Problems*

Numerical problems

21.1 The data below apply to the formation of urea from ammonium cyanate, $NH_4CNO \rightarrow NH_2CONH_2$. Initially 22.9 g of ammonium cyanate was dissolved 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
m(urea)/g	0	7.0	12.1	13.8	17.7

21.2 The data below apply to the reaction $(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$. Determine the order of the reaction, the rate constant, and the molar concentration of $(CH_3)_3CBr$ after 43.8 h.

t	0	3.15	6.20	10.00	18.30	30.80
$[(CH_3)_3CBr]/(10^{-2} \text{ mol dm}^{-3})$	10.39	8.96	7.76	6.39	3.53	2.07

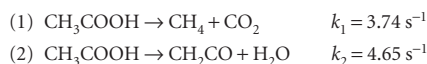**21.3** The thermal decomposition of an organic nitrile produced the following data:

$t/(10^3 \text{ s})$	0	2.00	4.00	6.00	8.00	10.00	12.00	∞
[nitrile]/(mol dm^{-3})	1.50	1.26	1.07	0.92	0.81	0.72	0.65	0.40

Determine the order of the reaction and the rate constant.

21.4 The following data have been obtained for the decomposition of $N_2O_5(g)$ at 67°C according to the reaction $2 N_2O_5(g) \rightarrow 4 NO_2(g) + O_2(g)$. 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.

t/min	0	1	2	3	4	5
$[N_2O_5]/(\text{mol dm}^{-3})$	1.000	0.705	0.497	0.349	0.246	0.173

21.5 The gas-phase decomposition of acetic acid at 1189 K proceeds by way of two parallel reactions:

(1) $CH_3COOH \rightarrow CH_4 + CO_2$ $k_1 = 3.74 \text{ s}^{-1}$
(2) $CH_3COOH \rightarrow CH_2CO + H_2O$ $k_2 = 4.65 \text{ s}^{-1}$

What is the maximum percentage yield of the ketene CH_2CO obtainable at this temperature?

21.6 Sucrose is readily hydrolysed 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:

t/min	0	14	39	60	80	110	140	170	210
[sucrose]/(mol dm^{-3})	0.316	0.300	0.274	0.256	0.238	0.211	0.190	0.170	0.146

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

21.7 The composition of a liquid-phase reaction $2 A \rightarrow B$ was followed by a spectrophotometric method with the following results:

t/min	0	10	20	30	40	∞
$[B]/(\text{mol dm}^{-3})$	0	0.089	0.153	0.200	0.230	0.312

Determine the order of the reaction and its rate constant.

21.8 The ClO radical decays rapidly by way of the reaction, $2 ClO \rightarrow Cl_2 + O_2$. The following data have been obtained:

$t/(10^{-3} \text{ s})$	0.12	0.62	0.96	1.60	3.20	4.00	5.75
$[ClO]/(10^{-6} \text{ mol dm}^{-3})$	8.49	8.09	7.10	5.79	5.20	4.77	3.95

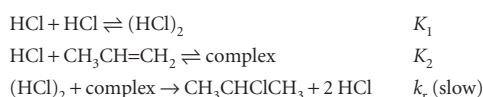Determine the rate constant of the reaction and the half-life of a ClO radical.

21.9 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:

p_0/Torr	200	200	400	400	600	600
t/s	100	200	100	200	100	200
p/Torr	186	173	373	347	559	520

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?

21.10 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 δt, the concentration of product follows $[P]/[A] = k_r[A]^{m-1}[B]^n\delta t$ if the reaction is mth-order in A and nth-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 $\delta t \approx 100$ h (which is short on the timescale of the reaction) the latter ratio rose from zero to 0.05, 0.03, 0.01 for $p(HCl) = 10$ atm, 7.5 atm, 5.0 atm, respectively. What are the orders of the reaction with respect to each reactant?

21.11 Show that the following mechanism can account for the rate law of the reaction in Problem 21.10:

$$HCl + HCl \rightleftharpoons (HCl)_2 \qquad\qquad K_1$$
$$HCl + CH_3CH{=}CH_2 \rightleftharpoons \text{complex} \qquad K_2$$
$$(HCl)_2 + \text{complex} \rightarrow CH_3CHClCH_3 + 2 HCl \qquad k_r \text{ (slow)}$$

What further tests could you apply to verify this mechanism?

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

$k_r/(10^{-3} \text{ s}^{-1})$	2.46	45.1	576
θ/°C	0	20.0	40.0

21.13 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 1.44×10^7 dm^3 mol^{-1} s^{-1} at 300.3 K, 3.03×10^7 dm^3 mol^{-1} s^{-1} at 341.2 K, and 6.9×10^7 dm^3 mol^{-1} s^{-1} at 392.2 K. Find the pre-exponential factor and activation energy of the reaction.

21.14 In the experiments described in Problems 21.10 and 21.11 an inverse temperature dependence of the reaction rate was observed, the overall rate of reaction at 70°C being approximately 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}.

21.15 Use mathematical software or an electronic spreadsheet to examine the time dependence of [I] in the reaction mechanism $A \rightarrow I \rightarrow P$ (k_a, k_b). 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 $k_a = 10 \text{ s}^{-1}$ and $k_b = 1 \text{ s}^{-1}$. (b) Increase the ratio k_b/k_a steadily by decreasing the value of k_a and examine the plot of [I] against t at each turn. What approximation about $d[I]/dt$ becomes increasingly valid?

21.16 Consider the dimerization $2 A \rightleftharpoons A_2$, with forward rate constant k_a and reverse rate constant k_a'. (a) Derive the following expression for the relaxation time in terms of the total concentration of protein, $[A]_{tot} = [A] + 2[A_2]$:

$$\frac{1}{\tau^2} = k_a'^2 + 8k_a k_a' [A]_{tot}$$

(b) Describe the computational procedures that lead to the determination of the rate constants k_a and k_a' from measurements of τ for different values of $[A]_{tot}$. (c) Use the data provided below and the procedure you outlined in part (b) to calculate the rate constants k_a and k_a', and the equilibrium constant K for formation of hydrogen-bonded dimers of 2-pyridone:

$[P]/(\text{mol dm}^{-3})$	0.500	0.352	0.251	0.151	0.101
τ/ns	2.3	2.7	3.3	4.0	5.3

21.17 In Problem 21.9 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 *et al.*, *Proc. R. Soc.* **A217**, 563 (1953)):

p/Torr	84.1	11.0	2.89	0.569	0.120	0.067
$10^4 k_r/s^{-1}$	2.98	2.23	1.54	0.857	0.392	0.303

Test the Lindemann theory with these data.

21.18 Dansyl chloride, which absorbs maximally at 330 nm and fluoresces maximally at 510 nm, can be used to label aminoacids 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). The ratio of intensities is equal to the ratio of the rates of photon emission.

t/ns	5.0	10.0	15.0	20.0
I_f/I_0	0.45	0.21	0.11	0.05

(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?

21.19 When benzophenone is illuminated with ultraviolet radiation 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?

$[Q]/(\text{mol dm}^{-3})$	0.0010	0.0050	0.0100
$I_f/(\text{arbitrary units})$	0.41	0.25	0.16

21.20 An electronically excited state of Hg can be quenched by N_2 according to

$$Hg^* (g) + N_2 (g, v = 0) \rightarrow Hg (g) + N_2 (g, v = 1)$$
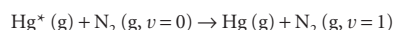
in which energy transfer from Hg^* excites N_2 vibrationally. Fluorescence lifetime measurements of samples of Hg with and without N_2 present are summarized below ($T = 300$ K):

$$p_{N_2} = 0.0 \text{ atm}$$

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

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

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 are perfect. Determine the rate constant for the energy transfer process.

21.21 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:

R/nm	1.2	1.5	1.8	2.8	3.1	3.4	3.7	4.0	4.3	4.6
η_T	0.99	0.94	0.97	0.82	0.74	0.65	0.40	0.28	0.24	0.16

Are the data described adequately by eqn 21.86? If so, what is the value of R_0 for the naphthyl–dansyl pair?

Theoretical problems

21.22 Show that $t_{1/2}$ is given by eqn 21.17 for a reaction that is nth-order in A. Then deduce an expression for the time it takes for the concentration of a substance to fall to one-third the initial value in an nth-order reaction.

21.23 The equilibrium $A \rightleftharpoons B$ 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 $[A]_0$ and $[B]_0$. What is the final composition of the system?

21.24 Derive an integrated expression for a second-order rate law $v = k[A][B]$ for a reaction of stoichiometry $2 A + 3 B \rightarrow P$.

21.25 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.

21.26 Show that the definition of E_a given in eqn 21.30 reduces to eqn 21.29 for a temperature-independent activation energy.

21.27 Set up the rate equations for the reaction mechanism:

$$A \underset{k_a'}{\overset{k_a}{\rightleftharpoons}} B \underset{k_b'}{\overset{k_b}{\rightleftharpoons}} CH$$
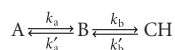
Show that the mechanism is equivalent to

$$A \underset{k_r'}{\overset{k_r}{\rightleftharpoons}} C$$
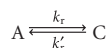
under specified circumstances.

21.28 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 $\frac{3}{4}$ 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.

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

21.30 Consider the dimerization $2 A \rightleftharpoons A_2$ with forward rate constant k_r and backward rate constant k_r'. Show that the relaxation time is:

$$\tau = \frac{1}{k_r' + 4k_r[A]_{eq}}$$

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

21.32 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.

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

21.34 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 $d[A]/dt = -k_r[A]^2[OH]$.

21.35 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_a, but that the reverse reaction $B \rightarrow A$ is bimolecular and second-order with a rate $k_r[B]^2$. What is the stationary state concentration of B? Why does this 'photostationary state' differ from the equilibrium state?

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

Applications to: biochemistry and environmental science

21.37 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 faeces. 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 analysed for remaining drug and the data are shown below, where c is the drug concentration measured at a time t after the injection.

t/min	30	60	120	150	240	360	480
c/(ng cm^{-3})	699	622	413	292	152	60	24

(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.

21.38 Consider a mechanism for the helix–coil transition in polypeptides that begins in the middle of the chain:

$$hhhh\ldots \rightleftharpoons hchh\ldots$$
$$hchh\ldots \rightleftharpoons cccc\ldots$$
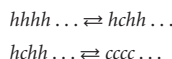
The first conversion from h to c, also called a nucleation step, is relatively slow, so neither step may be rate-determining. (a) Set up the rate equations for this mechanism. (b) Apply the steady-state approximation and show that, under these circumstances, the mechanism is equivalent to $hhhh\ldots \rightleftharpoons cccc\ldots$.

21.39‡ 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 *et al.* (*Inorg. Chem.* **34**, 4543 (1995)) report that the reaction $2\,HSO_3^- + O_2 \rightarrow 2\,SO_4^{2-} + 2\,H^+$ follows the rate law $v = k_r[HSO_3^-]^2[H^+]^2$. Given pH = 5.6 and an oxygen molar concentration of 2.4×10^{-4} mol dm^{-3} (both presumed constant), an initial HSO_3^- molar concentration of 5×10^{-5} mol dm^{-3}, and a rate constant of 3.6×10^6 dm^9 mol^{-3} s^{-1}, what is the initial rate of reaction? How long would it take for HSO_3^- to reach half its initial concentration?

21.40 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?

21.41‡ Ultraviolet radiation photolyses O_3 to O_2 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 yield is 0.94 at 220 K, the concentration about 8×10^{-9} mol dm^{-3}, the molar absorption coefficient 260 dm^3 mol^{-1} cm^{-1}, and the flux of 305 nm radiation about 1×10^{14} photons cm^{-2} s^{-1}. Data from W.B. DeMore *et al.*, *Chemical kinetics and photochemical data for use in stratospheric modeling: Evaluation Number 11*, JPL Publication 94-26 (1994).