}}{R}$$

$K = e^{\frac{\Delta H_{ads}}{RT}}$

$\ln K$ vs $\frac{1}{T}$ $\quad R$

$\ln K^\circ = -\frac{\Delta H^\circ}{RT} + \frac{\Delta}{R}$

1) surfaces in general not uniform

→ different kinds of adsorption sites

2) rate of ads. and des. can depend on occupation of nearby sites

3) ads. molecules can diffuse over the surface

→ more complicated mechanisms than the Langmuir ones are needed

Example for adsorption calculation next class

mparison of the isotherms predicted using nondissociative and dissociative mechanisms rresponding to the same ratio of k_a/k_d. Finally, different Langmuir isotherms can be col-ted and evaluated over a range of temperatures to determine K as a function of T. With s information, a van't Hoff plot of $\ln K$ versus $1/T$ should provide a straight line of slope $\Delta H_{ads}/R$. Through this analysis, the enthalpy of adsorption ΔH_{ads} can be determined.

The assumptions employed in the Langmuir model may not be rigorously obeyed in ıl heterogeneous systems. First, surfaces are generally not uniform, resulting in the :sence of more than one type of adsorption site. Second, the rate of adsorption and sorption may depend on the occupation state of nearby adsorption sites. Finally, it s been established that adsorbed molecules can diffuse on the surface and then sorb corresponding to a kinetic process of adsorption that is more complicated than : Langmuir mechanism envisions.

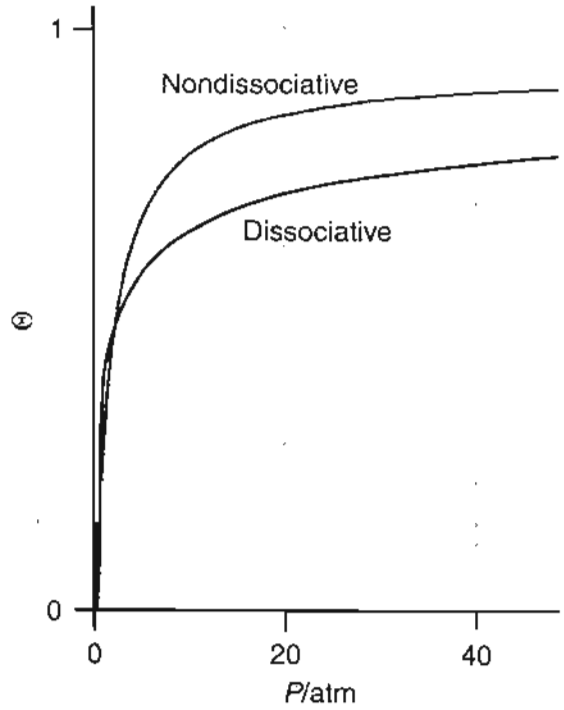


FIGURE 36.12
Comparison of Langmuir isotherms for nondissociative and dissociative adsorption with $k_a/k_d = 0.5\ \text{atm}^{-1}$.

XAMPLE PROBLEM 36.2

e following data were obtained for the adsorption of Kr on charcoal at 193.5 K. ing the Langmuir model, construct the adsorption isotherm, and determine V_m and : equilibrium constant for adsorption/desorption.

V_{ads} ($\text{cm}^3\ \text{g}^{-1}$)	P (Torr)
5.98	2.45
7.76	3.5
10.1	5.2
12.35	7.2
16.45	11.2
18.05	12.8
19.72	14.6
21.1	16.1

- Example for Adsorption
- Radical Chain Reactions

example: emperical data of V_{ads} (adsorbed volume) at different pressures

V_{ads} (cm^3/g)	5.98	7.76	10.1	12.35	16.45	18.05	19.72	21.1
P(Torr)	2.45	3.5	5.2	7.2	11.2	12.8	14.6	16.1

at 193.5 K

plot (linear regression) the langmuir isotherm and determine V_m (mono layer occupation) and K

$$\theta = \frac{V_{ads}}{V_m}$$

plot of V_{ads} vs P → isotherm.

Transp. Langmuir works for Kr on charcoal

reciprocal plot: $\theta = \frac{KP}{1+KP}$

$$\rightarrow \frac{1}{\theta} = 1 + \frac{1}{KP} \qquad \frac{1}{\theta} = \frac{V_m}{V_{ads}}$$

$$\frac{1}{V_{ads}} = \frac{1}{V_m} + \frac{1}{KV_m}\frac{1}{P}$$

$\frac{1}{V_{ads}}$ or vs $\frac{1}{P}$: straight line slope $= \frac{1}{KV_m}$

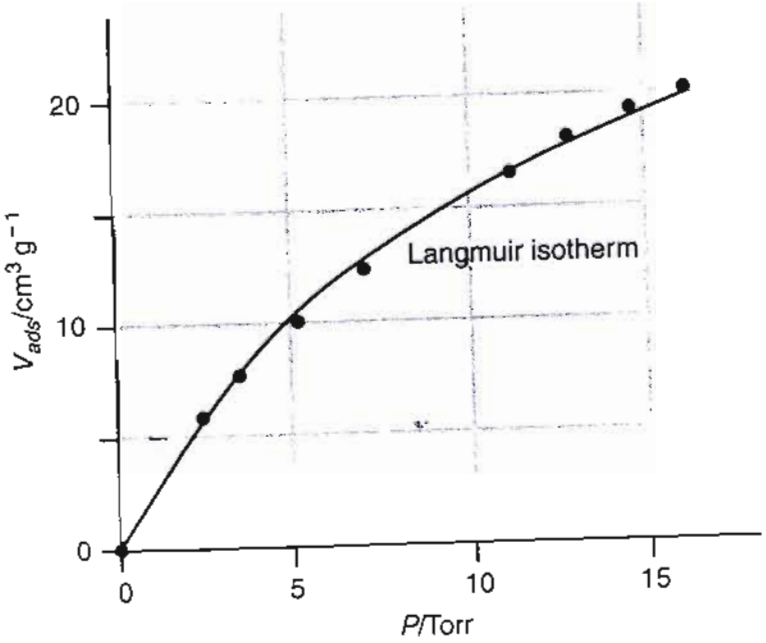
intercept $= \frac{1}{V_m}$ Transp. of plot

intercept $= \frac{1}{V_m} = 0.0293 \ g/cm^3 \rightarrow V_m = 34.1 \ cm^3/g$

slope $= 0.3449 \ \frac{Torr\,g}{cm^3} \rightarrow K = 9.38 \cdot 10^{-2} \ \frac{1}{Torr}$

Solution

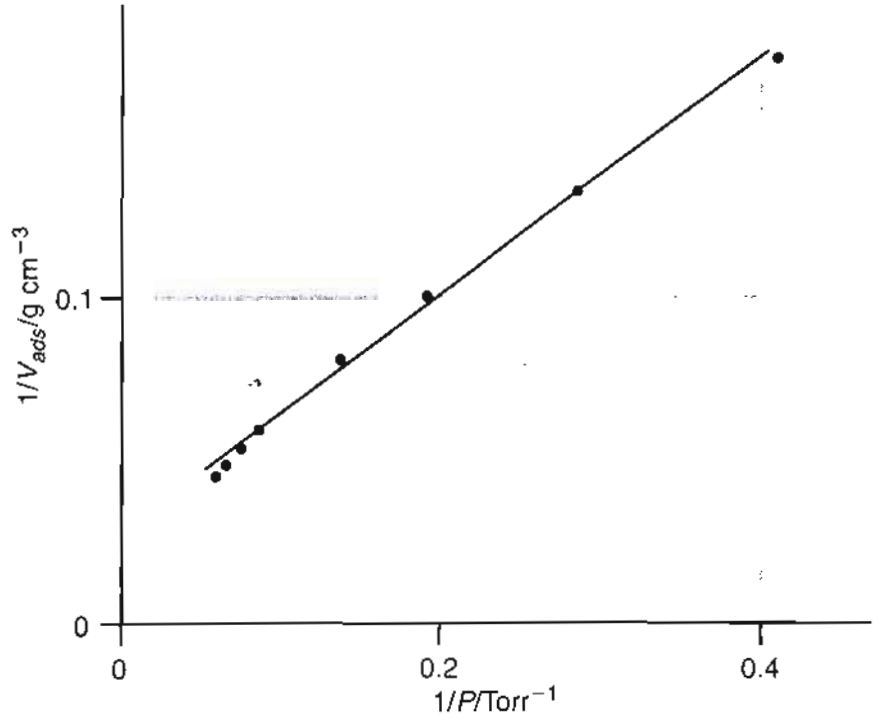
The fractional coverage is related to the experimentally measured V_{ads}. The adsorption isotherm is given by a plot of V_{ads} versus P, which can be compared to the behavior predicted by Equation (36.83) as illustrated here:



Although the comparison of the adsorption isotherm to Equation (36.83) illustrates that the Langmuir model is consistent with the adsorption of Kr on charcoal, determination of the Langmuir parameters is difficult because parameters such as V_m are unknown. This information is more readily determined by using the reciprocal of Equation (36.83):

$$\frac{1}{V_{ads}} = \left(\frac{1}{KV_m}\right)\frac{1}{P} + \frac{1}{V_m}$$

This equation demonstrates that a plot of $(V_{ads})^{-1}$ versus $(P)^{-1}$ should yield a straight line with slope equal to $(KV_m)^{-1}$ and y intercept equal to $(V_m)^{-1}$. A plot of the data in reciprocal form with the best fit line is shown next:



The y intercept obtained from the best fit line is 0.0293 g cm^{-3} such that V_m = 34.1 cm^3 g^{-1}. The slope of the best fit line is 0.3449 Torr g cm^{-3}. Using V_m determined from the y intercept, K is found to be 8.38 × 10^{-2} Torr^{-1}.

finally: termination step

2 radicals combine to a non-radical product

complex mechanism with 5 steps, but rather simple rate law

consumption of ethane:

$$-\frac{d[C_2H_6]}{dt} = k_1[C_2H_6] + k_2[CH_3\cdot][C_2H_6] + k_4[C_2H_6][H\cdot] - k_5[H\cdot][C_2H_5\cdot]$$

1 term from each step that involves C_2H_6

rate of consumption: + when C_2H_6 is consumed
- when " " formed

$CH_3\cdot$: reactive intermediate $\Rightarrow$ SSA

$$\frac{d[CH_3\cdot]}{dt} \overset{SSA}{=} 0 = 2k_1[C_2H_6] - k_2[CH_3\cdot][C_2H_6] \quad (1)$$

$$[CH_3\cdot] = \frac{2k_1}{k_2} \quad [C_2H_6] \text{ cancels}$$

2 at k_1 because each step forms 2 $CH_3\cdot$

rate of formation $\Rightarrow$ formation step +
consumption step -

for $C_2H_5\cdot$ and $H\cdot$ also SSA:

$$\frac{d[C_2H_5\cdot]}{dt} = 0 = k_2[CH_3\cdot][C_2H_6] - k_3[C_2H_5\cdot] + k_4[H\cdot][C_2H_6] - k_5[H\cdot][C_2H_5\cdot] \quad (2)$$

$$\frac{d[H\cdot]}{dt} = 0 = k_3[C_2H_5\cdot] - k_4[H\cdot][C_2H_6] - k_5[H\cdot][C_2H_5\cdot] \quad (3)$$

(1) + (2) + (3): underlined stays, rest cancels

$$0 = 2k_1[C_2H_6] - 2k_5[H\cdot][C_2H_5\cdot]$$

$$[H\cdot] = \frac{k_1[C_2H_6]}{k_5[C_2H_5\cdot]}$$

into (3): $0 = k_3[C_2H_5^\cdot] - k_4[C_2H_6]\frac{k_1[C_2H_6]}{k_5[C_2H_5^\cdot]} - k_5[C_2H_5^\cdot]\frac{k_1[C_2H_6]}{k_5[C_2H_5^\cdot]}$

$0 = k_3[C_2H_5^\cdot] - k_4 k_1 \frac{[C_2H_6]^2}{k_5[C_2H_5^\cdot]} - k_1[C_2H_6] \;\Big|\cdot \frac{[C_2H_5^\cdot]}{k_3}$

$0 = [C_2H_5^\cdot]^2 - \frac{k_4 k_1 [C_2H_6]^2}{k_5 \cdot k_3} - \frac{k_1}{k_3}[C_2H_6][C_2H_5^\cdot]$

with $x = [C_2H_5^\cdot]$ $\quad a = \frac{k_4 k_1 [C_2H_6]^2}{k_5 k_3}$ $\quad b = \frac{k_1}{k_3}[C_2H_6]$

this is $x^2 - a - bx = 0$

$x^2 - bx - a = 0$

$x_{1,2} = \frac{1}{2}\left(b \pm \sqrt{b^2 + 4a}\right) = \frac{1}{2}b \pm \sqrt{\left(\frac{b}{2}\right)^2 + a}$

$-(-b)$ $\qquad -4(-a)$

$x = [C_2H_5^\cdot]$ must be >0 $\Rightarrow$ + <u>not</u> −

$[C_2H_5^\cdot] = \left(\frac{k_1}{2k_3} + \sqrt{\left(\frac{k_1}{2k_3}\right)^2 + \frac{k_1 k_4}{k_3 k_5}}\right)[C_2H_6]$

1. term has factor $[C_2H_6]$, both in the root have $[C_2H_6]^2$

<u>experiment</u> k_1 small $\Rightarrow$ smallest power counter the root which is $\sqrt{k_1}$ is kept, higher powers (like $\sim k_1$) are neglected

$\rightarrow [C_2H_5^\cdot] = \sqrt{\frac{k_1 k_4}{k_3 k_5}}[C_2H_6]$

$\rightarrow [H^\cdot] = \frac{k_1[C_2H_6]}{k_5[C_2H_5^\cdot)} = \frac{k_1}{k_5}\left(\sqrt{\frac{k_1 k_4}{k_3 k_5}}\right)^{-1} = \sqrt{\frac{k_1 k_3}{k_4 k_5}}$

$\frac{k_1}{k_5}\sqrt{\frac{k_3 k_5}{k_1 k_4}}$

$$-\frac{d[C_2H_6]}{dt} = \left[k_1 + k_2[CH_3^\cdot] + k_4\sqrt{\frac{k_1 k_3}{k_4 k_5}}\right][C_2H_6] \quad (31) - 8$$

$$- k_5[C_2H_5^\cdot][H^\cdot] \rightarrow \sqrt{\frac{k_1 k_3 k_4}{k_5}}$$

before: $-\frac{d[C_2H_6]}{dt} = k_1[C_2H_6] + k_2[CH_3^\cdot][C_2H_6]$

it was found:

$$+ k_4[C_2H_6][H^\cdot] - k_5[H^\cdot][C_2H_5^\cdot]$$

$$k_5[C_2H_5^\cdot][H^\cdot] = k_5\sqrt{\frac{k_1 k_4}{k_3 k_5}}[C_2H_6]\sqrt{\frac{k_1 k_3}{k_4 k_5}}\sqrt{\frac{k_1 k_3}{k_4 k_5}}$$

$$\sqrt{\frac{k_1 k_4 k_5^2}{k_3 k_5}} = \sqrt{\frac{k_1 k_4 k_5}{k_3}}$$

$$k_5[C_2H_5^\cdot][H^\cdot] = \sqrt{\frac{k_1 k_4 k_5}{k_3}}\sqrt{\frac{k_1 k_3}{k_4 k_5}}[C_2H_6]$$

$$= k_1\sqrt{\frac{k_4 k_5}{k_3}}\sqrt{\frac{k_3}{k_4 k_5}}[C_2H_6] = k_1[C_2H_6]$$

$\Rightarrow$ since $-k_5[C_2H_5^\cdot][H^\cdot]$ cancels with $k_1[C_2H_6]$

$$\Rightarrow -\frac{d[C_2H_6]}{dt} = \left[k_2[CH_3^\cdot] + \sqrt{\frac{k_1 k_3 k_4}{k_5}}\right][C_2H_6]$$

it was $[CH_3^\cdot] = \frac{2k_1}{k_2} \Rightarrow k_2[CH_3^\cdot] = 2k_1$

can be neglected (k_1 small from experiment)

$\rightarrow k_1 \ll \sqrt{k_1}$

$$\rightarrow -\frac{d[C_2H_6]}{dt} = \sqrt{\frac{k_1 k_3 k_4}{k_5}}[C_2H_6]$$

1. order in C_2H_6 = experiment

$\theta = f(p)$ at $T = \text{const.}$:

adsorption isotherm

Langmuir model: $R(g) + M(\text{surface}) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} RM(\text{surface})$

$R(g)$: gas-phase reactant, $M(\text{surface})$ free surface site

$RM(\text{surface})$ occupied surface site

Approximations in Langmuir model:

1. Adsorption only in 1 Layer (monolayer)
2. Uniform surface (all sites equal)
3. No interactions between occupied sites

rate of adsorption $\sim k_a$ ~~fractio~~ no. of free sites $N(1-\theta)$

$\sim P$ No.

N: total # of surface sites

$$\left(\frac{d\theta}{dt}\right)_{ads} = k_a P N (1-\theta)$$

desorption: $\left(\frac{d\theta}{dt}\right)_{des} = -k_d \theta N$

equilibrium: $\frac{d\theta}{dt} = 0 = k_a P N(1-\theta) - k_d N\theta = 0$

$(k_a P N + k_d N)\theta = k_a P N$ all with θ added to the left

$$\rightarrow \quad \theta = \frac{k_a P}{k_a P + k_d} = \frac{(k_a/k_d)P}{(k_a/k_d)P + 1} = \frac{KP}{1+KP} \qquad K = \frac{k_a}{k_d}$$

K equilibrium constant for adsorption

Transp: Langmuir isotherms

if k_d increases $\Rightarrow$ K decreases $\Rightarrow$ P must be larger for $\theta = 1$ (full monolayer coverage)

$$\left(\frac{d\theta}{dt}\right)_{des}$$

At equilibrium, the change in fractional cove

$$\frac{d\theta}{dt} = 0 = k_a PN$$

$$(k_a PN + k_d N)\theta$$

$$\theta = \frac{k_a P}{k_a P + k_d}$$

$$\theta = \frac{}{K}$$

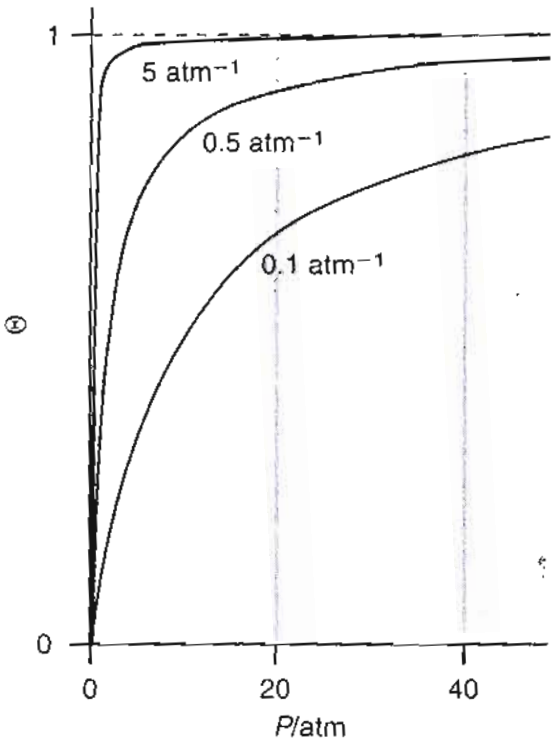


FIGURE 36.11
Langmuir isotherms for a range of k_a/k_d.

where K is the equilibrium constant defined for the **Langmuir isotherm.** Figure 36.11 values of k_a/k_d. Notice that as the rate co adsorption, higher pressures must be emplo be understood based on the competition bet orption. Correspondingly, if the rate consta becomes independent of pressure for lower v

In many instances adsorption is accomp process that is referred to as **chemisorption** an

$$R_2(g) + 2M\,(surface) =$$

Kinetic analysis of this mechanism (see the en ing expression for θ:

$$\theta = \frac{(KP}{1 + (K}$$

Inspection of Equation (36.84) reveals that the strate weaker pressure dependence compared t

[redacted]

competition between adsorption and desorption if k_d is large (more R escapes surface)

after adsorption dissociation can happen (chemisorption)

$$R_2(g) + 2M(\text{surface}) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} 2\,RM(\text{surface})$$

then $\theta = \dfrac{\sqrt{KP}}{1+\sqrt{KP}}$ $\quad \dfrac{1}{\theta}$ vs $\dfrac{1}{\sqrt{P}}$ straight line

$$\text{slope} = \frac{1}{\sqrt{K}}$$

$$\frac{1}{\theta} = \frac{1}{\sqrt{KP}} + 1$$

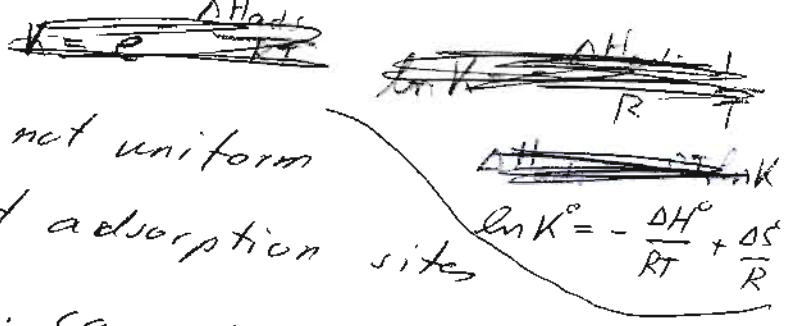
→ weaker P dependence

Transp.

different isotherms → $K = f(T)$

→ van't Hoff plot $\ln K$ vs $\frac{1}{T}$ straight line

$$\text{slope} = -\frac{\Delta H_{ads}}{R}$$



1) surfaces in general not uniform
   → different kinds of adsorption sites
2) rate of ads. and des. can depend on occupation of near by sites
3) ads. molecules can diffuse over the surface
   → more complicated mechanisms than the Langmuir ones are needed

Example for adsorption calculation next class

mparison of the isotherms predicted using nondissociative and dissociative mechanisms rresponding to the same ratio of k_a/k_d. Finally, different Langmuir isotherms can be col- ted and evaluated over a range of temperatures to determine K as a function of T. With s information, a van't Hoff plot of $\ln K$ versus $1/T$ should provide a straight line of slope $\Delta H_{ads}/R$. Through this analysis, the enthalpy of adsorption ΔH_{ads} can be determined.

The assumptions employed in the Langmuir model may not be rigorously obeyed in ıl heterogeneous systems. First, surfaces are generally not uniform, resulting in the :sence of more than one type of adsorption site. Second, the rate of adsorption and sorption may depend on the occupation state of nearby adsorption sites. Finally, it s been established that adsorbed molecules can diffuse on the surface and then sorb corresponding to a kinetic process of adsorption that is more complicated than : Langmuir mechanism envisions.

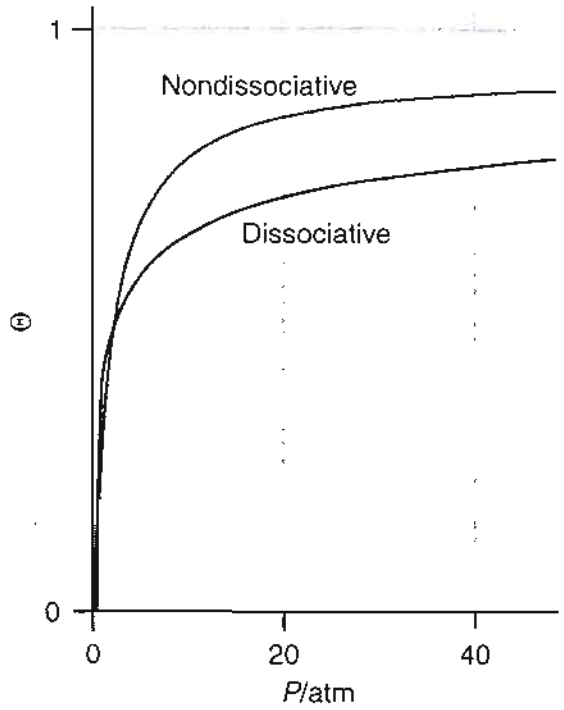


FIGURE 36.12
Comparison of Langmuir isotherms for nondissociative and dissociative adsorption with $k_a/k_d = 0.5\ \text{atm}^{-1}$.

XAMPLE PROBLEM 36.2

e following data were obtained for the adsorption of Kr on charcoal at 193.5 K. ing the Langmuir model, construct the adsorption isotherm, and determine V_m and : equilibrium constant for adsorption/desorption.

V_{ads} ($\text{cm}^3\ \text{g}^{-1}$)	P (Torr)
5.98	2.45
7.76	3.5
10.1	5.2
12.35	7.2
16.45	11.2
18.05	12.8
19.72	14.6
21.1	16.1

- Example for Adsorption
- Radical Chain Reactions

example: emperical data of V_{ads} (adsorbed volume) at different pressures

V_{ads} (cm^3/g)	5.98	7.76	10.1	12.35	16.45	18.05	19.72	21.1
P(Torr)	2.45	3.5	5.2	7.2	11.2	12.8	14.6	16.1

at 193.5 K

plot (linear regression) the Langmuir isotherm and determine V_m (mono layer occupation) and K

$$\theta = \frac{V_{ads}}{V_m}$$

plot of V_{ads} vs P → isotherm

Transp. Langmuir works for Kr on charcoal

reciprocal plot: $\theta = \frac{KP}{1+KP}$

$$\rightarrow \frac{1}{\theta} = 1 + \frac{1}{KP} \qquad \frac{1}{\theta} = \frac{V_m}{V_{ads}}$$

$$\frac{1}{V_{ads}} = \frac{1}{V_m} + \frac{1}{KV_m}\frac{1}{P}$$

$\frac{1}{V_{ads}}$ or vs $\frac{1}{P}$: straight line slope $= \frac{1}{KV_m}$

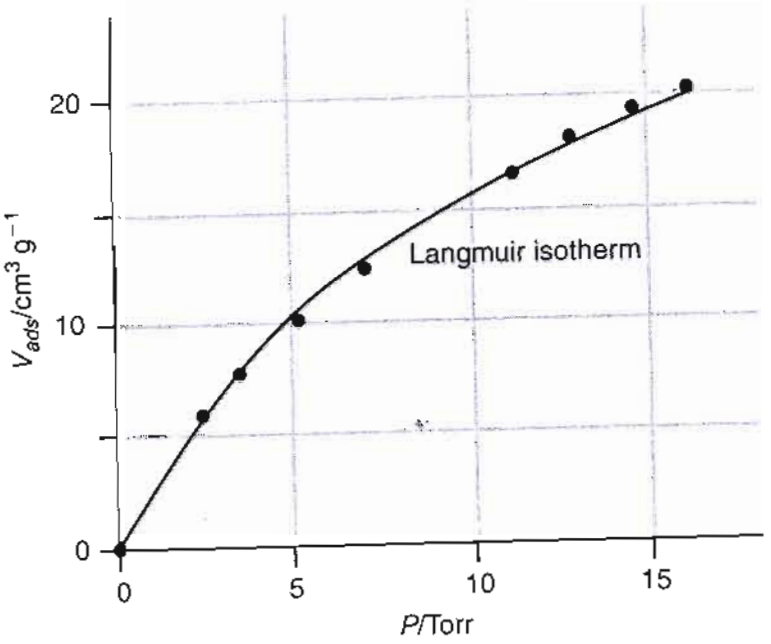
intercept $= \frac{1}{V_m}$ Transp. of plot

intercept $= \frac{1}{V_m} = 0.0293\ g/m^3 \rightarrow V_m = 34.1\ cm^3/g$

slope $= 0.3449\ \frac{Torr\,g}{cm^3} \rightarrow K = 8.38 \cdot 10^{-2}\ \frac{1}{Torr}$

Solution

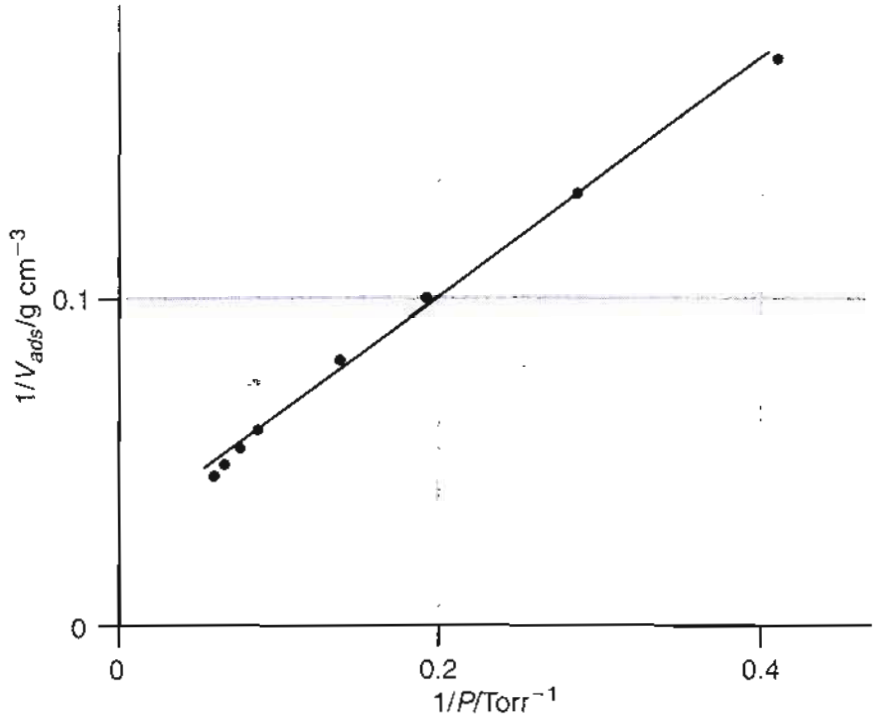
The fractional coverage is related to the experimentally measured V_{ads}. The adsorption isotherm is given by a plot of V_{ads} versus P, which can be compared to the behavior predicted by Equation (36.83) as illustrated here:



Although the comparison of the adsorption isotherm to Equation (36.83) illustrates that the Langmuir model is consistent with the adsorption of Kr on charcoal, determination of the Langmuir parameters is difficult because parameters such as V_m are unknown. This information is more readily determined by using the reciprocal of Equation (36.83):

$$\frac{1}{V_{ads}} = \left(\frac{1}{KV_m}\right)\frac{1}{P} + \frac{1}{V_m}$$

This equation demonstrates that a plot of $(V_{ads})^{-1}$ versus $(P)^{-1}$ should yield a straight line with slope equal to $(KV_m)^{-1}$ and y intercept equal to $(V_m)^{-1}$. A plot of the data in reciprocal form with the best fit line is shown next:



The y intercept obtained from the best fit line is 0.0293 g cm^{-3} such that $V_m = 34.1$ cm^3 g^{-1}. The slope of the best fit line is 0.3449 Torr g cm^{-3}. Using V_m determined from the y intercept, K is found to be 8.38×10^{-2} Torr^{-1}.

Radical Chain Reactions

radicals: molecules with 1 or more unpaired electrons

triplet O_2: biradical

because of the unpaired electrons, radicals are usually extremely reactive

1934 Rice & Herzberg could show that the behavior of many organic reactions is consistent with radicals in the mechanism

(example: decomposition of ethane:

overall: $C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)$

also small amounts of CH_4 are formed

initiation: $C_2H_6 \xrightarrow{k_1} 2\,CH_3^{\bullet}$

$^{\bullet}$ is for 1 unpaired electron

propagation $CH_3^{\bullet} + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5^{\bullet}$

$C_2H_5^{\bullet} \xrightarrow{k_3} C_2H_4 + H^{\bullet}$ (1)

$H^{\bullet} + C_2H_6 \xrightarrow{k_4} C_2H_5^{\bullet} + H_2$ (2)

termination $H^{\bullet} + C_2H_5^{\bullet} \xrightarrow{k_5} C_2H_6$

here: overall reaction from propagation reactions (1) and (2)

initiation step: radicals are produced from reactants

here: 1. step: $2\,CH_3^{\bullet}$ radicals produced from C_2H_6

radicals react with almost all other molecules

→ non-radical byproducts in small amounts, like CH_4

Finally: termination step

2 radicals combine to a non-radical product

complex mechanism with 5 steps, but rather simple rate law

consumption of ethane:

$$-\frac{d[C_2H_6]}{dt} = k_1[C_2H_6] + k_2[CH_3\cdot][C_2H_6] + k_4[C_2H_6][H\cdot] - k_5[H\cdot][C_2H_5\cdot]$$

1 term from each step that involves C_2H_6

rate of consumption: + when C_2H_6 is consumed
- when " " formed

$CH_3\cdot$: reactive intermediate $\Rightarrow$ SSA

$$\frac{d[CH_3\cdot]}{dt} \overset{SSA}{=} 0 = \underline{2k_1[C_2H_6]} - k_2[CH_3\cdot][C_2H_6] \quad (1)$$

$$[CH_3\cdot] = \frac{2k_1}{k_2} \quad [C_2H_6] \text{ cancels}$$

2 at k_1 because each step forms 2 $CH_3\cdot$

rate of formation $\Rightarrow$ formation step +
consumption step -

for $C_2H_5\cdot$ and $H\cdot$ also SSA:

$$\frac{d[C_2H_5\cdot]}{dt} = 0 = k_2[CH_3\cdot][C_2H_6] - k_3[C_2H_5\cdot] + \underline{k_4[H\cdot][C_2H_6]} - \underline{k_5[H\cdot][C_2H_5\cdot]} \quad (2)$$

$$\frac{d[H\cdot]}{dt} = 0 = \underline{k_3[C_2H_5\cdot]} - \underline{k_4[H\cdot][C_2H_6]} - \underline{k_5[H\cdot][C_2H_5\cdot]} \quad (3)$$

(1) + (2) + (3): underlined stays, rest cancels

$$0 = 2k_1[C_2H_6] - 2k_5[H\cdot][C_2H_5\cdot]$$

$$[H\cdot] = \frac{k_1[C_2H_6]}{k_5[C_2H_5\cdot]}$$

into (3): $0 = k_3[C_2H_5^\cdot] - k_4[C_2H_6]\frac{k_1[C_2H_6]}{k_5[C_2H_5^\cdot]} - k_5[C_2H_5^\cdot]\frac{k_1[C_2H_6]}{k_5[C_2H_5^\cdot]}$ (3') +

$$0 = k_3[C_2H_5^\cdot] - k_4 k_1 \frac{[C_2H_6]^2}{k_5[C_2H_5^\cdot]} - k_1[C_2H_6] \quad \Big| \cdot \frac{[C_2H_5^\cdot]}{k_3}$$

$$0 = [C_2H_5^\cdot]^2 - \frac{k_4 k_1 [C_2H_6]^2}{k_5 \cdot k_3} - \frac{k_1}{k_3}[C_2H_6][C_2H_5^\cdot]$$

with $x = [C_2H_5^\cdot]$ $\quad a = \frac{k_4 k_1 [C_2H_6]^2}{k_5 k_3}$ $\quad b = \frac{k_1}{k_3}[C_2H_6]$

this is $x^2 - a - bx = 0$

$$x^2 - bx - a = 0$$

$$x_{1,2} = \frac{1}{2}\left(b \pm \sqrt{b^2 + 4a}\right) = \frac{1}{2}b \pm \sqrt{\left(\frac{b}{2}\right)^2 + a}$$

($-(-b)$; $-4(-a)$)

$x = [C_2H_5^\cdot]$ must be $>0 \Rightarrow$ + not −

$$[C_2H_5^\cdot] = \left(\frac{k_1}{2k_3} + \sqrt{\left(\frac{k_1}{2k_3}\right)^2 + \frac{k_1 k_4}{k_3 k_5}}\right)[C_2H_6]$$

1. term has factor $[C_2H_6]$, both in the root have $[C_2H_6]^2$

<u>experiment</u> k_1 small $\Rightarrow$ smallest power under the root which is $\sqrt{k_1}$ is kept, higher powers (like $\sim k_1$) are neglected

$$\rightarrow [C_2H_5^\cdot] = \sqrt{\frac{k_1 k_4}{k_3 k_5}}[C_2H_6]$$

$$\rightarrow [H^\cdot] = \frac{k_1[C_2H_6]}{k_5[C_2H_5^\cdot]} = \frac{k_1}{k_5}\left(\sqrt{\frac{k_1 k_4}{k_3 k_5}}\right)^{-1} = \sqrt{\frac{k_1 k_3}{k_4 k_5}}$$

$$\frac{k_1}{k_5}\sqrt{\frac{k_3 k_5}{k_1 k_4}}$$

$$-\frac{d[C_2H_6]}{dt} = \left[k_1 + k_2[CH_3^\cdot] + k_4\sqrt{\frac{k_1 k_3}{k_4 k_5}}\right][C_2H_6] \quad (31) - 8$$

$$- k_5[C_2H_5^\cdot][H^\cdot] \rightarrow \sqrt{\frac{k_1 k_3 k_4}{k_5}}$$

before: $-\frac{d[C_2H_6]}{dt} = k_1[C_2H_6] + k_2[CH_3^\cdot][C_2H_6]$

it was found:

$$+ k_4[C_2H_6][H^\cdot] - k_5[H^\cdot][C_2H_5^\cdot]$$

$$k_5[C_2H_5^\cdot][H^\cdot] = k_5\sqrt{\frac{k_1 k_4}{k_3 k_5}}[C_2H_6]\sqrt{\frac{k_1 k_3}{k_4 k_5}}$$

$$\sqrt{\frac{k_1 k_4 k_5^2}{k_3 k_5}} = \sqrt{\frac{k_1 k_4 k_5}{k_3}}$$

$$k_5[C_2H_5^\cdot][H^\cdot] = \sqrt{\frac{k_1 k_4 k_5}{k_3}}\sqrt{\frac{k_1 k_3}{k_4 k_5}}[C_2H_6]$$

$$= k_1\sqrt{\frac{k_4 k_5}{k_3}}\sqrt{\frac{k_3}{k_4 k_5}}[C_2H_6] = k_1[C_2H_6]$$

$\Rightarrow$ since $-k_5[C_2H_5^\cdot][H^\cdot]$ cancels with $k_1[C_2H_6]$

$$\Rightarrow -\frac{d[C_2H_6]}{dt} = \left[k_2[CH_3^\cdot] + \sqrt{\frac{k_1 k_3 k_4}{k_5}}\right][C_2H_6]$$

it was $[CH_3^\cdot] = \frac{2k_1}{k_2} \Rightarrow k_2[CH_3^\cdot] = 2k_1$

can be neglected (k_1 small from experiment)

$\rightarrow k_1 \ll \sqrt{k_1}$

$$\rightarrow -\frac{d[C_2H_6]}{dt} = \sqrt{\frac{k_1 k_3 k_4}{k_5}}[C_2H_6]$$

1. order in C_2H_6 = experiment

$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$ (31) g

exp.: $\frac{1}{2}$ order in Cl_2

consistent with the following mechanism?

$$Cl_2 \xrightarrow{k_1} 2Cl\cdot$$

$$Cl\cdot + CH_4 \xrightarrow{k_2} HCl + CH_3\cdot$$

$$CH_3\cdot + Cl_2 \xrightarrow{k_3} CH_3Cl + Cl\cdot$$

$$2Cl\cdot \xrightarrow{k_4} Cl_2$$

rate of formation of HCl:

$$R = \frac{d[HCl]}{dt} = k_2[Cl\cdot][CH_4]$$

$Cl\cdot$ is intermediate and must be eliminated

$$\frac{d[Cl\cdot]}{dt} = 2k_1[Cl_2] - k_2[Cl\cdot][CH_4] + k_3[CH_3\cdot][Cl_2] - 2k_4[Cl\cdot]^2$$

SSA used for $CH_3\cdot$:

$$\frac{d[CH_3\cdot]}{dt} = 0 = -k_3[CH_3\cdot][Cl_2] + k_2[Cl\cdot][CH_4]$$

$$\rightarrow [CH_3\cdot] = \frac{k_2[Cl\cdot][CH_4]}{k_3[Cl_2]}$$

SSA for $Cl\cdot$

$$0 = 2k_1[Cl_2] - k_2[Cl\cdot][CH_4] + k_3[CH_3\cdot][Cl_2] - 2k_4[Cl\cdot]^2$$

$$0 = 2k_1[Cl_2] - k_2[Cl\cdot][CH_4] + k_3\frac{k_2[Cl\cdot][CH_4]}{k_3[Cl_2]}[Cl_2] - 2k_4[Cl\cdot]^2$$

$$0 = 2k_1[Cl_2] - k_2[Cl\cdot][CH_4] + k_2[Cl\cdot][CH_4] - 2k_4[Cl\cdot]^2$$

$$0 = 2k_1[Cl_2] - 2k_4[Cl\cdot]^2$$

$$\rightarrow [Cl\cdot] = \sqrt{\frac{k_1}{k_4}[Cl_2]}$$

$$R = \frac{d(CH_3Cl)}{dt} = k_2[Cl\cdot][CH_4]$$

$$= k_2\sqrt{\frac{k_1}{k_4}[Cl_2]}\,[CH_4]$$

$\frac{1}{2}$ order in Cl_2 as in experiment

1 order in CH_4

$\frac{3}{2}$ order overall

$$k_{apparent} = k_2\sqrt{\frac{k_1}{k_4}}$$

$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$ (31) ~~=0~~ (32) -1

exp.: $\frac{1}{2}$ order in Cl_2

consistent with the following mechanism?

$$Cl_2 \xrightarrow{k_1} 2Cl\cdot$$

$$Cl\cdot + CH_4 \xrightarrow{k_2} HCl + CH_3\cdot$$

$$CH_3\cdot + Cl_2 \xrightarrow{k_3} CH_3Cl + Cl\cdot$$

$$2Cl\cdot \xrightarrow{k_4} Cl_2$$

rate of formation of HCl:

$$R = \frac{d[HCl]}{dt} = k_2[Cl\cdot][CH_4]$$

$Cl\cdot$ is intermediate and must be eliminated

$$\frac{d[Cl\cdot]}{dt} = 2k_1[Cl_2] - k_2[Cl\cdot][CH_4] + k_3[CH_3\cdot][Cl_2] - 2k_4[Cl\cdot]^2$$

SSA used for $CH_3\cdot$:

$$\frac{d[CH_3\cdot]}{dt} = 0 = -k_3[CH_3\cdot][Cl_2] + k_2[Cl\cdot][CH_4]$$

$$\rightarrow [CH_3\cdot] = \frac{k_2[Cl\cdot][CH_4]}{k_3[Cl_2]}$$

SSA for $Cl\cdot$

$$0 = 2k_1[Cl_2] - k_2[Cl\cdot][CH_4] + k_3[CH_3\cdot][Cl_2] - 2k_4[Cl\cdot]^2$$

$$0 = 2k_1[Cl_2] - k_2[Cl\cdot][CH_4] + k_3\frac{k_2[Cl\cdot][CH_4]}{k_3[Cl_2]}[Cl_2] - 2k_4[Cl\cdot]^2$$

$$0 = 2k_1[Cl_2] - k_2[Cl\cdot][CH_4] + k_2[Cl\cdot][CH_4] - 2k_4[Cl\cdot]^2$$

$$0 = 2k_1[Cl_2] - 2k_4[Cl\cdot]^2$$

(31) – 70

3.2 – 2.

$$\rightarrow [Cl\cdot] = \sqrt{\frac{k_1}{k_4}[Cl_2]}$$

$$R = \frac{d[CH_3Cl]}{dt} = k_2[Cl\cdot][CH_4]$$

$$= k_2\sqrt{\frac{k_1}{k_4}[Cl_2]}\,[CH_4]$$

$\frac{1}{2}$ order in Cl_2 as in experiment

1 order in CH_4

$\frac{3}{2}$ order overall

$$k_{apparent} = k_2\sqrt{\frac{k_1}{k_4}}$$

- Photochemistry: Photophysical Processes

A monomer of a polymer can be activated with a radical initiator

yielding a monomer radical

reaction with another monomer ~~radical~~

→ dimer

reaction with again another one

→ trimer → → → polymer chain:

$I \xrightarrow{k_i} 2R\cdot$ initiation, initiator I

$R\cdot + M \xrightarrow{k_1} R + M\cdot$ activated monomer

then chain propagation → dimer and so on

$M\cdot + M \xrightarrow{k_p} M_2\cdot$

$M_2\cdot + M \xrightarrow{k_p} M_3\cdot$

$M_{N-1}\cdot + M \xrightarrow{k_p} M_N\cdot$

k_p is assumed to be the same, independent of chain length

rate of activated monomer production ($M\cdot$):

$$\left(\frac{d[M\cdot]}{dt}\right)_{production} = 2\phi k_i [I]$$

ϕ probability for the generated radical (by initiator) to start a chain reaction

active oligomers can combine to terminate the chain reaction: 2 radicals → polymer:

terminations $M_N\cdot + M_M\cdot \xrightarrow{k_t} M_{M+N}$

also activated ~~can~~ monomers can combine and terminate the chain

→ rate of active monomer loss with k_t

$$\left(\frac{d[M\cdot]}{dt}\right)_{decay} = -2k_t[M\cdot]^2, \quad 2M\cdot \xrightarrow{k_t} M_2$$

→ the total rate of formation of activated monomers is the sum:

$$\frac{d[M\cdot]}{dt} = 2\phi k_i[I] - 2k_t[M\cdot]^2$$

M· is an intermediate → SSA

$$2\phi k_i[I] - 2k_t(M\cdot)^2 = 0$$

$$\rightarrow [M\cdot] = \sqrt{\frac{\phi k_i[I]}{k_t}}$$

but if monomer consumption by the chain reaction:

$$\frac{d[M\cdot]}{dt} = -k_p[M\cdot][M]$$

$$= -k_p\sqrt{\frac{\phi k_i}{k_t}}\sqrt{[I]}[M]$$

rate of monomer consumption is of $\frac{3}{2}$ order

$\frac{1}{2}$ in initiator, 1 in the monomer

a measure of polymerization efficiency is the kinetic chain length ν

ν = average # of ~~monomer~~ monomers in the ~~poly~~ polymer chain over # of activated monomers produced:

$$\nu = \frac{-\left(\frac{d[M\cdot]}{dt}\right)_{propagation}}{\left(\frac{d[M\cdot]}{dt}\right)_{production}}$$

$$= \frac{k_p [M\cdot][M]}{2\phi k_i [I]}$$

$$= (SSA)\ \frac{k_p [M\cdot][M]}{2k_t [M\cdot]^2} \qquad SSA: 2\phi k_i [I] = 2k_t [M\cdot]^2$$

$$= \frac{k_p [M]}{2k_t [M\cdot]} = \frac{k_p [M]}{2k_t \sqrt{\frac{\phi k_i}{k_t}}\sqrt{[I]}}$$

since $[M\cdot] = \sqrt{\frac{\phi k_i}{k_t}}\sqrt{[I]}$

$$= \frac{k_p [M]}{2\sqrt{\phi k_i k_t}\sqrt{I}}$$

decrease of initiation and termination rate constants → longer chain, increase of ν

most easy: polymerizations done always with low initiator concentrations

(more easy is low [I], than change in k_i k_t)

low [I] keeps the number of activated monomers low (~~acti~~ too many ~~mach~~ activated monomers would terminate the chain reaction quickly)

Photochemistry

initiation of a reaction by absorption of a photon by an atom or molecule

→ photons act like reactants

photochemical reactions are important (3c) - ①
as / or in

- first event in vision: photon absorbed by the visual pigment rhodopsin
- Photosynthesis: conversion of light energy into chemical energy by plants and bacteria
- many photochemical reaction take place in the atmosphere like ozone, O_3, production and decomposition.

when a molecule absorbs a photon, the energy of the photon is transferred to the molecule

Planck equation: $E_{Photon} = h\nu = \frac{hc}{\lambda}$

Planck's constant, $h = 6.626 \cdot 10^{-34}\ Js$

speed of light in vacuum) $c = 2.998 \cdot 10^{8} \frac{m}{s}$

ν: frequency of light, λ wavelength of light

$c = \lambda\nu$ 1 mol Photons = 1 einstein

energy of 1 einstein of photons: $E_{einstein} = N_A h\nu$

intensity of light: $\frac{\text{energy}}{(\text{area} \cdot \text{time})}$

Watt: $1\ W = 1\ \frac{J}{s}$

→ intensity unit: $1\ \frac{W}{cm^2}$

simplest photochemical reaction:

reactant absorbs photon → products

$$A \xrightarrow{h\nu} P$$

rate of reactant photoexcitation:

$$R = -\frac{d[A]}{dt} = \frac{I_{abs} \cdot 1000}{\ell}$$

r_{abs} $\frac{einstein}{(cm^2\ s)}$

l : optical path length which the light travels through the sample in cm

factor 1000 : to yield the unit of the rate in $\frac{M}{s}$

from : $1L = 1\,dm^3 = 1000\,cm^3 \rightarrow$ factor of 1000

Lambert-Beer law : intensity of light transmitted through a sample (outgoing intensity after passing through the sample) :

$$I_{trans} = I_0\, 10^{-\varepsilon l [A]}$$

I_0 : incident intensity before passing the sample of A

ε : molar absorptivity of A which is changing with wavelength λ

$I_{abs} = I_0 - I_{tran}$ absorbed intensity

$$\rightarrow I_{abs} = I_0 \left(1 - 10^{-\varepsilon l [A]}\right)$$

series expansion of the power of 10 :

$$10^{-\varepsilon l [A]} = 1 - 2.303\,\varepsilon l [A] + (2.303\,\varepsilon l [A])^2 \cdot \frac{1}{2!} \mp \cdots$$

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$$-\frac{d[A]}{dt} = \frac{I_0 \cdot 2.303\,\varepsilon\, l\,[A]}{l} = I_0\, 2.303\,[A]\varepsilon$$

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conversion to $1M = 1\,\frac{mol}{L}$ must be done

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Sometimes, it is better to refer to molecules instead of concentrations

$$-\frac{d}{dt}\left(n_A/V\right) = I_0 \cdot 2.303\,\varepsilon\,\frac{n_A}{V}$$

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+ number of molecules $A = n_A N_A$, N_A Avogadro's number

$$-\frac{d}{dt}\, n_A N_A = I_0\, 2.303\,\frac{\varepsilon}{N_A}\, n_A N_A$$

ε : molar absorptivity

ε/N_A absorptivity per molecule

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A number of A molecules

$\rightarrow A = A_0 e^{-I_0 \sigma_A t}$

absorption cross section of A: $\sigma_A = 2.303 \frac{\varepsilon}{N_A}$

rate constant for absorption $k_a = I_0 \sigma_A$

I_0 in # of photons / ($cm^2 s$)

light absorption can occur when an energy level difference of the molecule is equal to $h\nu$

Transp. Jablonski diagram:

shows e⁻ electronic transition, vertical: energy

ground state: singlet ($2S+1=1$) S_0, 1. excited singlet S_1

lowest triplet T_1, singlet: all e⁻ paired $\Rightarrow S=0$, $2S+1=1$

$2S+1$ multiplicity

Triplet: 2 e⁻ unpaired $\rightarrow S=1 \rightarrow 2S+1=3$

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exception: O_2 with T_0 ground state

bold horizontal lines: lowest vibrational level of a state, lighter lines: higher vibrational states, Each vibrational level has a rotational level structure which is left out.

solid and wavy lines connect the states

solid lines: light emission fluorescence ($S \rightarrow S$) and phosphorescence ($S \leftrightarrow T$ delayed: forbidden)

Wavy lines: Intersystem crossing, Internal conversion

VR = Vibrational Relaxation: transitions without light emission

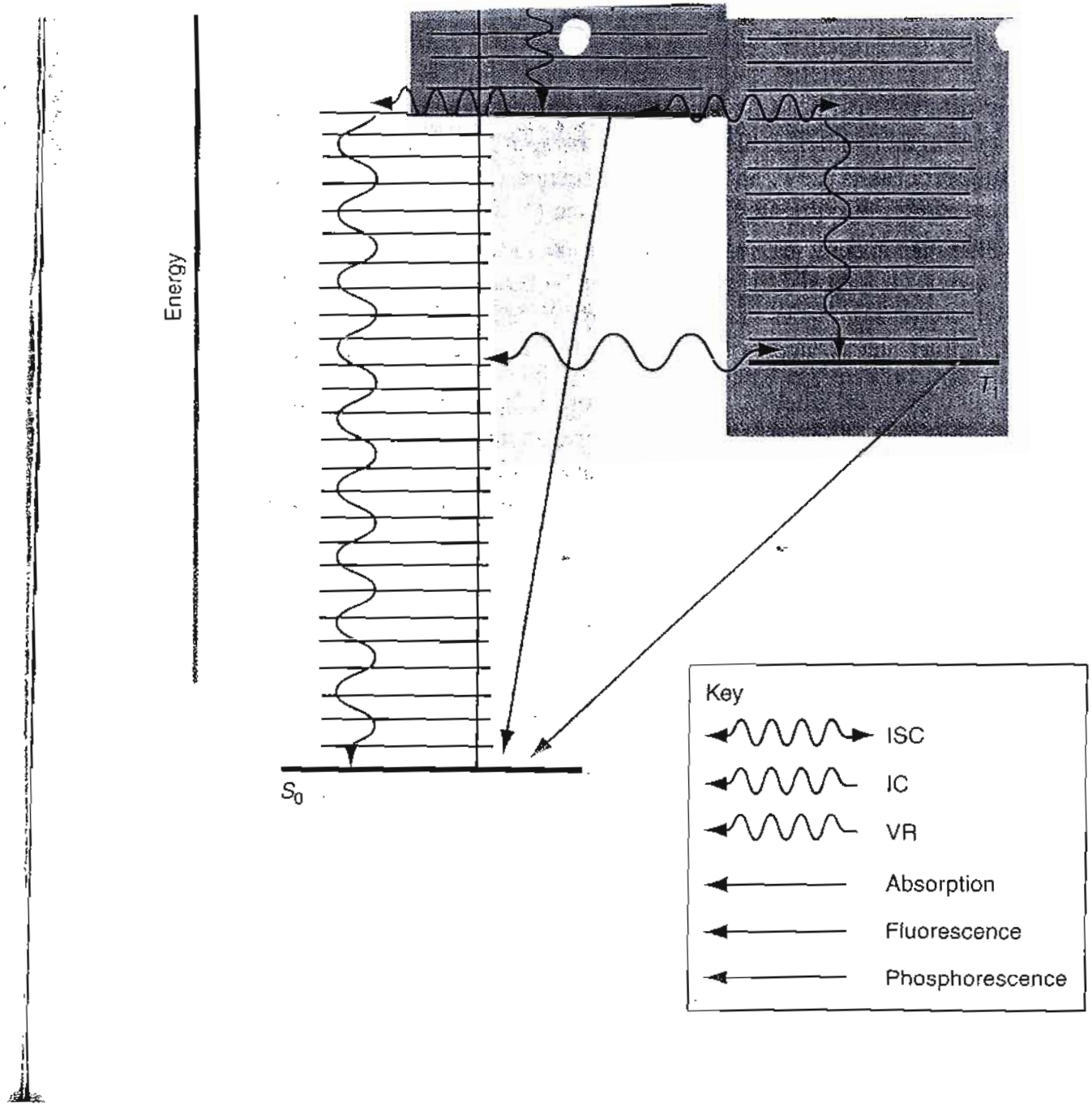

FIGURE 36.17
A Jablonski diagram depicting variou photophysical processes, where S_0 is the ground electronic singlet state, S_1 the first excited singlet state, and T_1 i first excited triplet state. Radiative processes are indicated by the straigh lines. The nonradiative processes of i system crossing (ISC), internal conve (IC), and vibrational relaxation (VR) indicated by the wavy lines.

- Radical Chain Polymerization

- Photochemistry: Photophysical Processes

A monomer of a polymer can be activated with a radical initiator

yielding a monomer radical

reaction with another monomer ~~radical~~

→ dimer

reaction with again another one

→ trimer → → → polymer chain:

$I \xrightarrow{k_i} 2R\cdot$ initiation, initiator I

$R\cdot + M \xrightarrow{k_1} R + M\cdot$ activated monomer

then chain propagation → dimer and so on

$M\cdot + M \xrightarrow{k_p} M_2\cdot$

$M_2\cdot + M \xrightarrow{k_p} M_3\cdot$

$M_{N-1}\cdot + M \xrightarrow{k_p} M_N\cdot$

k_p is assumed to be the same, independent of chain length

rate of activated monomer production ($M\cdot$):

$$\left(\frac{d[M\cdot]}{dt}\right)_{production} = 2\phi k_i [I]$$

ϕ probability for the generated radical (by initiator) to start a chain reaction

active oligomers can combine to terminate the chain reaction 2 radicals → polymer:

termination: $M_N\cdot + M_M\cdot \xrightarrow{k_t} M_{M+N}$

also activated monomers can combine and terminate the chain

→ rate of active monomer loss with k_t

$$\left(\frac{d[M\cdot]}{dt}\right)_{decay} = -2k_t[M\cdot]^2, \quad 2M\cdot \xrightarrow{k_t} M_2$$

→ the total rate of formation of activated monomers is the sum:

$$\frac{d[M\cdot]}{dt} = 2\phi k_i[I] - 2k_t[M\cdot]^2$$

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$$2\phi k_i[I] - 2k_t(M\cdot)^2 = 0$$

$$\rightarrow [M\cdot] = \sqrt{\frac{\phi k_i[I]}{k_t}}$$

but if monomer consumption by the chain reaction:

$$\frac{d[M\cdot]}{dt} = -k_p[M\cdot][M]$$

$$= -k_p\sqrt{\frac{\phi k_i}{k_t}}\sqrt{[I]}[M]$$

rate of monomer consumption is $\frac{3}{2}$ order

$\frac{1}{2}$ in initiator, 1 in the monomer

a measure of polymerization efficiency is the kinetic chain length ν

ν = average # of monomers in the polymer chain over # of activated monomers produced:

$$\nu = \frac{-\left(\frac{d[M\cdot]}{dt}\right)_{propagation}}{\left(\frac{d[M\cdot]}{dt}\right)_{production}}$$

$$= \frac{k_p [M\cdot][M]}{2\phi k_i [I]}$$

$$= (SSA)\ \frac{k_p [M\cdot][M]}{2k_t [M\cdot]^2} \qquad SSA: 2\phi k_i [I] = 2k_t [M\cdot]^2$$

$$= \frac{k_p [M]}{2k_t [M\cdot]} = \frac{k_p [M]}{2k_t \sqrt{\frac{\phi k_i}{k_t}}\sqrt{[I]}}$$

since $[M\cdot] = \sqrt{\frac{\phi k_i}{k_t}}\sqrt{[I]}$

$$= \frac{k_p [M]}{2\sqrt{\phi k_i k_t}\sqrt{I}}$$

decrease of initiation and termination rate constants → longer chain, increase of ν

most easy: polymerizations done always with low initiator concentrations

(more easy is low [I], than change in k_i, k_t)

low [I] keeps the number of activated monomers low (~~acti~~ too many ~~much~~ activated monomers would terminate the chain reaction quickly)

Photochemistry

initiation of a reaction by absorption of a photon by an atom or molecule

→ photons act like reactants

photochemical reactions are important (3c) - Ø
as / or in

- first event in vision: photon absorbed by the visual pigment rhodopsin
- Photosynthesis: conversion of light energy into chemical energy by plants and bacteria
- many photochemical reaction take place in the atmosphere like ozone, O_3, production and decomposition.

When a molecule absorbs a photon, the energy of the photon is transferred to the molecule

Planck equation: $E_{Photon} = h\nu = \frac{hc}{\lambda}$

Planck's constant, $h = 6,626 \cdot 10^{-34}\ Js$

speed of light in vacuum) $c = 2,998 \cdot 10^{8} \frac{m}{s}$

ν: frequency of light, λ wavelength of light

$c = \lambda\nu$ 1 mol Photons = 1 einstein

energy of 1 einstein of photons: $E_{einstein} = N_A h\nu$

Intensity of light: $\frac{\text{energy}}{(\text{area} \cdot \text{time})}$

Watt: $1\ W = 1\ \frac{J}{s}$

→ intensity unit: $1\ \frac{W}{cm^2}$

simplest photochemical reaction:

reactant absorbs photon → products

$$A \xrightarrow{h\nu} P$$

rate of reactant photoexcitation:

$$R = -\frac{d[A]}{dt} = \frac{I_{abs} \cdot 1000}{\ell}$$

r_{abs} $\frac{einstein}{(cm^2\ s)}$

l : optical path length which the light travels through the sample in cm

factor 1000 : to yield the unit of the rate in $\frac{M}{s}$

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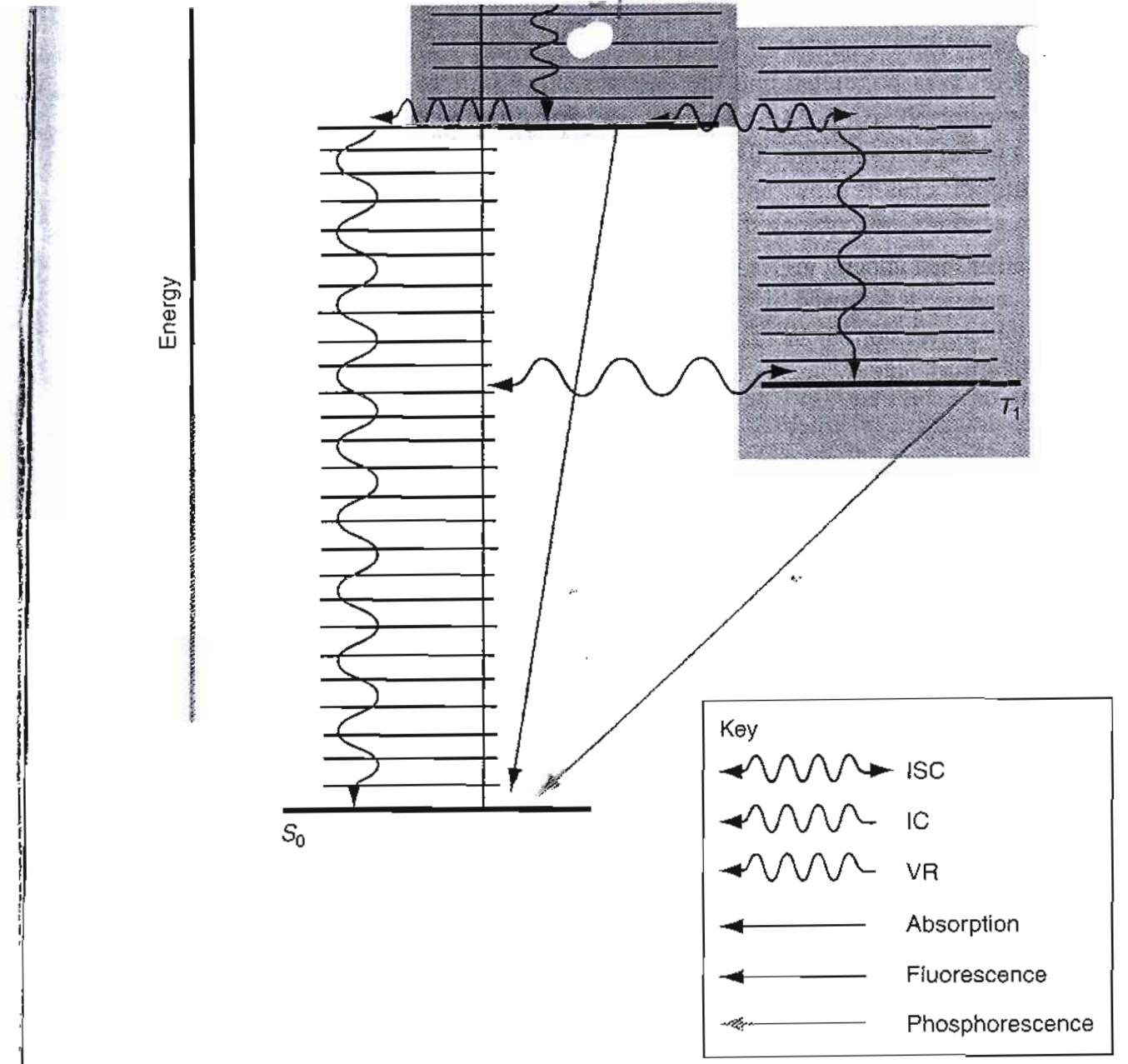


FIGURE 36.17
A Jablonski diagram depicting various photophysical processes, where S_0 is the ground electronic singlet state, S_1 is the first excited singlet state, and T_1 is t first excited triplet state. Radiative processes are indicated by the straight lines. The nonradiative processes of int system crossing (ISC), internal convers (IC), and vibrational relaxation (VR) a indicated by the wavy lines.

- Discussion of the Jablonski Diagram
- Fluorescence and fluorescence quenching
- Fluorescence life-time τ_f (measurement)

Absorption of light decreases population of S_0
= depletion of S_0

⇒ population of S_1 is increased, usually in higher vibrational levels than the lowest one of S_1

the intensity is given by the Frank-Condon factor (= transition probability):
direct $S_0 \rightarrow T_1$ excitation is ~~tro~~ forbidden ~~by~~
by spin selection rules

$$\mu_{gv\,JM,\,ev'J'M'} = \int \Psi_g \chi_{gv} \Theta_{JM} \underline{\mu} \Psi_e \chi_{ev'} \Theta_{J'M'} \, d\tau_{el} \, d\tau_{vib} \cdot d\tau_{rot}$$

Ψ_e, Ψ_g: electronic wave functions of ground (g) and excited state (e)

χ_{gv}, $\chi_{ev'}$: vibrational wave functions in the two electronic states

Θ_{JM}, $\Theta_{J'M'}$: rotational wave functions in the vibrational states

$\underline{\mu}_{ge}$: from integration over $d\tau_{el}$, assuming that Ψ_e and Ψ_g do not depend on vibrational levels

$$\underline{\mu}_{gv\,JM,\,ev'J'M'} = \int \Theta_{JM} \underline{\mu}_{ge} \Theta_{J'M'} \, d\tau_{rot} \cdot S_{vv'}$$

$S_{vv'} = \int \chi_{gv} \chi_{ev'} \, d\tau_{vib}$ also vibrational states assume independent of rotational states

When S_1 is populated: relaxation or thermal equilibration occurs very fast ($\approx 100\,fs$) → Boltzmann distribution for population of vibrational levels

ΔE_{vib} is assumed to be so large, that only the lowest vibrational state is highly populated in S_1

decay of S_1 along 3 pathways:

path 1 $S_1 \rightarrow S_0 + h\nu$ fluorescence $k_f[S_1]$

radiative decay → photon emission = spontaneous emission

path 2 intersystem crossing (isc) which populates T_1

change of e^- spin ⇒ isc is ~~forbidd~~ forbidden and ~~is~~ thus much slower than fluorescence

but is comparative in systems where T is already populated

after isc: relaxation to lowest T_1 vibrational level

isc: $S_1 \rightarrow T_1$ $k^S_{isc}[S_1]$ from T_1 radiative decay can occur, but much slower than fluorescence:

phosphorescence: $T_1 \rightarrow S_0 + h\nu$ forbidden

($\approx 10^{-6}$ s, while $S_1 \rightarrow S_0$ happens in $\approx 10^{-9}$ s)

phosphorescence: $T_1 \rightarrow S_0 + h\nu$ $k_p[T_1]$

path 3 $S_1 \rightarrow S_0$ can happen without photon emission:

internal conversion (ic) or non-radiative decay

can also happen from T_1

internal conversion: $S_1 \rightarrow S_0$ $k_{ic}[S_1]$

intersystem crossing: $T_1 \rightarrow S_0$ $k^T_{isc}[T_1]$

Transp: rate constants in the processes

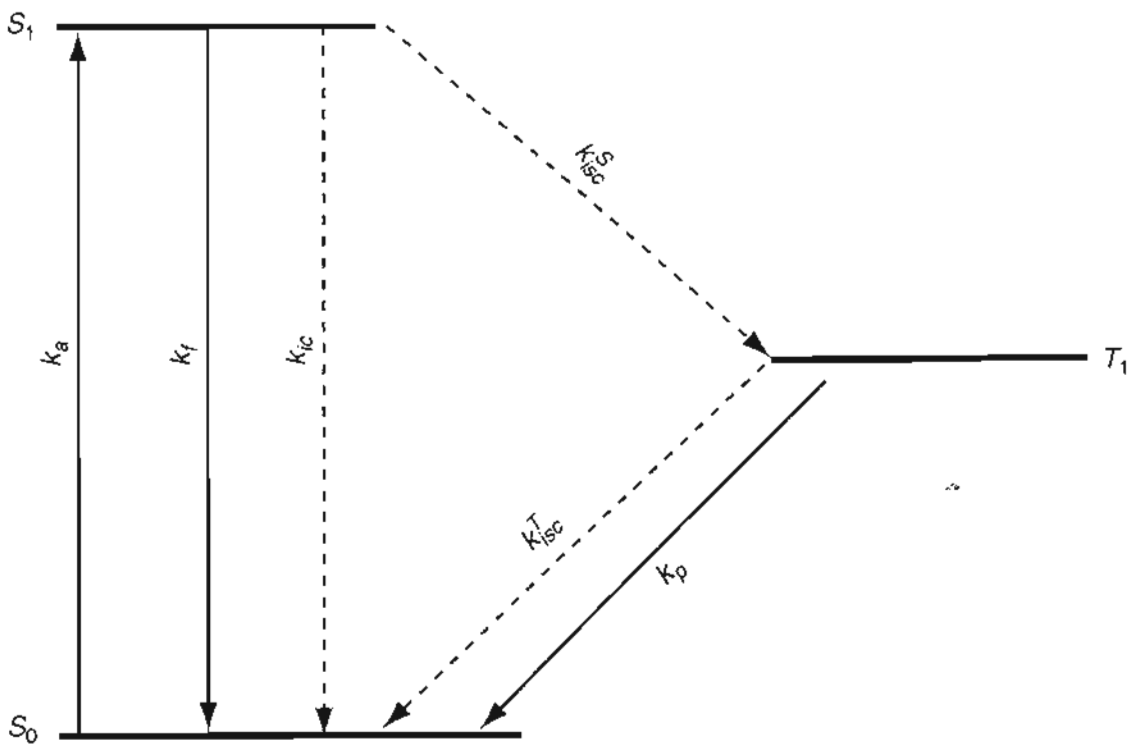


FIGURE 36.18
Kinetic description of photophysical processes. Rate constants are indicated for absorption (k_a), fluorescence (k_f), internal conversion (k_{ic}), intersystem crossing from S_1 to T_1 (k^S_{isc}), intersystem crossing from T_1 to S_0 (k^T_{isc}), and phosphorescence (k_p).

36.9.2 Fluorescence and Fluorescence Quenching

The photophysical processes outlined in Table 36.1 are present for any molecular system. To study excited state lifetimes, another photophysical process is introduced: **collisional quenching.** In this process, a collision occurs between a species Q and a molecule populating an excited electronic state. The result of the collision is the

collisional quenching collision partner takes excitation energy, no photon emission

⇒ adding of a quencher Q is needed:

$$S_1 + Q \xrightarrow{k_q} S_0 + Q$$

$$R_q = -\frac{d[S_1]}{dt} = k_q[S_1][Q]$$

S_1 can be seen as intermediate: $[S_1]$ = const. made by constant illumination ⇒ SSA

$$\frac{d[S_1]}{dt} = k_a[S_0] - (k_f + \underbrace{k_{isc}^s + k_{ic}^s}_{+k_{ic}^s} + k_q[Q])[S_1] = 0$$

→ fluorescence lifetime:

$$\frac{1}{\tau_f} = k_f + k_{isc}^s + k_q[Q] + k_{ic}^s$$

$$\frac{d[S_1]}{dt} = 0 = k_a[S_0] - \frac{1}{\tau_f}[S_1]$$

$$\rightarrow [S_1] = k_a[S_0]\tau_f$$

fluorescence intensity $\therefore I_f \sim [S_1]$, $I_f = k_f[S_1]$

with SSA result: $I_f = k_a[S]_0 k_f \tau_f$

$$k_f\tau_f = \frac{k_f}{k_f + k_{ic} + k_{isc}^s + k_q[Q]} = \Phi_f$$

Φ_f: quantum yield for fluorescence

S_1 decay is like a branching reaction

Φ_f = ratio of rate constant k_f to Σ of all processes

similar to reaction yield defined before (⇐35.8) in parallel reactions discussion

ϕ_f also defined as

$$\frac{\#\text{ of fluorescence photons}}{\#\text{ of photons absorbed}}$$

$$\frac{1}{I_f} = \frac{1}{k_a[S_0]}\left[1 + \frac{k_{ic} + k_{isc}^S}{k_f}\right] + \frac{k_q[Q]}{k_a[S_0]k_f}$$

if $\phi_f \to 1$, so that $k_f \gg k_{ic}$, $k_f \gg k_{isc}^S$, then

I_f is measured as function of $[Q]$

usually given relative to I_f^0 (without Q)

$$\frac{I_f^0}{I_f} = 1 + \frac{k_q}{k_f}[Q] \quad , \quad I_f^0 = k_a[S_0]\phi_f$$

(with $\phi_f \approx 1$, where $\phi_f = k_f \tau_f$)

Transp. Stern - Volmer plot $\frac{I_f^0}{I_f}$ vs $[Q]$

$$\text{slope} = \frac{k_q}{k_f}$$

Measurement of τ_f

before continous illumination was assumed

often easier is use of a short light ~~pb~~ pulse

if pulsetime short as compared to S_1 decay rate, then $I_f(t)$ shows directly the decay of S_1

pulses as short as 4 fs ($4 \cdot 10^{-15}$ s) possible

→ excitation in times much shorter than the S_1 decay

after excitation in short time, $[S_1]$ will be smaller than its SSA value

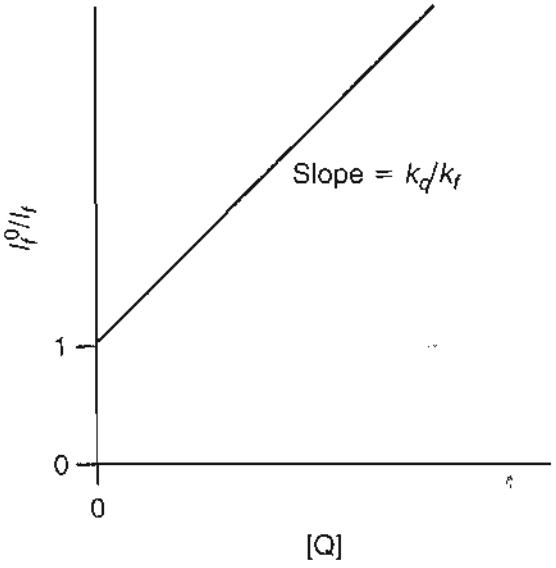


FIGURE 36.19
A Stern–Volmer plot. Intensity of fluorescence as a function of quencher concentration is plotted relative to the intensity in the absence of quencher. The slope of the line provides a measure of the quenching rate constant relative to the rate constant for fluorescence.

$$I_f = k_a$$

Inspection of the last two factors in E relationship:

$$k_f \tau_f = \frac{\qquad}{k_f + k_{ic} +}$$

The product of the fluorescence rate const the radiative rate constant divided by the s to the decay of S_1. In effect, S_1 decay can ratio of rate constants contained in Equati yield for fluorescence Φ_f, similar to th Section 35.8. The fluorescence quantum y emitted as fluorescence divided by the n this definition to Equation (36.165) demo will be large for molecules in which k_f is s corresponding to S_1 decay. Inverting Equa the following expression is obtained:

$$\frac{1}{I_f} = \frac{1}{k_a[S_0]}\left(1 + \frac{k}{}\right.$$

For a fluorophore with a quantum yield ap rescence quenching experiments, fluoresc [Q]. Measurements are generally perform sity observed in the absence of quencher I

$$\frac{I_f^0}{I_f} = 1$$

Equation (36.167) reveals that a plot of th [Q] will yield a straight line, with slope **Stern–Volmer plots,** an example of whic

36.9.3 Measurement of τ_f

In the development presented in the pre system of interest was subjected to con approximation could be applied to $[S_1]$. F toexcite the system with a temporally sh temporal duration of the pulse is short co this state can be measured directly by mo tion of time. Optical pulses as short as 4 f excitation on a timescale that is significan

After excitation by a temporally short in $[S_1]$ will be finite. In addition, the rate c

further: rate constant for absorption is $k_a \approx 0$

$$\rightarrow \frac{d[S_1]}{dt} = -(k_f + k_{ic} + k_{isc}^S + k_q[Q])[S_1]$$

$$= -\frac{[S_1]}{\tau_f}$$

$$\int_{[S_1]_0}^{[S_1]} \frac{d[S_1]}{[S_1]} = -\frac{1}{\tau_f}\int_0^t dt \rightarrow \ln\frac{[S_1]}{[S_1]_0} = -\frac{t}{\tau_f}$$

$$[S_1] = [S_1]_0 e^{-t/\tau_f}$$

$I_f \sim [S_1]$ decays exponentially with time constant τ_f

<u>when</u> $k_f \gg k_{ic}$ and $k_f \gg k_{isc}^S$

<u>then</u> $\frac{1}{\tau_f} \approx k_f + k_q[Q]$

$\lim_{k_f \gg k_{ic}, k_{isc}^S}$: $\tau_f = \frac{1}{k_f + k_q[Q]}$

→ measurement of fluorescence lifetime at known quencher concentration $[Q]$ + slope of a Stern-Volmer plot

<u>enough</u> to determine k_f and k_q

reciprocal equation:

$$\frac{1}{\tau_f} = k_f + k_q[Q]$$

$\frac{1}{\tau_f}$ vs $[Q]$ → straight line with slope = k_q and intercept = k_f

fluorescence of pyrene in solution with C_6Br_6 as quencher:

$[C_6Br_6]$ (mM)	0.5	1.0	2.0	3.0	5.0
τ_f	$2.66 \cdot 10^{-7}$ s	$1.87 \cdot 10^{-7}$	$1.17 \cdot 10^{-7}$	$8.50 \cdot 10^{-8}$	$5.51 \cdot 10^{-8}$
	266 ns	187 ns	117 ns	85.0 ns	55.1 ns

k_f, k_q ?

plot data as $\frac{1}{\tau_f}$ vs $[C_6Br_6]$

Transparency plot

linear regression fit (e.g. like with Excel in Lab)

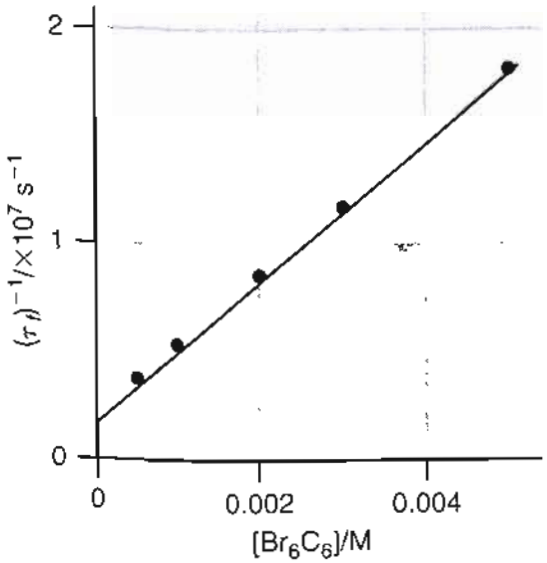
→ slope = $3.00 \cdot 10^9 \, s^{-1} = k_q = 3.00 \cdot 10^9 \frac{1}{10^9 \, ns} = 3.00 \, ns^{-1}$

intercept = $1.98 \cdot 10^6 \, s^{-1} = k_f = 1.96 \cdot 10^6 \frac{1}{10^6 \, \mu s} = 1.96 \, \mu s^{-1}$

0.0[illegible]5	2.66×10^{-7}
0.001	1.87×10^{-7}
0.002	1.17×10^{-7}
0.003	8.50×10^{-8}
0.005	5.51×10^{-8}

Solution

Using Equation (36.171), a plot of $(\tau_f)^{-1}$ versus [Q] for this system is as follows:



The best fit to the data by a straight line corresponds to a slope of $3.00 \times 10^9\ s^{-1}$, which is equal to k_q by Equation (36.171), and a y intercept of $1.98 \times 10^6\ s^{-1}$, which is equal to k_f.

- Single Molecule Fluorescence
- Fluorescence Resonance Energy Transfer (FRET)

Population change of the excited singlets, with time: $[S_1] = [S_1]_0 e^{-t/\tau_f}$

this is not for just 1 molecule, but for a collection (ensemble) of molecules

Transp. Single molecule fluorescence ~~measured~~ observed with a confocal tunneling microscope

excitation source and image occur at the same focal distances, so that fluorescence from the sample area which are not direct in ~~the~~ the focus can be rejected (taken out of picture)

laser excitation + efficient detectors → observation of single molecule fluorescence possible in a spatial extension of ~~the shown factors~~ of ≈ 300 nm (the beam area)

= fluorescence not from collection of molecules but from just one

Transp. I_f (fluorescence intensity) vs time from 1 molecule at continous photo excitation

The fluorescence is observed after the light is turned on:

molecule cycles between S_0 and S_1, because of the continous excitation and relaxation (fluorescence)

This goes on until the fluorescence suddenly stops

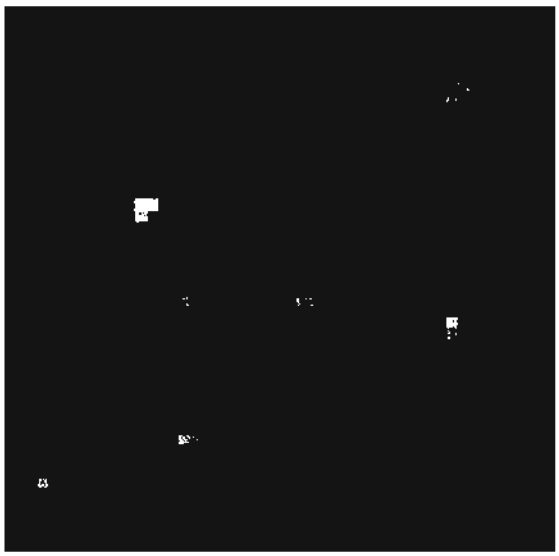


FIGURE 36.20
Microscope image of single Rhodamine B dye molecules on glass. Image was obtained using a confocal scanning microscope with the bright spots in the image corresponding to molecular fluorescence. The image dimension is 5 μm by 5 μm.

36.9.4 Single-Molecule Fluoresc

Equation (36.169) describes how the populat time, and the fluorescence intensity is predicte predicted behavior is for a collection, or ense troscopic techniques and advances in light de fluorescence from a single molecule. Figure cules obtained using a confocal scanning mi excitation source and image occur at identic from sample areas not directly in focus can be nation with laser excitation and efficient detec cence from a single molecule. In Figure fluorescence from single molecules. The spa mined by the diameter of the light beam at the

What does the fluorescence from a single Instead of a population of molecules in S_1 bei rescence is derived from a single molecule. Fi cence intensity from a single molecule with cc observed after the light field is turned on, an due to photoexcitation and subsequent rela constant fluorescence intensity continues unti point, depopulation of the S_1 state results in th the molecule that does not fluoresce. Eventual times corresponding to the eventual recovery c with excitation resulting in the repopulation of continues until a catastrophic event occurs in cule is lost. This catastrophic event is referre irreversible photochemical conversion of the n

Clearly, the fluorescence behavior observ ent than the behavior predicted for an ensem field involves the application of single-molecu not reflected by the ensemble. Such studies ar dynamics from an ensemble of molecules ha In addition, molecules can be studied in isola dow into the connection between molecular a

36.9.5 Fluorescence Resonance

Another fluorescence quenching technique in chromophore to another thereby reducing th photoexcited chromophore and correspondi mophore. This process, known as **fluorescen** has been extensively used to measure the str

Clearly, the fluorescence behavior observed in Figure 36.21 is dramatically different than the behavior predicted for an ensemble of molecules. Current interest in this field involves the application of single-molecule techniques to elucidate behavior that is not reflected by the ensemble. Such studies are extremely useful for isolating molecular dynamics from an ensemble of molecules having inherently inhomogeneous behavior. In addition, molecules can be studied in isolation of the bulk, thereby providing a window into the connection between molecular and ensemble behavior.

36.9.5 Fluorescence Resonance Energy Transfer

Another fluorescence quenching technique involves the transfer of excitation from one chromophore to another thereby reducing the excited-state population of the initially photoexcited chromophore and correspondingly the fluorescence from this chromophore. This process, known as **fluorescence resonance energy transfer,** or FRET, has been extensively used to measure the structure and dynamics of many biological

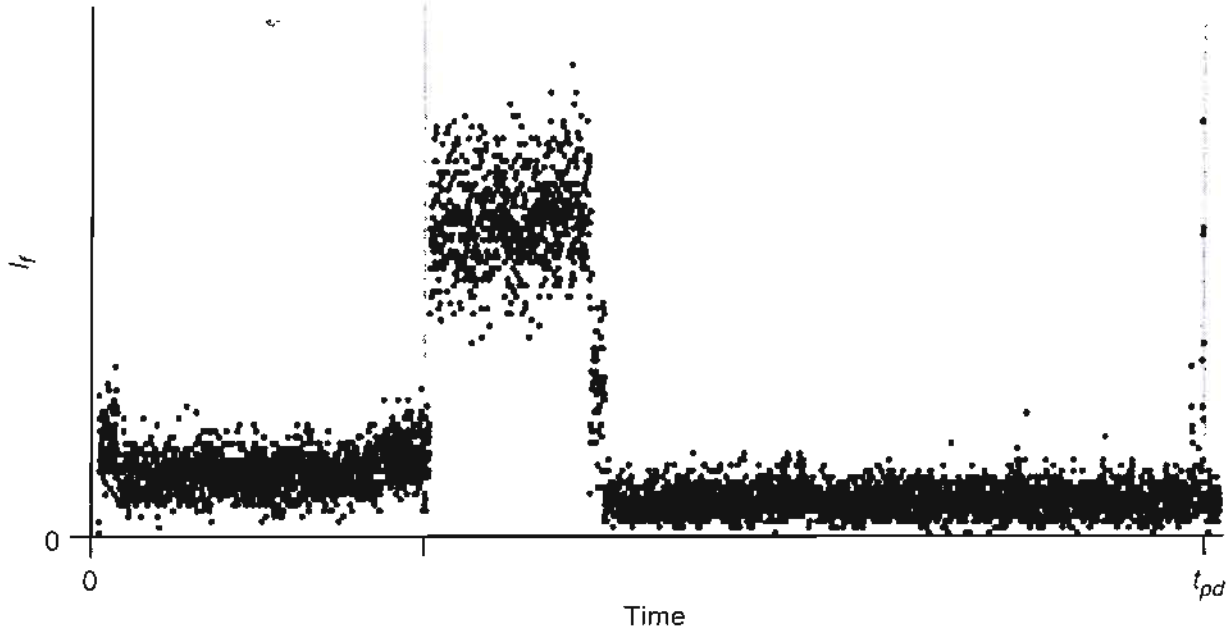


FIGURE 36.21
Fluorescence from a single Rhodamine B dye molecule. Steady illumination of the single molecule occurs at t_{on}, resulting in fluorescence, I_f. The fluorescence continues until decay of the S_1 state leads to population of a nonfluorescent state. At the end of the time axis, a brief period of fluorescence is observed corresponding to decay of the nonfluorescent state to populate S_0 followed by photoexcitation, resulting in the population of S_1 and fluorescence. However, this second period of fluorescence ends abruptly due to photodestruction of the molecule as evidenced by the absence of fluorescence after the decay event (t_{pd}).

Then depopulation of S_1 happens to $S_1 \rightarrow T_1$ or another state which does not fluorence later, when S_0 is populated again by relaxation from T_1 or higher states, excitation yields S_1 again and fluorescence happens again, until the molecule is photo destructed (irreversible conversion to a non-fluorescence active other molecule)

single molecule fluorescence very different from prediction for a collection of molecules: exponential fluorescence decay

useful for isolation of single molecule dynamics which can be erratic (random)

Fluorescence Resonant Energy Transfer (FRET)

This is also a quenching Technique, but by transfer of the excitation from one chromophor ("color" center which absorbs light and is the excitation donor) to another one

→ reduction of S_1 population in the donor and thus also of the donor fluorescence (FRET)

Observation of structures and dynamics of many biological systems

Mechanism to describe energy transfer between donor (D) and acceptor (A) chromophores:

$h\nu + D \xrightarrow{h\nu} D^*$ $\quad D^* \xrightarrow{k_f} D + h\nu$ | $D^* \xrightarrow{k_{nr}} D$ (non-radiative)

$D^* + A \xrightarrow{k_{FRET}} D + A^*$ $\quad A^* \xrightarrow{k_f} A + h\nu$

Initially S_1 of the Donor is populated

decay of $S_1(D)$ can be by fluorescence (k_f) or by non-radiative decay (nr: internal crossing and intersystem crossing) and by FRET leading to $S_1(A)$. decay of $S_1(A)$ via fluorescence of A as before with D.

Fluorsecence quantum yield ϕ_f:

$\phi_f = k_f \cdot (k_f + k_{nr})^{-1}$ parallel reaction (35. 8 last class)

FRET experiments are usually done with donors having high ϕ_f, so that $k_f \gg k_{nr} \Rightarrow \phi_f \to 1$

When there is A present, then: 1 more parallel reaction

$\phi_{f,FRET} = k_f (k_f + k_{nr} + k_{FRET})^{-1}$ ϕ_f of D !

efficiency of ~~energy~~ excitation transfer: $Eff = 1 - \frac{\phi_{f,FRET}}{\phi_f}$

when $k_{FRET} > k_f$, then Eff approaches 1 ($\phi_{fFRET} \to \frac{k_f}{k_{fret}} \ll \phi_f$)

Förster theory (late 1940s) $Eff \to 1 - \frac{k_f}{k_{FRT}} \to 1$ ($k_{FRET} \gg k_f$)

basic ideas: there is a dependence of Eff on the distance between D and A and there should be overlap between the absorption band of A not and the fluorescence band of D

→ S_0-S_1 energy gaps of D and A should be similar

also the relative orientation of D and A towards each other influences the Eff

r: distance between D and A

r_0: distance at which Eff = 0.5

r_0 is pair dependent and different for different DA pairs

further r_0 depends on the spectral overlap between D fluorescence band and A absorption band and the relative orientation of D to A

$$r_0(\text{Å}) = 8.79 \cdot 10^{-5} \left(\frac{\kappa^2 J \phi_f}{n^4} \right)^{1/6}$$

κ: relative orientation of transition dipole moments of D and A

$\kappa = 0$: D and A perpendicular $\kappa = 2$: parallel orientation of moments, $\kappa = \frac{1}{3}$ for random orientation

κ can be difficult to obtain ⇒ usually $\frac{1}{3}$, the random orientation value is used

ϕ_f: fluorescence quantum yield of D

n: refractive index of the medium in which FRET occurs

J: overlap between donor fluorescence and acceptor absorption

Transp. 49 r_0 values for FRET pairs

~~for use of FRET to measure distances~~

TABLE 36.2 Values of R_0 for FRET Pairs

Donor	Acceptor	r_0 (Å)
EDANS	DABCYL	33
Pyrene	Coumarin	39
Dansyl	Octadecylrhodamine	43
IAEDANS	Fluorescein	46
Fluorescein	Tetramethylrhodamine	55

IAEDANS = 5-(((2-iodoacetyl)amino)ethyl)amino)naphthalene-1-sulfonic acid

EDANS = 5-((2-aminoethyl)amino)naphthalene-1-sulfonic acid

DABCYL = 4-((4-(dimethylamino)phenyl)azo)benzoic acid, succinimidyl ester

generally assumed. Also in the expression for r_0, Φ_f is the fluorescence quantum yi the donor, n is the refractive index of the medium in which the transfer occurs, and J overlap integral between the donor fluorescence and acceptor absorption expressed as

$$J = \int \varepsilon_A(\lambda) F_D(\lambda) \lambda^4 d\lambda \qquad (36$$

In this expression, ε_A is the extinction coefficient of the acceptor, F_D is the flu cence spectrum of the donor, and the integral is performed over all wavelengths value of this integral, and correspondingly the value for r_0, will vary as a functi donor–acceptor pair. To illustrate the connection between donor emission, acc absorption, and the overlap integral, Figure 36.22 presents the emission and absor for the fluorescein/tetramethylrhodamine (TMR) FRET pair, and provides an illu tion of J for this FRET pair.

A collection of FRET donor–acceptor pairs are presented in Table 36.2. When

overlap between bands:

$$J = \int \varepsilon_A(\lambda)\, F_D(\lambda)\, \lambda^4\, d\lambda \quad \text{over all } \lambda$$

see Transp.

ε_A: extinction coefficient of A

F_D: fluorescence spectrum of D

DA distance dependence of Eff in Förster theory:

$$Eff \sim \frac{r_0^6}{r_0^6 + r^6}$$

For the use of FRET to measure distances one must choose a FRET pair with r_0 close to the distance of interest

$r \gg r_0$: $Eff(FRET) = 0 \Rightarrow \phi_f(D)$ is not changed because of A

$r_0 \gg r$: very high Eff for D^* quenching

→ little emission from D^*

use of FRET for structural changes by substrate binding to an enzyme?

The mutant form of an enzyme has a tyrosine (D) and a tryptophane (A) residue which are 11 Å apart

distance change (measurable by FRET) due to substrate?

fluorescence of tyrosine overlaps with absorption of tryptophane

→ FRET pair with $r_0 = 9$ Å

A collection of FRET donor ceptor pairs are presented in Table 36.2. When u FRET to measure distance, it is critical to choose a donor–acceptor pair whose r_0 is clo the length scale of interest. For distances where $r \gg r_0$, the FRET efficiency will be that the fluorescence quantum yield of the donor will be largely unaffected by the pres of the acceptor. In the other limit where $r_0 \gg r$, the quenching of the donor fluoresc from energy transfer will be extremely efficient and little emission from the donor wi observed. The overlap between the fluorescein emission and TMR absorption is shown

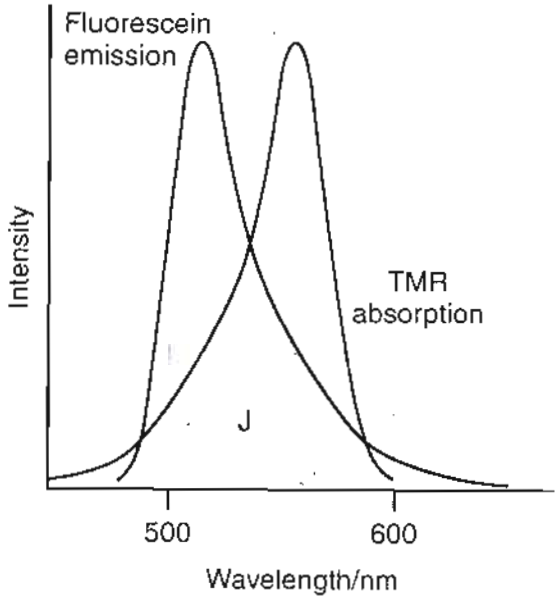


FIGURE 36.22
Illustration of the overlap integral ($J(\lambda)$) for the fluorescein/tetramethylrhodamine (TMR) FRET donor–acceptor pair.

EXAMPLE PROBLEM 36.5

You are designing a FRET experiment to determine the magnitude of the structural change introduced by substrate binding to an enzyme. Using site-specific mutagene you have constructed a mutant form of the enzyme that possesses a single tyrosine residue and a single tryptophan residue, and these residues are separated by 11 Å. would like to determine if the distance between these residues changes with substra binding. The fluorescence of tyrosine overlaps with the tryptophan absorption; ther fore, these two amino acids form a FRET pair for which $r_0 = 9$ Å, determined usir the absorption and emission spectra in combination with Equation (36.181). Calcul the FRET efficiency at 11 Å separation and how much this distance must increase i order for the efficiency to decrease by 20%, the experimental detection limit.

Solution

Using the initial separation distance and r_0, the efficiency is determined as follows:

$$Eff = \frac{r_0^6}{r_0^6 + r^6} = \frac{(9\ \text{Å})^6}{(9\ \text{Å})^6 + (11\ \text{Å})^6} = 0.23$$

The detection limit corresponds to $Eff = 0.18$. Solving for r yields:

$$Eff = 0.18 = \frac{r_0^6}{r_0^6 + r^6} = \frac{(9\ \text{Å})^6}{(9\ \text{Å})^6 + r^6}$$

1) What is FRET Eff at 11 Å distance?

2) r-increase for Eff decreased by 20%, the detection limit?

$$Eff = \frac{r_0^6}{r_0^6 + r^6} = \frac{9^6}{9^6 + 11^6} = 0.23$$

for 20% decrease Eff = 0.18 needed:

20% decrease ⇒ $0.8 \cdot 0.23 = 0.184$ (0.8 = 20% reduction in Eff; 1 → 0.8)

$$0.18 \frac{r_0^6}{r^6 + r_0^6} = \frac{(9Å)^6}{(9Å)^6 + r^6}$$

$$\frac{(9Å)^6}{0.18} = (9Å)^6 + r^6$$

$$0.18 = \frac{(9Å)^6}{(9Å)^6 + r^6}$$

$2.42 \cdot 10^6 Å^6 = r^6 \rightarrow r = 11.6 Å$

→ measurement only possible for small r change (detection limit)

→ r_0 of FRET pair must be close to r

important application of FRET: Photosynthesis, chloroplasts of green plants and ~~are~~ of algae (photosynthetic organelles) light harvesting pigments in their membranes absorb visible and near IR light

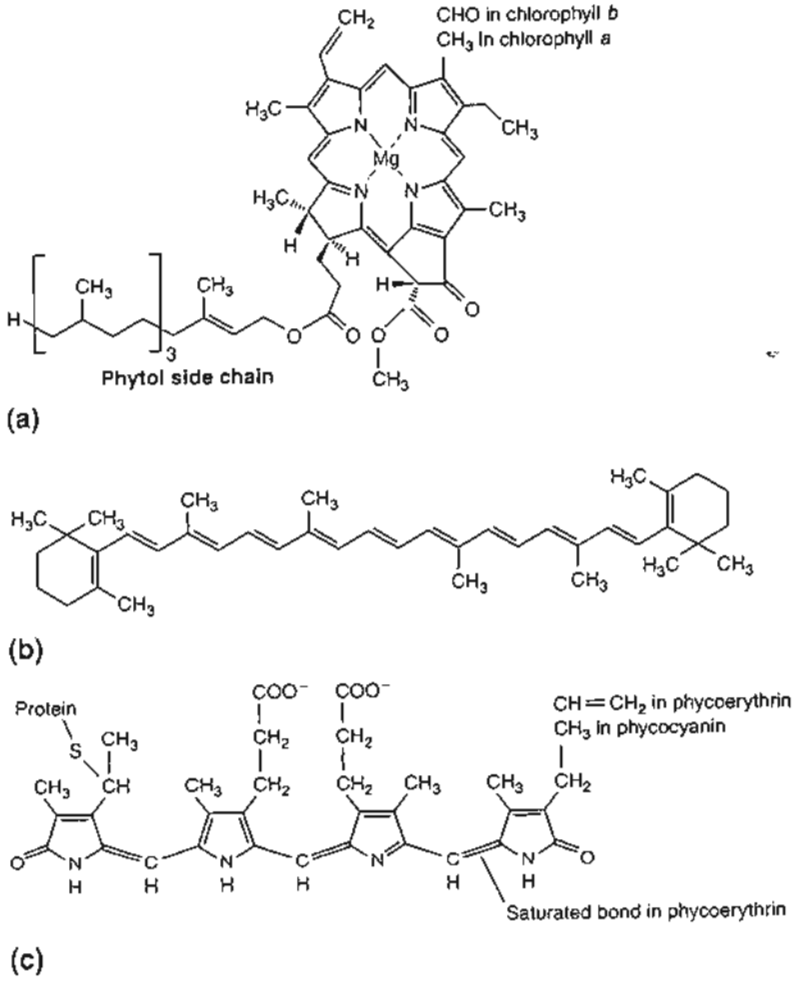
Transp: chlorophyll a and b as well as carotenoids like β-carotene are harvesting (collecting) light in light harvesting complexes of cylindrical structures

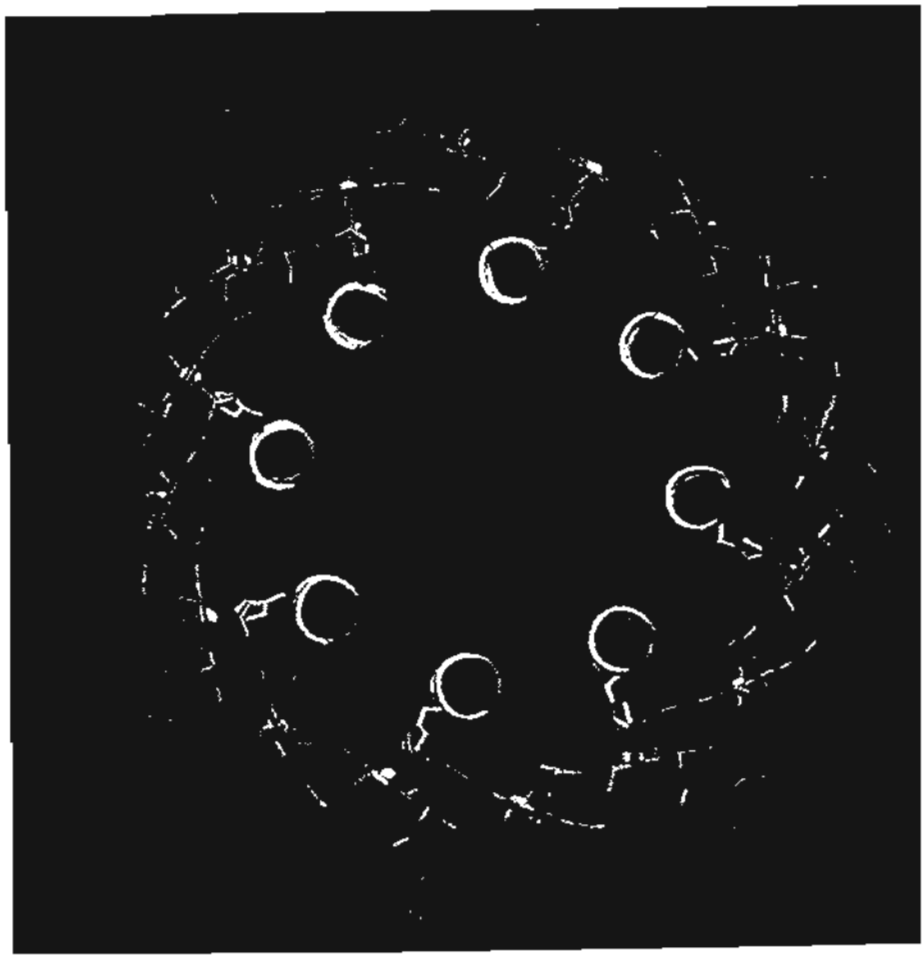
photon absorption: ~~in~~ transfer between pigments and out of the complex

mechanism used to absorb light and deliver the energy to the reaction center

intensity of sunlight is such that the probability of a chlorophyll molecule absorbing a photon is extremely modest. Incorporating numerous chlorophylls into a single light-harvesting complex provides for maximum collection efficiency. Resonance energy transfer results in the migration of absorbed photon energy from the light-harvesting complex to the reaction center as illustrated in Figure 36.24. Once the energy is transferred to the reaction center, it initiates an electron transfer process that is the start of

plant pigments. **Right.** X-ray crystal structure of the light-harvesting complex II of purple photosynthetic bacteria. The pigments, including bacteriochlorophyll (green) are held in this spatially complex arrangement by the surrounding protein (parts of which are shown in red and whi





The intensity of sun light is such that the probability of chlorophyll to absorb a photon is quite low

→ for large light collection efficiency many chlorophylls are involved in FRET in just 1 complex

→ absorbed photon energy moves from light harvesting pigment to reaction center.

Transp.

start of chem. reactions in photosynthesis:

energy arrives in reaction center

→ start of electron transfer processes

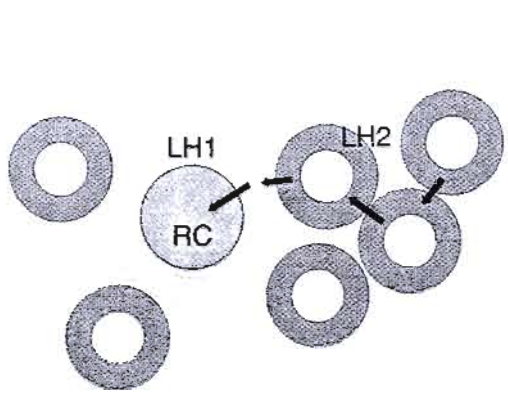


FIGURE 36.24
Schematic illustration of resonance energy transfer in photosynthesis where the energy initially obtained by photon absorption of a light-harvesting pigment is transferred to the reaction center through a series of resonance energy transfer steps.

the chemical transformations involved in photosynthesis. This electron t
will be further explored in the upcoming section on electron transfer.

36.9.6 Photochemical Processes

As discussed earlier, photochemical processes are distinct from photophy
in that the absorption of a photon results in chemical transformation of t
a photochemical process that occurs through the first excited singlet sta
chemical reaction can be viewed kinetically as another reaction branch,
decay of S_1. The corresponding expression for the rate corresponding to t
ical reaction branch is

$$R_{photochem.} = k^{S}_{photo}[S_1]$$

where k_{photo} is the rate constant for the photochemical reaction. For
processes occurring through T_1, a rate expression similar to Equation (
constructed as follows:

$$R_{photochem.} = k^{T}_{photo}[T_1]$$

The absorption of a photon can also provide sufficient energy to initiate a
tion. However, given the range of photophysical processes that occurs,
photon is not sufficient to guarantee that the photochemical reaction
extent of photochemistry is quantified by the overall **quantum yield** ϕ, w
as the number of reactant molecules consumed in photochemical proces
absorbed. The overall quantum yield can be greater than one, as demo
photoinitiated decomposition of HI(g) that proceeds by the following me

$$HI + h\nu \rightarrow H\cdot + I\cdot$$
$$H\cdot + HI \rightarrow H_2 + I\cdot$$
$$I\cdot + I\cdot \rightarrow I_2$$

In this mechanism, absorption of a photon results in the

- Photochemical Processes
~~- Catalysis~~ - Review 36

= Chemical Change involved

if that happens in excited state S_1, then the process is just another branch of S_1 decay

photochemical rate:

$$R_{Photchem.} = k^{S}_{Photchem} [S_1]$$

but the photochem. process can also happen through the excited triplet state T_1:

$$\rightarrow R_{Photchem.} = k^{T}_{Photchem.} [T_1]$$

for many photochemical processes 1 photon is <u>not</u> enough to start a chemical reaction

overall quantum yield:

$$\phi = \frac{\#\text{ of reactants consumed in time } t}{\#\text{ of photons absorbed in same time } t}$$

$\phi > 1$ is also possible

e.g.: $HI + h\nu \rightarrow H\cdot + I\cdot$

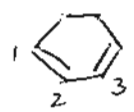
$H\cdot + HI \rightarrow H_2 + I\cdot$ <u>no chain reaction</u>

$2\,I\cdot \rightarrow I_2$

1 photon absorbed $\rightarrow$ 2 HI consumed

$\rightarrow \phi = 2$

1,3 cyclohexadiene + $h\nu$ $\rightarrow$ cis hexatriene



$=$ all π bonds <u>cis</u>

found in experiment:

2.5 mmol 1,3-cyclohexadiene are converted to cis-hexatriene in 27.0 s of irradiation with 100. W (Watt = $\frac{J}{s}$) of 280. nm light when all light is absorbed by the sample for conversion, what is ϕ

total photon energy absorbed:

$$E_{abs} = \text{Power} \cdot \Delta t = 100. \frac{J}{s} \cdot 27.0\,s = 2.70\,kJ$$

Photon energy:

$$E_{phot} = h\nu = \frac{hc}{\lambda} = \frac{6.626 \cdot 10^{-34}\,Js \cdot 2.998 \cdot 10^{8}\,\frac{m}{s}}{2.80 \cdot 10^{-7}\,m}$$

$$= 7.10 \cdot 10^{-19}\,J$$

no. of photons absorbed:

$$N_{Phot} = \frac{E_{abs}}{E_{Phot}} = \frac{2.70 \cdot 10^{3}\,J}{7.10 \cdot 10^{-19}\,J} = 3.80 \cdot 10^{21}$$

no. of moles of photons (einstein):

$$n_{Phot} = \frac{3.80 \cdot 10^{21}}{N_A} = \frac{3.80 \cdot 10^{21}}{6.022 \cdot 10^{23}} = 6.31 \cdot 10^{-3}\ \text{einstein}$$

$$\phi = \frac{2.50 \cdot 10^{-3}\ mol\ (reacted)}{6.31 \cdot 10^{-3}\ mol\ (photons\ absorbed)} = 0.396 \approx 0.40$$

biology: photo synthesis:

$$6\,CO_2(g) + 6\,H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6\,O_2(g)$$

$$\Delta G^\circ = +2870\ kJ$$

in green sulfur bacteria also CO_2 is used, but with H_2S and CH_2O production, not sugar

$$2\,H_2S(aq) + CO_2(g) \rightarrow CH_2O(g) + H_2O(l) + 2\,S(rhombic)$$

$$\Delta G^\circ = 88\ kJ$$

C in CO_2 is reduced

O in H_2O / S in H_2S oxidized

→ e^- transfer (Redox)

set-up of rate equations

$$\nu_A A + \nu_B B \xrightarrow{k} \nu_C C + \nu_D D$$

e.g. rate of formation of C:

k : product of reactant conc.

$$\frac{1}{\nu_C}\frac{d[C]}{dt} = k[A]^{\nu_A}[B]^{\nu_B} \qquad \nu_C > 0 \text{ for products}$$

rate of consumption of A:

$$-\frac{1}{|\nu_A|}\frac{d[A]}{dt} = k[A]^{\nu_A}[B]^{\nu_B} \qquad \nu_A < 0 \text{ for reactants}$$

$$A + B \xrightarrow{k} 2C$$

$$\Rightarrow \frac{1}{2}\frac{d[C]}{dt} = k[A][B]$$

$$\Rightarrow \frac{d[C]}{dt} = 2k[A][B]$$

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

mechanism

$$Cl_2 \xrightarrow{k_1} 2\,Cl\cdot$$

$$Cl\cdot + CH_4 \xrightarrow{k_2} HCl + CH_3\cdot$$

$$CH_3\cdot + Cl_2 \xrightarrow{k_3} CH_3Cl + Cl\cdot$$

$$2\,Cl\cdot \xrightarrow{k_4} Cl_2$$

$$\frac{d[HCl]}{dt} = k_2[Cl\cdot][CH_4]$$

↳ intermediate

= formed by k_1 and k_3

consumed by k_2 and k_4

intermediate = no reactant or product

but formed and consumed in the mechanism

$[Cl\cdot]$ must be eliminated for correct rate eq,

SSA: ~~$\frac{d[Cl\cdot]}{dt} = 0$~~ for $CH_3\cdot$: only in 2 reactions

$$\frac{d(CH_3\cdot)}{dt} = 0 = +k_2[Cl\cdot][CH_4] - k_3[CH_3\cdot][Cl_2]$$

formation ⊕ consumption ⊖

$$[CH_3\cdot] = \frac{k_2[Cl\cdot][CH_4]}{k_3[Cl_2]}$$

for $[Cl\cdot]$ → SSA:

$$\frac{d[Cl\cdot]}{dt} = 0 = 2k_1[Cl_2] - k_2[Cl\cdot][CH_4] + k_3[CH_3\cdot][Cl_2]$$

↑ 2 Cl· formed in 1 step

$-2k_4[Cl\cdot]^2$ 2 Cl· consumed in 1 step

$$0 = 2k_1[Cl_2] - k_2[Cl\cdot][CH_4] + k_3\frac{k_2[Cl\cdot][CH_4]}{k_3[Cl_2]}[Cl_2] - 2k_4[Cl\cdot]^2$$

$$0 = 2k_1[Cl_2] - k_2[Cl\cdot][CH_4] + k_3[Cl\cdot][CH_4] - 2k_4[Cl\cdot]^2$$

$$0 = 2k_1[Cl_2] - 2k_4[Cl\cdot]^2$$

$$[Cl\cdot] = \sqrt{\frac{k_1}{k_4}[Cl_2]}$$

$$[CH_3\cdot] = \frac{k_2\sqrt{\frac{k_1}{k_4}[Cl_2]}[CH_4]}{k_3[Cl_2]}$$

$$\rightarrow R = \frac{d(HCl)}{dt} = k_2\sqrt{\frac{k_1}{k_4}}\sqrt{[Cl_2]}[CH_4]$$

$\frac{1}{2}$ order in Cl_2

1. order in CH_4

$\frac{3}{2}$ order overall

$$k_{apparent} = k_2\sqrt{\frac{k_1}{k_4}}$$

$$R = \frac{k[A]}{k' + k''[A]}\frac{1}{[B]}$$

-1 order in B

no order in A

Catalyst's

$$S + C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SC$$ fast equilibrium

$$\Rightarrow K_1 = \frac{k_1}{k_{-1}} = \text{const.}$$

$$SC \xrightarrow{k_2} P + C$$

$$\frac{d[P]}{dt} = k_2[SC]$$ product formation

intermediate

$$K_1 = \frac{[S][C]}{[SC]} \Rightarrow [SC] = \frac{[S][C]}{K_1}$$

$$\rightarrow \frac{d[P]}{dt} = \frac{k_2[S][C]}{K_1}$$

Catalysis

$$S + C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SC$$

$$SC \xrightarrow{k_2} P + C$$

product formation $= R = \frac{d(P)}{dt} = k_2(SC)$ intermediate

SSA

$$\frac{d(SC)}{dt} = 0 = k_1(S)(C) - (k_{-1} + k_2)(SC)$$

$$(SC) = \frac{k_1}{k_{-1} + k_2}(S)(C) = \frac{(S)(C)}{K_m}$$

$$K_m = \frac{k_{-1} + k_2}{k_1}$$

$$\rightarrow R = \frac{k_2(S)(C)}{K_m}$$ into

with $(S)_o = (S) + (SC) + (P) - (S) =$

$$(C)_o = (C) + (SC) \Rightarrow (C) =$$

$$\rightarrow (SC) = \frac{(S)_o(C)_o}{(S)_o + (C)_o + K_m}$$

near $t = 0$

$$\rightarrow R_o = \frac{k_2(S)_o(C)_o}{(S)_o + (C)_o + K_m}$$

Pre-equilibrium

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \qquad \underline{\text{fast}}\ \text{equilibrium}$$

$$\Rightarrow K = \frac{k_1}{k_{-1}} = \text{const.}$$

$$I \xrightarrow{k_p} P$$

$$R = \frac{d(P)}{dt} = k_p [I] \qquad \text{intermediate}$$

$$K = \frac{[I]}{[A][B]}$$

$$\rightarrow [I] = K[A][B]$$

$$\rightarrow R = \frac{d(P)}{dt} = k_p K [A][B]$$

Lindemann

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M$$

$$A^* \xrightarrow{k_2} P$$

$$\frac{d(P)}{dt} = k_2 [A^*] \qquad \text{intermediate}$$

SSA $\quad \frac{d(A^*)}{dt} = 0 = k_1 [A][M] - (k_{-1}[M] + k_2)[A^*]$

$$[A^*] = \frac{k_1 [A][M]}{k_{-1}[M] + k_2} = k_{uni}[A]$$

$$k_{uni} = \frac{k_1 [M]}{k_{-1} [M] + k_2}$$

$$R = \frac{d[P]}{dt} = \frac{k_1 k_2 [M] [A]}{k_{-1} [M] + k_2}$$

$$= k_{uni} [A]$$

$$k_{uni} = \frac{k_1 k_2 [M]}{k_{-1} [M] + k_2}$$