Discussion questions

22.1 Consult literature sources and list the observed timescales during which the following processes occur: radiative decay of excited electronic states, molecular rotational motion, molecular vibrational motion, proton transfer reactions, the initial event of vision, energy transfer in photosynthesis, the initial electron transfer events in photosynthesis, the helix-to-coil transition in polypeptides, and collisions in liquids.

22.2 Write a brief report on a recent research article in which at least one of the following techniques was used to study the kinetics of a chemical reaction: stopped-flow techniques, flash photolysis, chemical quench-flow methods, freeze quench methods, temperature-jump methods, or pressure-jump methods. Your report should be similar in content and size to one of the Impact sections found throughout this text.

22.3 Describe the main features, including advantages and disadvantages, of the following experimental methods for determining the rate law of a reaction: the isolation method, the method of initial rates, and fitting data to integrated rate law expressions.

22.4 Distinguish between reaction order and molecularity.

22.5 Assess the validity of the following statement: the rate-determining step is the slowest step in a reaction mechanism.

22.6 Distinguish between a pre-equilibrium approximation and a steady-state approximation.

22.7 Distinguish between kinetic and thermodynamic control of a reaction.
22.8 Define the terms in and limit the generality of the expression \( \ln k = \ln A - \frac{E_a}{RT} \).

22.9 Distinguish between a primary and a secondary kinetic isotope effect. Discuss how kinetic isotope effects in general can provide insight into the mechanism of a reaction.

22.10 Discuss the limitations of the generality of the expression \( k = k_a k_b [A] / (k_b + k_a' [A]) \) for the effective rate constant of a unimolecular reaction \( A \rightarrow P \) with the following mechanism: \( A + A \rightarrow A^* + A (k_a, k_a') \), \( A^* \rightarrow P (k_b) \). Suggest an experimental procedure that may either support or refute the mechanism.

Exercises

22.1a The rate of the reaction \( A + 2 B \rightarrow 3 C + D \) was reported as 1.0 mol dm\(^{-3}\) s\(^{-1}\). State the rates of formation and consumption of the participants.

22.1b The rate of the reaction \( A + 3 B \rightarrow C + 2 D \) was reported as 1.0 mol dm\(^{-3}\) s\(^{-1}\). State the rates of formation and consumption of the participants.

22.2a The rate of formation of \( C \) in the reaction \( 2 A + B \rightarrow 2 C + 3 D \) is 1.0 mol dm\(^{-3}\) s\(^{-1}\). State the reaction rate, and the rates of formation or consumption of \( A, C, \) and \( D \).

22.2b The rate of consumption of \( B \) in the reaction \( A + 3 B \rightarrow C + 2 D \) is 1.0 mol dm\(^{-3}\) s\(^{-1}\). State the reaction rate, and the rates of formation or consumption of \( A, B, \) and \( D \).
22.3a The rate law for the reaction in Exercise 22.1a was found to be \( v = k[A][B] \). What are the units of \( k \)? Express the rate law in terms of the rates of formation and consumption of (a) A, (b) C.

22.3b The rate law for the reaction in Exercise 22.1b was found to be \( v = k[A][B]^2 \). What are the units of \( k \)? Express the rate law in terms of the rates of formation and consumption of (a) A, (b) C.

22.4a The rate law for the reaction in Exercise 22.2a was reported as \( \frac{d[C]}{dt} = k[A][B][C] \). Express the rate law in terms of the reaction rate; what are the units for \( k \) in each case?

22.4b The rate law for the reaction in Exercise 22.2b was reported as \( \frac{d[C]}{dt} = k[A][B][C]^{-1} \). Express the rate law in terms of the reaction rate; what are the units for \( k \) in each case?

22.5a At 518°C, the rate of decomposition of a sample of gaseous acetaldehyde, initially at a pressure of 363 Torr, was 1.07 Torr s\(^{-1}\) when 5.0 per cent had reacted and 0.76 Torr s\(^{-1}\) when 20.0 per cent had reacted. Determine the order of the reaction.

22.5b At 400 K, the rate of decomposition of a gaseous compound initially at a pressure of 12.6 kPa, was 9.71 Pa s\(^{-1}\) when 10.0 per cent had reacted and 7.67 Pa s\(^{-1}\) when 20.0 per cent had reacted. Determine the order of the reaction.

22.6a At 518°C, the half-life for the decomposition of a sample of gaseous acetaldehyde
(ethanal) initially at 363 Torr was 410 s. When the pressure was 169 Torr, the half-life was 880 s. Determine the order of the reaction.

22.6b At 400 K, the half-life for the decomposition of a sample of a gaseous compound initially at 55.5 kPa was 340 s. When the pressure was 28.9 kPa, the half-life was 178 s. Determine the order of the reaction.

22.7a The rate constant for the first-order decomposition of N₂O₅ in the reaction 2 N₂O₅(g) → 4 NO₂(g) + O₂(g) is \( k = 3.38 \times 10^{-5} \) s\(^{-1}\) at 25°C. What is the half life of N₂O₅? What will be the pressure, initially 500 Torr, after (a) 10 s, (b) 10 min after initiation of the reaction?

22.7b The rate constant for the first-order decomposition of a compound A in the reaction 2 A → P is \( k = 2.78 \times 10^{-7} \) s\(^{-1}\) at 25°C. What is the half life of A? What will be the pressure, initially 32.1 kPa after (a) 10 s, (b) 10 min after initiation of the reaction?

22.8a A second-order reaction of the type A + B → P was carried out in a solution that was initially 0.050 mol dm\(^{-3}\) in A and 0.080 mol dm\(^{-3}\) in B. After 1.0 h the concentration of A had fallen to 0.020 mol dm\(^{-3}\). (a) Calculate the rate constant. (b) What is the half-life of the reactants?

22.8b A second-order reaction of the type A + 2 B → P was carried out in a solution that was initially 0.075 mol dm\(^{-3}\) in A and 0.030 mol dm\(^{-3}\) in B. After 1.0 h the concentration of A had fallen to 0.015 mol dm\(^{-3}\). (a) Calculate the rate constant. (b) What is the half-life of the reactants?

22.9a If the rate laws are expressed with (a) concentrations in moles per decimetre cubed, (b)
pressures in kilopascals, what are the units of the second-order and third-order rate constants?

**22.9b** If the rate laws are expressed with (a) concentrations in molecules per metre cubed, (b) pressures in newtons per metre squared, what are the units of the second-order and third-order rate constants?

**22.10a** The second-order rate constant for the reaction

\[
\text{CH}_3\text{COOC}_2\text{H}_5(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{CH}_3\text{CO}_2^-\text{(aq)} + \text{CH}_3\text{CH}_2\text{OH}(\text{aq})
\]

is 0.11 dm³ mol⁻¹ s⁻¹. What is the concentration of ester after (a) 10 s, (b) 10 min when ethyl acetate is added to sodium hydroxide so that the initial concentrations are [NaOH] = 0.050 mol dm⁻¹ and [CH₃COOC₂H₅] = 0.100 mol dm⁻³?

**22.10b** The second-order rate constant for the reaction A + 2 B → C + D is 0.21 dm³ mol⁻¹ s⁻¹. What is the concentration of C after (a) 10 s, (b) 10 min when the reactants are mixed with initial concentrations are [A] = 0.025 mol dm⁻¹ and [B] = 0.150 mol dm⁻³?

**22.11a** A reaction 2 A → P has a second-order rate law with \( k = 3.50 \times 10^{-4} \) dm³ mol⁻¹ s⁻¹. Calculate the time required for the concentration of A to change from 0.260 mol dm⁻³ to 0.011 mol dm⁻³.

**22.11b** A reaction 2 A → P has a third-order rate law with \( k = 3.50 \times 10^{-4} \) dm⁶ mol⁻² s⁻¹. Calculate the time required for the concentration of A to change from 0.077 mol dm⁻³ to 0.021 mol dm⁻³.
22.12a Show that \( t_{1/2} \propto 1/[A]^{n-1} \) for a reaction that is \( n \)th-order in A.

22.12b Deduce an expression for the time it takes for the concentration of a substance to fall to one-third its initial value in an \( n \)th-order reaction.

22.13a The \( pK_a \) of \( NH_4^+ \) is 9.25 at 25°C. The rate constant at 25°C for the reaction of \( NH_4^+ \) and \( \text{OH}^- \) to form aqueous \( NH_3 \) is \( 4.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \). Calculate the rate constant for proton transfer to \( NH_3 \). What relaxation time would be observed if a temperature jump were applied to a solution of 0.15 mol dm\(^{-3}\) \( NH_3(aq) \) at 25°C?

22.13b The equilibrium \( A \_ B + C \) at 25°C is subjected to a temperature jump which slightly increases the concentrations of B and C. The measured relaxation time is 3.0 \( \mu \text{s} \). The equilibrium constant for the system is \( 2.0 \times 10^{-16} \) at 25°C, and the equilibrium concentrations of B and C at 25°C are both \( 2.0 \times 10^{-4} \text{ mol dm}^{-3} \). Calculate the rate constants for steps (1) and (2).

22.14a The rate constant for the decomposition of a certain substance is \( 2.80 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) at 30°C and \( 1.38 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) at 50°C. Evaluate the Arrhenius parameters of the reaction.

22.14b The rate constant for the decomposition of a certain substance is \( 1.70 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) at 24°C and \( 2.01 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) at 37°C. Evaluate the Arrhenius parameters of the reaction.

22.15a The base-catalysed bromination of nitromethane-d\(_3\) in water at room temperature (298 K) proceeds 4.3 times more slowly than the bromination of the undeuterated material. Account for this difference. Use \( k_{f}(\text{C–H}) = 450 \text{ N m}^{-1} \).
22.15b Predict the order of magnitude of the isotope effect on the relative rates of displacement of (a) $^{1}$H and $^{3}$H, (b) $^{16}$O and $^{18}$O. Will raising the temperature enhance the difference? Take $k_{d}(C–H) = 450 \text{ N m}^{-1}$, $k_{d}(C–O) = 1750 \text{ N m}^{-1}$.

22.16a The effective rate constant for a gaseous reaction which has a Lindemann–Hinshelwood mechanism is $2.50 \times 10^{-4} \text{ s}^{-1}$ at 1.30 kPa and $2.10 \times 10^{-5} \text{ s}^{-1}$ at 12 Pa. Calculate the rate constant for the activation step in the mechanism.

22.16b The effective rate constant for a gaseous reaction which has a Lindemann–Hinshelwood mechanism is $1.7 \times 10^{-3} \text{ s}^{-1}$ at 1.09 kPa and $2.2 \times 10^{-4} \text{ s}^{-1}$ at 25 Pa. Calculate the rate constant for the activation step in the mechanism.

Problems

Numerical problems

22.1 The data below apply to the formation of urea from ammonium cyanate, $\text{NH}_4\text{CNO} \rightarrow \text{NH}_2\text{CONH}_2$. Initially 22.9 g of ammonium cyanate was dissolved in in enough water to prepare 1.00 dm$^3$ of solution. Determine the order of the reaction, the rate constant, and the mass of ammonium cyanate left after 300 min.

| $t$/min | 0 | 20.0 | 50.0 | 65.0 | 150 |

---

1 Problems denoted with the symbol ‡ were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.
22.2 The data below apply to the reaction, \((\text{CH}_3)_3\text{CBr} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH} + \text{HBr}\). Determine the order of the reaction, the rate constant, and the molar concentration of \((\text{CH}_3)_3\text{CBr}\) after 43.8 h.

<table>
<thead>
<tr>
<th>(t/\text{h})</th>
<th>0</th>
<th>3.15</th>
<th>6.20</th>
<th>10.00</th>
<th>18.30</th>
<th>30.80</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{(CH}_3)_3\text{CBr}]/(10^{-2} \text{ mol dm}^{-3}))</td>
<td>10.39</td>
<td>8.96</td>
<td>7.76</td>
<td>6.39</td>
<td>3.53</td>
<td>2.07</td>
</tr>
</tbody>
</table>

22.3 The thermal decomposition of an organic nitrile produced the following data:

<table>
<thead>
<tr>
<th>(t/(10^3 \text{ s}))</th>
<th>0</th>
<th>2.00</th>
<th>4.00</th>
<th>6.00</th>
<th>8.00</th>
<th>10.00</th>
<th>12.00</th>
<th>(\infty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[nitrile]/(mol dm(^{-3}))</td>
<td>1.50</td>
<td>1.26</td>
<td>1.07</td>
<td>0.92</td>
<td>0.81</td>
<td>0.72</td>
<td>0.65</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Determine the order of the reaction and the rate constant.

22.4 The following data have been obtained for the decomposition of \(\text{N}_2\text{O}_5(\text{g})\) at 67°C according to the reaction \(2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})\). Determine the order of the reaction, the rate constant, and the half-life. It is not necessary to obtain the result graphically, you may do a calculation using estimates of the rates of change of concentration.

<table>
<thead>
<tr>
<th>(t/\text{min})</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(\text{N}_2\text{O}_5)]/(mol dm(^{-3}))</td>
<td>1.000</td>
<td>0.705</td>
<td>0.497</td>
<td>0.349</td>
<td>0.246</td>
<td>0.173</td>
</tr>
</tbody>
</table>

22.5 A first order decomposition reaction is observed to have the following rate constants at the indicated temperatures. Estimate the activation energy.

<table>
<thead>
<tr>
<th>(k/(10^{-3} \text{ s}^{-1}))</th>
<th>2.46</th>
<th>45.1</th>
<th>576</th>
</tr>
</thead>
</table>
22.6 The gas phase decomposition of acetic acid at 1189 K proceeds by way of two parallel reactions:

(1) \( \text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2 \quad k_1 = 3.74 \text{ s}^{-1} \)

(2) \( \text{CH}_3\text{COOH} \rightarrow \text{H}_2\text{C}=\text{O} + \text{H}_2\text{O} \quad k_2 = 4.65 \text{ s}^{-1} \)

What is the maximum percentage yield of the ketene \( \text{CH}_2\text{CO} \) obtainable at this temperature?

22.7 Sucrose is readily hydrolyzed to glucose and fructose in acidic solution. The hydrolysis is often monitored by measuring the angle of rotation of plane-polarized light passing through the solution. From the angle of rotation the concentration of sucrose can be determined. An experiment on the hydrolysis of sucrose in 0.50 M HCl(aq) produced the following data:

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>[Sucrose] (mol dm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.316</td>
</tr>
<tr>
<td>14</td>
<td>0.300</td>
</tr>
<tr>
<td>39</td>
<td>0.274</td>
</tr>
<tr>
<td>60</td>
<td>0.256</td>
</tr>
<tr>
<td>80</td>
<td>0.238</td>
</tr>
<tr>
<td>110</td>
<td>0.211</td>
</tr>
<tr>
<td>140</td>
<td>0.190</td>
</tr>
<tr>
<td>170</td>
<td>0.170</td>
</tr>
<tr>
<td>210</td>
<td>0.146</td>
</tr>
</tbody>
</table>

Determine the rate constant of the reaction and the half-life of a sucrose molecule.

22.8 The composition of a liquid phase reaction \( 2 \text{A} \rightarrow \text{B} \) was followed by a spectrophotometric method with the following results:

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>[B] (mol dm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.089</td>
</tr>
<tr>
<td>10</td>
<td>0.153</td>
</tr>
<tr>
<td>20</td>
<td>0.200</td>
</tr>
<tr>
<td>30</td>
<td>0.230</td>
</tr>
<tr>
<td>40</td>
<td>0.312</td>
</tr>
</tbody>
</table>

Determine the order of the reaction and its rate constant.

22.9 The ClO radical decays rapidly by way of the reaction, \( 2 \text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2 \). The following
data have been obtained:

\[
t/(10^3 \text{ s}) \quad 0.12 \quad 0.62 \quad 0.96 \quad 1.60 \quad 3.20 \quad 4.00 \quad 5.75
\]

\[
[\text{ClO}]/(10^6 \text{ mol dm}^{-3}) \quad 8.49 \quad 8.09 \quad 7.10 \quad 5.79 \quad 5.20 \quad 4.77 \quad 3.95
\]

Determine the rate constant of the reaction and the half-life of a ClO radical.

22.10 Cyclopropane isomerizes into propene when heated to 500°C in the gas phase. The extent of conversion for various initial pressures has been followed by gas chromatography by allowing the reaction to proceed for a time with various initial pressures:

\[
\begin{array}{cccccccc}
p_0/\text{Torr} & 200 & 200 & 400 & 400 & 600 & 600 \\
t/\text{s} & 100 & 200 & 100 & 200 & 100 & 200 \\
p/\text{Torr} & 186 & 173 & 373 & 347 & 559 & 520
\end{array}
\]

where \(p_0\) is the initial pressure and \(p\) is the final pressure of cyclopropane. What is the order and rate constant for the reaction under these conditions?

22.11 The addition of hydrogen halides to alkenes has played a fundamental role in the investigation of organic reaction mechanisms. In one study (M.J. Haugh and D.R. Dalton, *J. Amer. Chem. Soc.* 97, 5674 (1975)), high pressures of hydrogen chloride (up to 25 atm) and propene (up to 5 atm) were examined over a range of temperatures and the amount of 2-chloropropane formed was determined by NMR. Show that if the reaction \(A + B \rightarrow P\) proceeds for a short time \(\Delta t\), the concentration of product follows \([P]/[A] = k[A]^{m-1}[B]^n\Delta t\) if the reaction is \(m\)th-order in \(A\) and \(n\)th-order in \(B\). In a series of runs the ratio of [chloropropane] to [propene] was independent of [propene] but the ratio of [chloropropane] to [HCl] for constant amounts of propene depended on [HCl]. For \(\Delta t = 100\) h (which is short on the time scale of the reaction) the latter ratio rose from zero to 0.05, 0.03, 0.01 for \(p(\text{HCl}) = 10\) atm, 7.5 atm, 5.0 atm. What are the
orders of the reaction with respect to each reactant?

22.12 Use mathematical software or an electronic spreadsheet to examine the time dependence of [I] in the reaction mechanism \( A \rightarrow I \rightarrow P \) \((k_1, k_2)\). You may either integrate eqn 22.* numerically (see Appendix 2) or use eqn 22.* directly. In all of the following calculations, use \([A]_0 = 1 \text{ mol dm}^{-3}\) and a time range of 0 to 5 s. (a) Plot [I] against \( t \) for \( k_1 = 10 \text{ s}^{-1} \) and \( k_2 = 1 \text{ s}^{-1} \). (b) Increase the ratio \( k_2/k_1 \) steadily by decreasing the value of \( k_1 \) and examine the plot of [I] against \( t \) at each turn. What approximation about \( d[I]/dt \) becomes increasingly valid?

22.13 Show that the following mechanism can account for the rate law of the reaction in Problem 22.9:

\[
\begin{align*}
\text{HCl} + \text{HCl} &\rightleftharpoons (\text{HCl})_2 \quad K_1 \\
\text{HCl} + \text{CH}_3\text{CH}=\text{CH}_2 &\rightleftharpoons \text{complex} \quad K_2 \\
(\text{HCl})_2 + \text{complex} &\rightarrow \text{CH}_3\text{CHClCH}_3 + 2 \text{HCl} \quad k \text{ (slow)}
\end{align*}
\]

What further tests could you apply to verify this mechanism?

22.14 Consider the dimerization \( 2 \text{A} \rightleftharpoons \text{A}_2 \), with forward rate constant \( k_a \) and backward rate constant \( k_b \). (a) Derive the following expression for the relaxation time in terms of the total concentration of protein, \([A]_{\text{tot}} = [A] + 2[A_2]\):
constant $K$ for formation of hydrogen-bonded dimers of 2-pyridone:

\[
\frac{[P]}{(\text{mol L}^{-1})} \quad 0.500 \quad 0.352 \quad 0.251 \quad 0.151 \quad 0.101
\]

$\tau/\text{ns}$ \quad 2.3 \quad 2.7 \quad 3.3 \quad 4.0 \quad 5.3

### 22.15
In the experiments described in Problems 22.11 and 22.13 an inverse temperature dependence of the reaction rate was observed, the overall rate of reaction at 70°C being roughly one-third that at 19°C. Estimate the apparent activation energy and the activation energy of the rate determining step given that the enthalpies of the two equilibria are both of the order of -14 kJ mol\(^{-1}\).

### 22.16
The second-order rate constants for the reaction of oxygen atoms with aromatic hydrocarbons have been measured (R. Atkinson and J.N. Pitts, *J. Phys. Chem.* 79, 295 (1975)). In the reaction with benzene the rate constants are $1.44 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300.3 K, $3.03 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 341.2 K, and $6.9 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 392.2 K. Find the pre-exponential factor and activation energy of the reaction.

### 22.17
In Problem 22.10 the isomerization of cyclopropane over a limited pressure range was examined. If the Lindemann mechanism of first-order reactions is to be tested we also need data at low pressures. These have been obtained (H.O. Pritchard, R.G. Sowden, and A.F. Trotman-Dickenson, *Proc. R. Soc.* A217, 563 (1953)):

\[
p/\text{Torr} \quad 84.1 \quad 11.0 \quad 2.89 \quad 0.569 \quad 0.120 \quad 0.067
\]

\[
10^4 k_{\text{eff}}/\text{s}^{-1} \quad 2.98 \quad 2.23 \quad 1.54 \quad 0.857 \quad 0.392 \quad 0.303
\]

Test the Lindemann theory with these data.
22.18‡ P.W. Seakins, M.J. Pilling, L.T. Niiranen, D. Gutman, and L.N. Krasnoperov (*J. Phys. Chem.* 96, 9847 (1992)) measured the forward and reverse rate constants for the gas-phase reaction \( \text{C}_2\text{H}_5(\text{g}) + \text{HBr}(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) + \text{Br}(\text{g}) \) and used their findings to compute thermodynamic parameters for \( \text{C}_2\text{H}_5 \). The reaction is bimolecular in both directions with Arrhenius parameters \( A = 1.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \), \( E_a = -4.2 \text{ kJ mol}^{-1} \) for the forward reaction and \( k' = 1.4 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \), \( E_a = 53.3 \text{ kJ mol}^{-1} \) for the reverse reaction. Compute \( \Delta_f H_,\text{S}_m^-,\text{ and }\Delta_f G^- \) of \( \text{C}_2\text{H}_5 \) at 298 K.

22.19 Two products are formed in reactions in which there is kinetic control of the ratio of products. The activation energy for the reaction leading to Product 1 is greater than that leading to Product 2. Will the ratio of product concentrations \([P_1]/[P_2]\) increase or decrease if the temperature is raised?

### Theoretical problems

22.20 The reaction mechanism

\[
\text{A}_2 \rightarrow \text{A} + \text{A} \text{ (fast)} \\
\text{A} + \text{B} \rightarrow \text{P} \text{ (slow)}
\]

involves an intermediate A. Deduce the rate law for the reaction.

22.21 The equilibrium \( \text{A} \rightarrow \text{B} \) is first-order in both directions. Derive an expression for the concentration of A as a function of time when the initial molar concentrations of A and B are \([\text{A}]_0\) and \([\text{B}]_0\). What is the final composition of the system?

22.22 Derive an integrated expression for a second-order rate law \( v = k[\text{A}][\text{B}] \) for a reaction of stoichiometry \( 2 \text{A} + 3 \text{B} \rightarrow \text{P} \).
22.23 Derive the integrated form of a third-order rate law \( v = k[A]^2[B] \) in which the stoichiometry is \( 2 \, A + B \rightarrow P \) and the reactants are initially present in (a) their stoichiometric proportions, (b) with B present initially in twice the amount.

22.24 Set up the rate equations for the reaction mechanism:

\[
A \underset{k_a, k_a'}{\rightarrow} B \underset{k_b, k_b'}{\rightarrow} C
\]

Show that the mechanism is equivalent to

\[
A \underset{k_{\text{eff}}, k_{\text{eff}}'}{\rightarrow} C
\]

under specified circumstances.

22.25 Show that the ratio \( t_{1/2}/t_{3/4} \), where \( t_{1/2} \) is the half-life and \( t_{3/4} \) is the time for the concentration of A to decrease to \( 3/4 \) of its initial value (implying that \( t_{3/4} < t_{1/2} \)) can be written as a function of \( n \) alone, and can therefore be used as a rapid assessment of the order of a reaction.

22.26 Derive an equation for the steady state rate of the sequence of reactions \( A \rightarrow B \rightarrow C \), with \([A]\) maintained at a fixed value and the product D removed as soon as it is formed.

22.27 For the second-order reaction \( A + B \rightarrow \text{Products} \), the rate of reaction, \( v \), may be written

\[
v = k[A][B]
\]

where \( x \) is the decrease in concentration of A or B as a result of reaction. Find an expression for the maximum rate and the conditions under which it applies. Draw a graph of \( v \) against \( x \), and noting that \( v \) and \( x \) cannot be negative, identify the portion of the curve that corresponds to
22.28 Consider the dimerization $A \_ A_2$ with forward rate constant $k_a$ and backward rate constant $k_b$. Show that the relaxation time is:

$$$$

Applications to: archaeology, biochemistry, and environmental science

22.29 The half-life for the (first-order) radioactive decay of $^{14}$C is 5730 y (it emits $\beta$ rays with an energy of 0.16 MeV). An archaeological sample contained wood that had only 72 per cent of the $^{14}$C found in living trees. What is its age?

22.30 One of the hazards of nuclear explosions is the generation of $^{90}$Sr and its subsequent incorporation in place of calcium in bones. This nuclide emits $\beta$ rays of energy 0.55 MeV, and has a half-life of 28.1 y. Suppose 1.00 µg was absorbed by a newly born child. How much will remain after (a) 18 y, (b) 70 y if none is lost metabolically?

22.31 Pharmacokinetics is the study of the rates of absorption and elimination of drugs by organisms. In most cases, elimination is slower than absorption and is a more important determinant of availability of a drug for binding to its target. A drug can be eliminated by many mechanisms, such as metabolism in the liver, intestine, or kidney followed by excretion of breakdown products through urine or feces. As an example of pharmacokinetic analysis, consider the elimination of beta adrenergic blocking agents (beta blockers), drugs used in the treatment of hypertension. After intravenous administration of a beta blocker, the blood plasma of a patient
was analyzed for remaining drug and the data are shown below, where \( c \) is the drug concentration measured at a time \( t \) after the injection.

\[
\begin{array}{cccccccc}
  t/\text{min} & 30 & 60 & 120 & 150 & 240 & 360 & 480 \\
  c/(\text{ng cm}^{-3}) & 699 & 622 & 413 & 292 & 152 & 60 & 24 \\
\end{array}
\]

(a) Is removal of the drug a first- or second-order process? (b) Calculate the rate constant and half-life of the process. Comment: An essential aspect of drug development is the optimization of the half-life of elimination, which needs to be long enough to allow the drug to find and act on its target organ but not so long that harmful side-effects become important.

22.32 The absorption and elimination of a drug in the body may be modeled with a mechanism consisting of two consecutive reactions:

\[
\begin{align*}
  \text{A} & \rightarrow \text{B} \\
  \text{drug at site of administration} & \rightarrow \text{drug dispersed in blood} \\
  \text{B} & \rightarrow \text{C} \\
  \text{eliminated drug} & \rightarrow \text{drug}
\end{align*}
\]

where the rate constants of absorption (A \( \rightarrow \) B) and elimination are, respectively, \( k_1 \) and \( k_2 \). (a) Consider a case in which absorption is so fast that it may be regarded as instantaneous and elimination follows first-order kinetics. Show that, after administration of \( n \) equal doses separated by a time interval \( \tau \), the concentration of drug in blood rises exponentially and eventually reaches a constant level \([B]_\infty\) given by

\[
[B]_\infty = \frac{[B]_0}{1 - e^{-k_2 \tau}}
\]

where \([B]_0\) is the initial concentration of drug in the blood after administration of each dose. (b) Consider a drug for which \( k_2 = 0.0289 \text{ h}^{-1} \). Using the result from part (a), calculate the number of doses of a specified size that must be administered every 4 h to reach a level in blood given by
[B]₀/[A]₀ = 0.10. (c) Now consider a case in which absorption follows first-order kinetics and elimination follows zero-order kinetics. The mode of drug metabolism occurs when the drug is in excess with respect to the compounds with which it must react during elimination. Show that, with [B]₀ = 0, the concentration of drug in the blood is given by

\[ \frac{[B]}{[A]} = \frac{[B]_0}{[A]_0} = 0.10. \]

(c) Now consider a case in which absorption follows first-order kinetics and elimination follows zero-order kinetics. The mode of drug metabolism occurs when the drug is in excess with respect to the compounds with which it must react during elimination. Show that, with [B]₀ = 0, the concentration of drug in the blood is given by

Plot \([B]/[A]_0\) against \(t\) for the case \(k_1 = 10 \text{ h}^{-1}\) and \(k_2 = 8.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}\). Comment on the shape of the curve. (d) Using the model from part (c), set \(d[B]/dt = 0\) and show that the maximum concentration of drug in blood is given by

\[ [B]_{\text{max}} = \frac{[A]_0 - k_2/k_1 - k_2 t_{\text{max}}}{k_1} \]

where \(t_{\text{max}}\) is the time at which \([B] = [B]_{\text{max}}\).

22.33 Consider a mechanism for the helix–coil transition in which nucleation occurs in the middle of the chain:

\[
\begin{array}{c}
\text{hhhh} \ldots \_	ext{hchh} \ldots \\
\text{hchh} \ldots \_	ext{cccc} \ldots 
\end{array}
\]

We saw in Impact section 22.1 that this type of nucleation is relatively slow, so neither step may be rate determining. (a) Set up the rate equations for this mechanism. (b) Apply the steady-state approximation and show that, under these circumstances, the mechanism is equivalent to \(\text{hhhh} \ldots \_	ext{cccc} \ldots\). (c) Use your knowledge of experimental techniques and your results from parts (a) and (b) to support or refute the following statement: It is very difficult to obtain experimental evidence for intermediates in protein folding by performing simple rate measurements and one must resort to special flow, relaxation, or trapping techniques to detect intermediates directly.

22.34 Propose a set of experiments in which analysis of the line-shapes of NMR transitions
(Section 15.*) can be used to monitor fast events in protein folding and unfolding. What are the disadvantages and disadvantages of this NMR method over methods that use electronic and vibrational spectroscopy?

22.35 Consider the following mechanism for renaturation of a double helix from its strands A and B:

\[
A + B \rightarrow \text{unstable helix (fast)} \\
\text{Unstable helix} \rightarrow \text{stable double helix (slow)}
\]

Derive the rate equation for the formation of the double helix and express the rate constant of the renaturation reaction in terms of the rate constants of the individual steps.

22.36 *Prebiotic reactions* are reactions that might have occurred under the conditions prevalent on the Earth before the first living creatures emerged and which can lead to analogs of molecules necessary for life as we now know it. To qualify, a reaction must proceed with favorable rates and equilibria. M.P. Robertson and S.I. Miller (*Science* 268, 702(1995)) have studied the prebiotic synthesis of 5-substituted uracils, among them 5-hydroxymethyluracil (HMU). Amino acid analogs can be formed from HMU under prebiotic conditions by reaction with various nucleophiles, such as H₂S, HCN, indole, imidazole, etc. For the synthesis of HMU (the uracil analog of serine) from uracil and formaldehyde (HCHO), the rate of addition is given by log \( k/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \) = 11.75 -5488/(\(T/K\)) (at pH = 7), and log \( K = -1.36 + 1794/(T/K)\). For this reaction, calculate the rates and equilibrium constants over a range of temperatures corresponding to possible prebiotic conditions, such as 0–50°C, and plot them against temperature. Also, calculate the activation energy and the standard reaction Gibbs energy and enthalpy at 25°C. Prebiotic conditions are not likely to be standard conditions. Speculate about
how the actual values of the reaction Gibbs energy and enthalpy might differ from the standard values. Do you expect that the reaction would still be favourable?

22.37‡ Methane is a by-product of a number of natural processes (such as digestion of cellulose in ruminant animals, anaerobic decomposition of organic waste matter) and industrial processes (such as food production and fossil fuel use). Reaction with the hydroxyl radical OH is the main path by which CH$_4$ is removed from the lower atmosphere. T. Gierczak, R.K. Talukdar, S.C. Herndon, G.L. Vaghjiani, and A.R. Ravishankara (*J. Phys. Chem. A* 101, 3125 (1997)) measured the rate constants for the elementary bimolecular gas-phase reaction of methane with the hydroxyl radical over a range of temperatures of importance to atmospheric chemistry. Deduce the Arrhenius parameters $A$ and $E_a$ from the following measurements:

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$k$ ($10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>3.70</td>
</tr>
<tr>
<td>295</td>
<td>3.55</td>
</tr>
<tr>
<td>223</td>
<td>0.494</td>
</tr>
<tr>
<td>218</td>
<td>0.452</td>
</tr>
<tr>
<td>213</td>
<td>0.379</td>
</tr>
<tr>
<td>206</td>
<td>0.295</td>
</tr>
<tr>
<td>200</td>
<td>0.241</td>
</tr>
<tr>
<td>195</td>
<td>0.217</td>
</tr>
</tbody>
</table>

22.38‡ As we saw in Problem 22.37, reaction with the hydroxyl radical OH is the main path by which CH$_4$, a by product of many natural and industrial processes, is removed from the lower atmosphere. T. Gierczak, R.K. Talukdar, S.C. Herndon, G.L. Vaghjiani, and A.R. Ravishankara (*J. Phys. Chem. A* 101, 3125 (1997)) measured the rate constants for the bimolecular gas-phase reaction CH$_4$(g) + OH(g) → CH$_3$(g) + H$_2$O(g) and found $A = 1.13 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ and $E_a = 14.1$ kJ mol$^{-1}$ for the Arrhenius parameters. (a) Estimate the rate of consumption of CH$_4$. Take the average OH concentration to be $1.5 \times 10^{-21}$ mol dm$^{-3}$, that of CH$_4$ to be $4.0 \times 10^{-8}$ mol dm$^{-3}$, and the temperature to be -10° C. (b) Estimate the global annual mass of CH$_4$ consumed by this reaction (which is slightly less than the amount introduced to the atmosphere) given an effective volume for the Earth’s lower atmosphere of $4 \times 10^{21}$ dm$^3$. 
22.39‡ T. Gierczak, R.K. Talukdar, S.C. Herndon, G.L. Vaghjiani, and A.R. Ravishankara (J. Phys. Chem. A 101, 3125 (1997)) measured the rate constants for the bimolecular gas-phase reaction of methane with the hydroxyl radical in several isotopic variations. From their data, the following Arrhenius parameters can be obtained:

\[
\begin{align*}
A/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) & \quad E_a/(\text{kJ mol}^{-1}) \\
\text{CH}_4 + \text{OH} & \rightarrow \text{CH}_3 + \text{H}_2\text{O} & 1.13 \times 10^9 & 14.1 \\
\text{CD}_4 + \text{OH} & \rightarrow \text{CD}_3 + \text{DOH} & 6.0 \times 10^8 & 17.5 \\
\text{CH}_4 + \text{OD} & \rightarrow \text{CH}_3 + \text{DOH} & 1.01 \times 10^9 & 13.6
\end{align*}
\]

Compute the rate constants at 298 K, and interpret the kinetic isotope effects.

22.40‡ The oxidation of HSO_3^- by O_2 in aqueous solution is a reaction of importance to the processes of acid rain formation and flue gas desulfurization. R.E. Connick, Y.-X. Zhang, S. Lee, R. Adamic, and P. Chieng (Inorg. Chem. 34, 4543 (1995)) report that the reaction \(2 \text{HSO}_3^- + \text{O}_2 \rightarrow 2 \text{SO}_4^{2-} + 2 \text{H}^+\) follows the rate law \(v = k[\text{HSO}_3^-]^2[\text{H}^+]^2\). Given a pH of 5.6 and an oxygen molar concentration of \(2.4 \times 10^{-4} \text{ mol dm}^{-3}\) (both presumed constant), an initial \(\text{HSO}_3^-\) molar concentration of \(5 \times 10^{-5} \text{ mol dm}^{-3}\), and a rate constant of \(3.6 \times 10^6 \text{ L}^3 \text{ mol}^{-3} \text{ s}^{-1}\), what is the initial rate of reaction? How long would it take for \(\text{HSO}_3^-\) to reach half its initial concentration?