Discussion questions

23.1 Identify any initiation, propagation, retardation, inhibition, and termination steps in the following chain mechanisms:

(a) 
1. \[ AH \rightarrow A^\cdot + H^\cdot \]
2. \[ A^\cdot \rightarrow B^\cdot + C \]
3. \[ AH + B^\cdot \rightarrow A^\cdot + D \]
4. \[ A^\cdot + B^\cdot \rightarrow P \]

(b) 
1. \[ A_2 \rightarrow A^\cdot + A^\cdot \]
2. \[ A^\cdot \rightarrow B^\cdot + C \]
3. \[ A^\cdot + P \rightarrow B^\cdot \]
4. \[ A^\cdot + B^\cdot \rightarrow P \]

23.2 Bearing in mind distinctions between the mechanisms of stepwise and chain polymerization, describe ways in which it is possible to control the molar mass of a polymer by manipulating the kinetic parameters of polymerization.

23.3 Discuss the features, advantages, and limitations of the Michaelis–Menten mechanism of enzyme action.

23.4 Distinguish between competitive, non-competitive, and uncompetitive inhibition of enzymes. Discuss how these modes of inhibition may be detected experimentally.

23.5 Distinguish between the primary quantum yield and overall quantum yield of a chemical
reaction. Describe an experimental procedure for the determination of the quantum yield.

23.6 Discuss experimental procedures that make it possible to differentiate between quenching by energy transfer, collisions, or electron transfer.

23.7 Summarize the main features of the Förster theory of resonance energy transfer. Then, discuss FRET in terms of Förster theory.

Exercises

In the following exercises and problems, it is recommended that rate constants are labelled with the number of the step in the proposed reaction mechanism, and any reverse steps are labelled similarly but with a prime.

23.1a Derive the rate law for the decomposition of ozone in the reaction $2 \text{O}_3 (g) \rightarrow 3 \text{O}_2 (g)$ on the basis of the following proposed mechanism:

(1) $\text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O} \quad k_1, k_1'$

(2) $\text{O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 \quad k_2$

23.1b On the basis of the following proposed mechanism, account for the experimental fact that the rate law for the decomposition $2 \text{N}_2\text{O}_5 (g) \rightarrow 4 \text{NO}_2 (g) + \text{O}_2 (g)$ is $v = k[\text{N}_2\text{O}_5]$.

(1) $\text{N}_2\text{O}_5 + \text{NO}_2 + \text{NO}_3 \quad k_1, k_1'$

(2) $\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO}_2 + \text{O}_2 + \text{NO} \quad k_2$

(3) $\text{NO} + \text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_2 + \text{NO}_2 \quad k_3$
23.2a  A slightly different mechanism for the decomposition of N\textsubscript{2}O\textsubscript{5} from that in Exercise 23.1b has also been proposed. It differs only in the last step, which is replaced by

\[(3) \text{NO} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO}_2 \quad k_3\]

Show that this mechanism leads to the same overall rate law.

23.2b  Consider the following mechanism for the thermal decomposition of R\textsubscript{2}:

\[(1) \text{R}_2 \rightarrow \text{R} + \text{R} \]
\[(2) \text{R} + \text{R}_2 \rightarrow \text{P}_B + \text{R}' \]
\[(3) \text{R}' \rightarrow \text{P}_A + \text{R} \]
\[(4) \text{R} + \text{R} \rightarrow \text{P}_A + \text{P}_B\]

where R\textsubscript{2}, P\textsubscript{A}, P\textsubscript{B} are stable hydrocarbons and R and R’ are radicals. Find the dependence of the rate of decomposition of R\textsubscript{2} on the concentration of R\textsubscript{2}.

23.3a  Refer to Fig. 23.* and determine the pressure range for branching chain explosion in the hydrogen-oxygen reaction at 800 K.

23.3b  Refer to Fig. 23.* and determine the pressure range for branching chain explosion in the hydrogen-oxygen reaction at (a) 700 K, (b) 900 K.

23.4a  The condensation reaction of propanone, (CH\textsubscript{3})\textsubscript{2}CO, in aqueous solution is catalysed by bases, B, which react reversibly with propanone to form the carbanion C\textsubscript{3}H\textsubscript{5}O\textsuperscript{−}. The carbanion then reacts with a molecule of propanone to give the product. A simplified version of the mechanism is
(1) \( AH + B \rightarrow BH^+ + A^- \)

(2) \( A^- + BH^+ \rightarrow AH + B \)

(3) \( A^- + AH \rightarrow \text{product} \)

where AH stands for propanone and A\(^-\) denotes its carbanion. Use the steady-state approximation to find the concentration of the carbanion and derive the rate equation for the formation of the product.

23.4b Consider the acid-catalysed reaction

(1) \( HA + H^- \rightarrow HAH^+ \quad k_1, k_1', \text{ both fast} \)

(2) \( HAH^+ + B \rightarrow BH^+ + AH \quad k_2, \text{ slow} \)

Deduce the rate law and show that it can be made independent of the specific term \([H^+]\).

23.5a Consider the following chain mechanism:

(1) \( AH \rightarrow A\cdot + H\cdot \)

(2) \( A\cdot \rightarrow B\cdot + C \)

(3) \( AH + B\cdot \rightarrow A\cdot + D \)

(4) \( A\cdot + B\cdot \rightarrow P \)

Use the steady-state approximation to deduce that the decomposition of AH is first order in AH.

23.5b Consider the following chain mechanism:

(1) \( A_2 \rightarrow A\cdot + A\cdot \)

(2) \( A\cdot \rightarrow B\cdot + C \)

(3) \( A\cdot + P \rightarrow B\cdot \)

(4) \( A\cdot + B\cdot \rightarrow P \)
Use the steady-state approximation to deduce that the rate law for the consumption of $A_2$.

23.6a The enzyme-catalysed conversion of a substrate at 25°C has a Michaelis constant of 0.035 mol dm$^{-3}$. The rate of the reaction is $1.15 \times 10^{-3}$ mol dm$^{-3}$ s$^{-1}$ when the substrate concentration is 0.110 mol dm$^{-3}$. What is the maximum velocity of this enzymolysis?

23.6b The enzyme-catalysed conversion of a substrate at 25°C has a Michaelis constant of 0.042 mol dm$^{-3}$. The rate of the reaction is $2.45 \times 10^{-4}$ mol dm$^{-3}$ s$^{-1}$ when the substrate concentration is 0.890 mol dm$^{-3}$. What is the maximum velocity of this enzymolysis?

23.7a In a photochemical reaction $A \rightarrow 2 \ B + C$, the quantum efficiency with 500 nm light is $2.1 \times 10^{2}$ mol einstein$^{-1}$ (1 einstein = 1 mol photons). After exposure of 300 mmol of $A$ to the light, 2.28 mmol of $B$ is formed. How many photons were absorbed by $A$?

23.7b In a photochemical reaction $A \rightarrow B + C$, the quantum efficiency with 500 nm light is $1.2 \times 10^{2}$ mol einstein$^{-1}$. After exposure of 200 mmol $A$ to the light, 1.77 mmol $B$ is formed. How many photons were absorbed by $A$?

23.8a In an experiment to measure the quantum efficiency of a photochemical reaction, the absorbing substance was exposed to 490 nm light from a 100 W source for 45 min. The intensity of the transmitted light was 40 per cent of the intensity of the incident light. As a result of irradiation, 0.344 mol of the absorbing substance decomposed. Determine the quantum efficiency.
23.8b In an experiment to measure the quantum efficiency of a photochemical reaction, the absorbing substance was exposed to 320 nm radiation from a 87.5 W source for 28.0 min. The intensity of the transmitted light was 0.257 that of the incident light. As a result of irradiation, 0.324 mol of the absorbing substance decomposed. Determine the quantum efficiency.

Problems

Numerical problems

23.1 Studies of combustion reactions depend on knowing the concentrations of H atoms and HO radicals. Measurements on a flow system using EPR for the detection of radicals gave information on the reactions

\[(1) \text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO} \quad k_1 = 2.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\]

\[(2) \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O} \quad k_2 = 1.55 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\]

\[(3) \text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H} \quad k_3 = 1.1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\]

(J.N. Bradley, W. Hack, K. Hoyermann, and H.G. Wagner, *J. Chem. Soc. Faraday Trans. I*, 1889 (1973)). Using initial H atom and NO2 concentrations of $4.5 \times 10^{-10}$ mol cm$^{-3}$ and $5.6 \times 10^{-10}$ mol cm$^{-3}$, respectively, compute and plot curves showing the O, O$_2$, and OH concentrations as a function of time in the range 0–10 ns.

23.2 In a flow study of the reaction between O atoms and Cl$_2$ (J.N. Bradley, D.A. Whytock, and T.A. Zaleski, *J. Chem. Soc. Faraday Trans. I*, 1251 (1973)) at high chlorine pressures, plots of ln [O]$_0$/[O] against distances $l$ along the flow tube, where [O]$_0$ is the oxygen concentration at zero
chlorine pressure, gave straight lines. Given the flow velocity as 6.66 m s\(^{-1}\) and the data below, find the rate coefficient for the reaction \(O + Cl_2 \rightarrow ClO + Cl\).

<table>
<thead>
<tr>
<th>(l/cm)</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>16</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\ln([O]_0/[O]))</td>
<td>0.27</td>
<td>0.31</td>
<td>0.34</td>
<td>0.38</td>
<td>0.45</td>
<td>0.46</td>
<td>0.50</td>
<td>0.55</td>
<td>0.56</td>
<td>0.60</td>
</tr>
</tbody>
</table>

with \([O]_0 = 3.3 \times 10^{-8}\) mol dm\(^{-3}\), \([Cl_2] = 2.54 \times 10^{-7}\) mol dm\(^{-3}\), \(p = 1.70\) Torr.

23.3 J.D. Chapple-Sokol, C.J. Giunta, and R.G. Gordon (*J. Electrochem. Soc.* **136**, 2993 (1989)) proposed the following radical chain mechanism for the initial stages of the gas-phase oxidation of silane by nitrous oxide:

1. \(N_2O \rightarrow N_2 + O\)
2. \(O + SiH_4 \rightarrow SiH_3 + OH\)
3. \(OH + SiH_4 \rightarrow SiH_3 + H_2O\)
4. \(SiH_3 + N_2O \rightarrow SiH_3O + N_2\)
5. \(SiH_3O + SiH_4 \rightarrow SiH_3OH + SiH_3\)
6. \(SiH_3 + SiH_3O \rightarrow (H_3Si)_2O\)

Label each step with its role in the chain. Use the steady-state approximation to show that this mechanism predicts the following rate law for \(SiH_4\) consumption (provided \(k_1\) and \(k_6\) are in some sense small):

23.4 The water formation reaction has been studied many times and continues to be of interest. Despite the many studies there is not uniform agreement on the mechanism. But as explosions are known to occur at certain critical values of the pressure, any proposed mechanism to be considered plausible must be consistent with the existence of these critical explosion limits. One such plausible mechanism is that of Example 23.*. Another is the following
(1) $H_2 \rightarrow H + H$
(2) $H + O_2 \rightarrow OH + O$
(3) $O + H_2 \rightarrow OH + H$
(4) $H + O_2 \rightarrow HO_2$
(5) $HO_2 + H_2 \rightarrow H_2O + OH$
(6) $HO_2 + \text{wall} \rightarrow \text{destruction}$
(7) $H + M \rightarrow \text{destruction}$

In a manner similar to that in Example 23.*, determine whether or not this mechanism can lead to explosions under appropriate conditions.

**23.5** For many years the reaction $H_2(g) + I_2(g) \rightarrow 2 HI(g)$ and its reverse were assumed to be elementary bimolecular reactions. However, J.H. Sullivan (*J. Chem. Phys.* 46, 73 (1967)) suggested that the following mechanism for the reaction, originally proposed by M. Bodenstein (*Z. Physik. Chem.* 29, 56 (1898)), provides a better explanation of the experimental results:

1. $I_2 \rightarrow I + I$ \hspace{1cm} $k_1, k_1'$
2. $I + I + H_2 \rightarrow HI + HI$ \hspace{1cm} $k_2$

Obtain the expression for the rate of formation of HI based on this mechanism. Under what conditions does this rate law reduce to the one for the originally accepted mechanism?

**23.6** The number of photons falling on a sample can be determined by a variety of methods, of which the classical one is chemical actinometry. The decomposition of oxalic acid ($\text{COOH})_2$, in the presence of uranyl sulphate, ($\text{UO}_2\text{SO}_4$), proceeds according to the sequence

1. $\text{UO}^{2+} + \text{hv} \rightarrow (\text{UO}^{2+})^*$
2. $(\text{UO}^{2+})^* + (\text{COOH})_2 \rightarrow \text{UO}^{2+} + \text{H}_2\text{O} + \text{CO}_2 + \text{CO}$
with a quantum efficiency of 0.53 at the wavelength used. The amount of oxalic acid remaining after exposure can be determined by titration (with KMnO₄) and the extent of decomposition used to find the number of incident photons. In a particular experiment, the actinometry solution consisted of 5.232 g anhydrous oxalic acid, 25.0 cm³ water (together with the uranyl salt). After exposure for 300 s the remaining solution was titrated with 0.212 M KMnO₄(aq), and 17.0 cm³ were required for complete oxidation of the remaining oxalic acid. The titration reaction is

\[
2 \text{ MnO}_4^-(aq) + 5 \text{ (COOH)}_2(aq) + 6 \text{ H}^+(aq) \rightarrow 10 \text{ CO}_2(g) + 8 \text{ H}_2\text{O}(l) + \text{ 2Mn}^{2+}(aq)
\]

What is the rate of incidence of photons at the wavelength of the experiment? Express the answer in photons/second and einstein/second.

23.7 Dansyl chloride, which absorbs maximally at 330 nm and fluoresces maximally at 510 nm, can be used to label amino acids in fluorescence microscopy and FRET studies. Tabulated below is the variation of the fluorescence intensity of an aqueous solution of dansyl chloride with time after excitation by a short laser pulse (with \( I_0 \) the initial fluorescence intensity).

<table>
<thead>
<tr>
<th>( t/\text{ns} )</th>
<th>5.0</th>
<th>10.0</th>
<th>15.0</th>
<th>20.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I_\ell/I_0 )</td>
<td>0.45</td>
<td>0.21</td>
<td>0.11</td>
<td>0.05</td>
</tr>
</tbody>
</table>

(a) Calculate the observed fluorescence lifetime of dansyl chloride in water. (b) The fluorescence quantum yield of dansyl chloride in water is 0.70. What is the fluorescence rate constant?

23.8 When benzophenone is illuminated with ultraviolet light it is excited into a singlet state. This singlet changes rapidly into a triplet, which phosphoresces. Triethylamine acts as a quencher for the triplet. In an experiment in methanol as solvent, the phosphorescence intensity varied with amine concentration as shown below. A time-resolved laser spectroscopy experiment had also shown that the half-life of the fluorescence in the absence of quencher is 29
µs. What is the value of $k_q$?

<table>
<thead>
<tr>
<th>$[Q]/(\text{mol dm}^{-3})$</th>
<th>0.0010</th>
<th>0.0050</th>
<th>0.0100</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_t/(\text{arbitrary units})$</td>
<td>0.41</td>
<td>0.25</td>
<td>0.16</td>
</tr>
</tbody>
</table>

23.9 An electronically excited state of Hg can be quenched by N$_2$ according to

$$\text{Hg}^* (\text{g}) + \text{N}_2 (\text{g}, v = 0) \rightarrow \text{Hg} (\text{g}) + \text{N}_2 (\text{g}, v = 1)$$

in which energy transfer from Hg* excites N$_2$ vibrationally. Fluorescence lifetime measurements of samples of Hg with and without N$_2$ present are summarized below ($T = 300$ K):

$p_{N_2} = 0.0$ atm

Relative fluorescence intensity | 1.000 | 0.606 | 0.360 | 0.22 | 0.135 |
$t/\mu s$ | 0.0 | 5.0 | 10.0 | 15.0 | 20.0 |

$p_{N_2} = 9.74 \times 10^{-4}$ atm

Relative fluorescence intensity | 1.000 | 0.585 | 0.342 | 0.200 | 0.117 |
$t/\mu s$ | 0.0 | 3.0 | 6.0 | 9.0 | 12.0 |

You may assume that all gases behave ideally. Determine the rate constant for the energy transfer process.

23.10 The Förster theory of resonance energy transfer and the basis for the FRET technique can be tested by performing fluorescence measurements on a series of compounds in which an energy donor and an energy acceptor are covalently linked by a rigid molecular linker of variable and known length. L. Stryer and R.P. Haugland, *Proc. Natl. Acad. Sci. USA* **58**, 719 (1967) collected the following data on a family of compounds with the general composition dansyl-(L-prolyl)$_n$-naphthyl, in which the distance $R$ between the naphthyl donor and the dansyl acceptor was varied from 1.2 nm to 4.6 nm by increasing the number of prolyl units in the linker:
Are the data described adequately by eqn 23.*? If so, what is the value of $R_0$ for the naphthyl-dansyl pair?

Theoretical problems

23.11 The Rice–Herzfeld mechanism for the dehydrogenation of ethane is specified in Section 23.*b, and it was noted there that it led to first-order kinetics. Confirm this remark, and find the approximations that lead to the rate law quoted there. How may the conditions be changed so that the reaction shows different orders?

23.12 The following mechanism has been proposed for the thermal decomposition of acetaldehyde (ethanal):

(1) $\text{CH}_3\text{CHO} \rightarrow \cdot\text{CH}_3 + \text{CHO}$

(2) $\cdot\text{CH}_3 + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \cdot\text{CH}_2\text{CHO}$

(3) $\cdot\text{CH}_2\text{CHO} \rightarrow \text{CO} + \cdot\text{CH}_3$

(4) $\cdot\text{CH}_3 + \cdot\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_3$

Find an expression for the rate of formation of methane and the rate of disappearance of acetaldehyde.

23.13 Express the root mean square deviation $\left\{\langle M^2 \rangle - \langle M \rangle^2\right\}^{1/2}$ of the molar mass of a condensation polymer in terms of $\rho$, and deduce its time-dependence.

23.14 Calculate the ratio of the mean cube molar mass to the mean square molar mass in terms
of (a) the fraction \( p \), (b) the chain length.

23.15 Calculate the average polymer length in a polymer produced by a chain mechanism in which termination occurs by a disproportionation reaction of the form \( M \cdot + \cdot M \rightarrow :M \).

23.16 Derive an expression for the time dependence of the degree of polymerization for a stepwise polymerization in which the reaction is acid-catalysed by the –COOH acid functional group. The rate law is \( \text{d}[A]/\text{d}t = -k[A]^2[\text{OH}] \).

23.17 Autocatalysis is the catalysis of a reaction by the products. For example, for a reaction \( A \rightarrow P \) it may be found that the rate law is \( v = k[A][P] \) and the reaction rate is proportional to the concentration of \( P \). The reaction gets started because there are usually other reaction routes for the formation of some \( P \) initially, which then takes part in the autocatalytic reaction proper. (a) Integrate the rate equation for an autocatalytic reaction of the form \( A \rightarrow P \), with rate law \( v = k[A][P] \), and show that

\[
\frac{[P]}{[P]_0} = \frac{a}{b} + \frac{b}{a} \ln \left( \frac{a}{b} \right)
\]

where \( a = ([A]_0 + [P]_0)k \) and \( b = [P]_0/[A]_0 \). *Hint:* Starting with the expression \( v = -\text{d}[A]/\text{d}t = k[A][P] \), write \( [A] = [A]_0 -x, [P] = [P]_0 + x \) and then write the expression for the rate of change of either species in terms of \( x \). To integrate the resulting expression, the following relation will be useful:

(b) Plot \( [P]/[P]_0 \) against \( at \) for several values of \( b \). Discuss the effect of autocatalysis on the shape...
of a plot of \([P]/[P]_0\) against \(t\) by comparing your results with those for a first-order process, in which \([P]/[P]_0 = 1 - e^{-kt}\). (c) Show that for the autocatalytic process discussed in parts (a) and (b), the reaction rate reaches a maximum at \(t_{\text{max}} = -(1/a) \ln b\). (d) An autocatalytic reaction \(A \rightarrow P\) is observed to have the rate law \(d[P]/dt = k[A]^2[P]\). Solve the rate law for initial concentrations \([A]_0\) and \([P]_0\). Calculate the time at which the rate reaches a maximum. (e) Another reaction with the stoichiometry \(A \rightarrow P\) has the rate law \(d[P]/dt = k[A][P]^2\); integrate the rate law for initial concentrations \([A]_0\) and \([P]_0\). Calculate the time at which the rate reaches a maximum.

23.18 Conventional equilibrium considerations do not apply when a reaction is being driven by light absorption. Thus the steady-state concentration of products and reactants might differ significantly from equilibrium values. For instance, suppose the reaction \(A \rightarrow B\) is driven by light absorption, and that its rate is \(I_\lambda\), but that the reverse reaction \(B \rightarrow A\) is bimolecular and second-order with a rate \(k[B]^2\). What is the stationary state concentration of \(B\)? Why does this ‘photostationary state’ differ from the equilibrium state?

23.19 Derive an expression for the rate of disappearance of a species \(A\) in a photochemical reaction for which the mechanism is:

1. initiation with light of intensity \(I\), \(A \rightarrow R_\cdot + R_\cdot\)
2. propagation, \(A + R_\cdot \rightarrow R_\cdot + B\)
3. termination, \(R_\cdot + R_\cdot \rightarrow R_2\)

Hence, show that rate measurements will give only a combination of \(k_2\) and \(k_3\) if a steady state is reached, but that both may be obtained if a steady state is not reached.

23.20 The photochemical chlorination of chloroform in the gas has been found to follow the
rate law $d[CCl_4]/dt = k[Cl_2]^{1/2}I_4^{1/2}$. Devise a mechanism that leads to this rate law when the chlorine pressure is high.

### 23.21

Photolysis of $Cr(CO)_6$ in the presence of certain molecules $M$, can give rise to the following reaction sequence:

1. $Cr(CO)_6 \rightarrow h\nu \rightarrow Cr(CO)_5 + CO$
2. $Cr(CO)_5 + CO \rightarrow Cr(CO)_6$
3. $Cr(CO)_5 + M \rightarrow Cr(CO)_5M$
4. $Cr(CO)_5M \rightarrow Cr(CO)_5 + M$

Suppose that the absorbed light intensity is so weak that $I \ll k_4[Cr(CO)_5M]$. Find the factor $f$ in the equation $d[Cr(CO)_5M]/dt = -f[Cr(CO)_5M]$. Show that a graph of $1/f$ against $[M]$ should be a straight line.

---

Applications to: biochemistry and environmental science

### 23.22

Models of population growth are analogous to chemical reaction rate equations. In the model due to Malthus (1798) the rate of change of the population $N$ of the planet is assumed to be given by $dN/dt = \text{births} - \text{deaths}$. The numbers of births and deaths are proportional to the population, with proportionality constants $b$ and $d$. Obtain the integrated rate law. How well does it fit the (very approximate) data below on the population of the planet as a function of time.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$N/10^9$</td>
<td>0.5</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
</tbody>
</table>

### 23.23

Many enzyme catalysed reactions are consistent with a modified version of the Michaelis–Menten mechanism in which the second step is also reversible. (a) For this mechanism show that
the rate of formation of product is given by

\[ v = k_b [E]_0, \quad v' = k_a' [E]_0, \quad K_M = (k_a' + k_b)/k_a, \quad \text{and} \quad K_M' = (k_a' + k_b)/k_b'. \]

(b) Find the limiting behaviour of this expression for large and small concentrations of substrate.

23.24 The following results were obtained for the action of an ATPase on ATP at 20°C, when the concentration of the ATPase was 20 nmol dm\(^{-3}\):

<table>
<thead>
<tr>
<th>[ATP]/(µmol dm(^{-3}))</th>
<th>0.60</th>
<th>0.80</th>
<th>1.4</th>
<th>2.0</th>
<th>3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v)/(µmol dm(^{-3}) s(^{-1}))</td>
<td>0.81</td>
<td>0.97</td>
<td>1.30</td>
<td>1.47</td>
<td>1.69</td>
</tr>
</tbody>
</table>

Determine the Michaelis constant, the maximum velocity of the reaction, the turnover number, and the catalytic efficiency of the enzyme.

23.25 Enzyme-catalyzed reactions are sometimes analyzed by use of the Eadie–Hofstee plot, in which \(v/[S]_0\) is plotted against \(v\). (a) Using the simple Michaelis–Menten mechanism, derive a relation between \(v/[S]_0\) and \(v\). (b) Discuss how the values of \(K_M\) and \(v_{\text{max}}\) are obtained from analysis of the Eadie–Hofstee plot. (c) Determine the Michaelis constant and the maximum velocity of the reaction of the reaction from Exercise 23.23 by using an Eadie–Hofstee plot to analyze the data.

23.26 In general, the catalytic efficiency of an enzyme depends on the pH of the medium in which it operates. One way to account for this behaviour is to propose that the enzyme and the enzyme-substrate complex are active only in specific protonation states. This situation can be summarized by the following mechanism:
\[
EH + S \rightarrow ESH \quad \text{rate} = k_a ESH \\
ESH \rightarrow E + P \quad \text{rate} = k_b
\]

\[
EH \rightarrow E^- + H^+
\]

\[
EH^+ \rightarrow EH + H^+
\]

\[
ESH \rightarrow ES^- + H^+
\]

\[
ESH^+ \rightarrow ESH + H^+
\]

in which only the EH and ESH forms are active. (a) For the mechanism above, show that

\[
\frac{v}{v_{\text{max}}} = \frac{K_{M}}{K_{M} + [S]}
\]

where \( v_{\text{max}} \) and \( K_M \) correspond to the form EH of the enzyme. (b) For pH values ranging from 0 to 14, plot \( v'_{\text{max}} \) against pH for a hypothetical reaction for which \( v_{\text{max}} = 1.0 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1} \), \( K_{ES,b} = 1.0 \times 10^{-6} \text{ mol dm}^{-3} \) and \( K_{ES,a} = 1.0 \times 10^{-8} \). Is there a pH at which \( v_{\text{max}} \) reaches a maximum value? If so, determine the pH. (c) Redraw the plot in part (b) by using the same value of \( v_{\text{max}} \), but \( K_{ES,b} = 1.0 \times 10^{-4} \text{ mol dm}^{-3} \) and \( K_{ES,a} = 1.0 \times 10^{-10} \text{ mol dm}^{-3} \). Account for any differences between this plot and the plot from part (b).

23.27 The enzyme carboxypeptidase catalyzes the hydrolysis of polypeptides and here we
consider its inhibition. The following results were obtained when the rate of the enzymolysis of carbobenzyo-glycyl-D-phenylalanine (CBGP) was monitored without inhibitor:

\[
\text{[CBGP]}_0/(10^{-2} \text{ mol dm}^{-3}) \quad 1.25 \quad 3.84 \quad 5.81 \quad 7.13
\]

Relative reaction rate 0.398 0.669 0.859 1.000

(All rates in this problem were measured with the same concentration of enzyme and are relative to the rate measured when \([\text{CBGP]}_0 = 0.0713 \text{ mol dm}^{-3}\) in the absence of inhibitor). When \(2.0 \times 10^{-3} \text{ mol dm}^{-3}\) phenylbutyrate ion was added to a solution containing the enzyme and substrate, the following results were obtained:

\[
\text{[CBGP]}_0/(10^{-2} \text{ mol dm}^{-3}) \quad 1.25 \quad 2.50 \quad 4.00 \quad 5.50
\]

Relative reaction rate 0.172 0.301 0.344 0.548

In a separate experiment, the effect of \(5.0 \times 10^{-2} \text{ mol dm}^{-3}\) benzoate ion was monitored and the results were:

\[
\text{[CBGP]}_0/(10^{-2} \text{ mol dm}^{-3}) \quad 1.75 \quad 2.50 \quad 5.00 \quad 10.00
\]

Relative reaction rate 0.183 0.201 0.231 0.246

Determine the mode of inhibition of carboxypeptidase by the phenylbutyrate ion and benzoate ion.

23.28 Many biological and biochemical processes involve autocatalytic steps (Problem 23.*). In the SIR model of the spread and decline of infectious diseases the population is divided into three classes; the susceptibles, S, who can catch the disease, the infectives, I, who have the disease and can transmit it, and the removed class, R, who have either had the disease and recovered, are dead, are immune or isolated. The model mechanism for this process implies the following rate laws:
What are the autocatalytic steps of this mechanism? Find the conditions on the ratio $a/r$ that decide whether the disease will spread (an epidemic) or die out. Show that a constant population is built into this system, namely that $S + I + R = N$, meaning that the time scales of births, deaths by other causes, and migration are assumed large compared to that of the spread of the disease.

23.29 In light-harvesting complexes, the fluorescence of a chlorophyll molecule is quenched by nearby chlorophyll molecules. Given that for a pair of chlorophyll $a$ molecules $R_0 = 5.6$ nm, by what distance should two chlorophyll $a$ molecules be separated to shorten the fluorescence lifetime from 1 ns (a typical value for monomeric chlorophyll $a$ in organic solvents) to 10 ps? ##

23.30 The light-induced electron transfer reactions in photosynthesis occur because chlorophyll molecules (whether in monomeric or dimeric forms) are better reducing agents in their electronic excited states. Justify this observation with the help of molecular orbital theory.

23.31 The emission spectrum of a porphyrin dissolved in $O_2$-saturated water shows a strong band at 650 nm and a weak band at 1270 nm. In separate experiments, it was observed that the electronic absorption spectrum of the porphyrin sample showed bands at 420 nm and 550 nm, and the electronic absorption spectrum of $O_2$-saturated water showed no bands in the visible range of the spectrum (and therefore no emission spectrum when excited in the same range). Based on these data alone, make a preliminary assignment of the emission band at 1270 nm. Propose additional experiments that test your hypothesis.
23.32‡ Ultraviolet radiation photolyzes O₃ to O₂ and O. Determine the rate at which ozone is consumed by 305 nm radiation in a layer of the stratosphere of thickness 1 km. The quantum efficiency is 0.94 at 220 K, the concentration about $8 \times 10^{-9}$ mol dm$^{-3}$, the molar absorption coefficient 260 dm$^3$ mol$^{-1}$ cm$^{-1}$, and the flux of 305 nm radiation about $1 \times 10^{14}$ photons cm$^{-2}$ s$^{-1}$.


23.33‡ Use the Chapman model to explore the behaviour of a model atmosphere consisting of pure O₂ at 10 Torr and 298 K that is exposed to measurable frequencies and intensities of UV radiation. (a) Look up the values of $k_2$, $k_4$, and $k_5$ in a source such as the *CRC Handbook of chemistry and physics* or *Chemical kinetics and photochemical data for use in stratospheric modeling* (the URL is available at the text’s web site). The rate constants $k_1$ and $k_3$ depend upon the radiation conditions; assume values of $1.0 \times 10^{-8}$ s$^{-1}$ and 0.016 s$^{-1}$, respectively. If you cannot find a value for $k_5$, formulate chemically sound arguments for exclusion of the fifth step from the mechanism. (b) Write the rate expressions for the concentration of each chemical species. (c) Assume that the UV radiation is turned on at $t = 0$, and solve the rate expressions for the concentration of all species as a function of time over a period of 4 h. Examine relevant concentrations in the very early time period $t < 0.1$ s. State all assumptions. Is there any ozone present initially? Why must the pressure be low and the UV radiation intensities high for the production of ozone? Draw graphs of the time variations of both atomic oxygen and ozone on both the very short and the long time scales. What is the percentage of ozone after 4.0 h of irradiation? *Hint:* You will need a software package for solving a ‘stiff’ system of differential equations. Stiff differential equations have at least two rate constants with very different values.
and result in different behaviours on different time scales, so the solution usually requires that the total time period be broken into two or more periods, one may be very short and another very long. For help with using mathematical software to solve systems of differential equations, see M.P. Cady and C.A. Trapp, *A Mathcad primer for physical chemistry*. Oxford University Press (1999).

23.34‡ Chlorine atoms react rapidly with ozone in the gas-phase bimolecular reaction \( \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \) with \( k = (1.7 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})e^{-260/(T/ K)} \) (W.B. DeMore, S.P. Sander, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard, A.R. Ravishankara, C.E. Kolb, and M.J. Molina, Chemical kinetics and photochemical data for use in stratospheric modeling: Evaluation Number 11, JPL Publication 94–26 (1994)). Estimate the rate of this reaction at (a) 20 km, where \([\text{Cl}] = 5 \times 10^{-17} \text{ mol dm}^{-3}, [\text{O}_3] = 8 \times 10^{-9} \text{ mol dm}^{-3}, \) and \( T = 220 \text{ K} \); (b) 45 km, where \([\text{Cl}] = 3 \times 10^{-15} \text{ mol dm}^{-3}, [\text{O}_3] = 8 \times 10^{-11} \text{ mol dm}^{-3}, \) and \( T = 270 \text{ K} \).

23.35‡ Because of its importance in atmospheric chemistry, the thermal decomposition of nitric oxide, \( 2 \text{NO(g)} \rightarrow \text{N}_2(g) + \text{O}_2(g) \), has been amongst the most thoroughly studied of gas phase reactions. The commonly accepted mechanism has been that of H. Wise and M.F. Freech (J. Chem. Phys. 22, 1724, (1952)):

\[
\begin{align*}
\text{(1)} \quad & \text{NO} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{O} & k_1 \\
\text{(2)} \quad & \text{O} + \text{NO} \rightarrow \text{O}_2 + \text{N} & k_2 \\
\text{(3)} \quad & \text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O} & k_3 \\
\text{(4)} \quad & \text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M} & k_4 \\
\text{(5)} \quad & \text{O}_2 + \text{M} \rightarrow \text{O} + \text{O} + \text{M} & k_4' \\
\end{align*}
\]

(a) Label the steps of this mechanism as initiation, propagation, etc. (b) Write down the full
expression for the rate of disappearance of NO. What does this expression for the rate become on
the basis of the assumptions that \( v_2 = v_3 \) when \([N]\) reaches its steady state concentration, that the
rate of the propagation step is more rapid than the rate of the initiation step, and that oxygen
atoms are in equilibrium with oxygen molecules? (c) Find an expression for the effective
activation energy, \( E_{a,\text{eff}} \), for the overall reaction in terms of the activation energies of the
individual steps of the reaction. (d) Estimate \( E_{a,\text{eff}} \) from the bond energies of the species involved.
(e) It has been pointed out by R.J. Wu and C.T. Yeh (Int. J. Chem. Kinet. 28, 89 (1996)) that the
reported experimental values of \( E_{a,\text{eff}} \) obtained by different authors have varied from 253 to 357
kJ mol\(^{-1}\). They suggest that the assumption of oxygen atoms and oxygen molecules being in
equilibrium is unwarranted and that the steady state approximation needs to be applied to the
entire mechanism. Obtain the overall rate law based on the steady state approximation and find
the forms that it assumes for low NO conversion (low \( O_2 \) concentration). (f) When the reaction
conversion becomes significant, Wu and Yeh suggest that two additional elementary steps,

\[
\begin{align*}
(6) \quad O_2 + M & \rightarrow O + O + M \quad k_6 \\
(7) \quad NO + O_2 & \rightarrow O + NO_2 \quad k_7
\end{align*}
\]

start to compete with step (1) as the initiation step. Obtain the rate laws based on these alternative
mechanisms and again estimate the apparent activation energies. Is the range of these different
theoretically estimated values for \( E_{a,\text{eff}} \) consistent with the range of values obtained
experimentally?