

22.18(a) For an electron donor–acceptor pair, $k_{\text{et}} = 2.02 \times 10^5 \text{ s}^{-1}$ when $r = 1.11 \text{ nm}$ and $k_{\text{et}} = 4.51 \times 10^5 \text{ s}^{-1}$ when $r = 1.23 \text{ nm}$. Assuming that $\Delta_r G^\circ$ and λ are the same in both experiments, estimate the value of β .

22.18(b) Refer to Exercise 22.18a. Estimate the value of k_{et} when $r = 1.48 \text{ nm}$.

22.19(a) The transfer coefficient of a certain electrode in contact with M^{3+} and M^{4+} in aqueous solution at 25°C is 0.39. The current density is found to be 55.0 mA cm^{-2} when the overpotential is 125 mV. What is the overpotential required for a current density of 75 mA cm^{-2} ?

22.19(b) The transfer coefficient of a certain electrode in contact with M^{2+} and M^{3+} in aqueous solution at 25°C is 0.42. The current density is found to be 17.0 mA cm^{-2} when the overpotential is 105 mV. What is the overpotential required for a current density of 72 mA cm^{-2} ?

22.20(a) Determine the exchange current density from the information given in Exercise 22.19a.

22.20(b) Determine the exchange current density from the information given in Exercise 22.19b.

22.21(a) To a first approximation, significant evolution or deposition occurs in electrolysis only if the overpotential exceeds about 0.6 V. To illustrate this criterion determine the effect that increasing the overpotential from 0.40 V to 0.60 V has on the current density in the electrolysis of a certain electrolyte solution, which is 1.0 mA cm^{-2} at 0.4 V and 25°C . Take $\alpha = 0.5$.

22.21(b) Determine the effect that increasing the overpotential from 0.50 V to 0.60 V has on the current density in the electrolysis of a certain electrolyte solution, which is 1.22 mA cm^{-2} at 0.50 V and 25°C . Take $\alpha = 0.50$.

22.22(a) Use the data in Table 22.3 for the exchange current density and transfer coefficient for the reaction $2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2$ on nickel at 25°C to determine what current density would be needed to obtain an overpotential of 0.20 V as calculated from (a) the Butler–Volmer equation, and (b) the Tafel equation (eqn 22.69). Is the validity of the Tafel approximation affected at higher overpotentials (of 0.4 V and more)?

22.22(b) Use the data in Table 22.3 for the exchange current density and transfer coefficient for the reaction $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ on platinum at 25°C to determine what current density would be needed to obtain an overpotential of

0.30 V as calculated from (a) the Butler–Volmer equation, and (b) the Tafel equation (eqn 22.69). Is the validity of the Tafel approximation affected at higher overpotentials (of 0.4 V and more)?

22.23(a) A typical exchange current density, that for H^+ discharge at platinum, is 0.79 mA cm^{-2} at 25°C . What is the current density at an electrode when its overpotential is (a) 10 mV, (b) 100 mV, (c) -5.0 V ? Take $\alpha = 0.5$.

22.23(b) The exchange current density for a $\text{Pt}|\text{Fe}^{3+}, \text{Fe}^{2+}$ electrode is 2.5 mA cm^{-2} . The standard potential of the electrode is $+0.77 \text{ V}$. Calculate the current flowing through an electrode of surface area 1.0 cm^2 as a function of the potential of the electrode. Take unit activity for both ions.

22.24(a) How many electrons or protons are transported through the double layer in each second when the $\text{Pt}|\text{H}_2|\text{H}^+$, $\text{Pt}|\text{Fe}^{3+}, \text{Fe}^{2+}$, and $\text{Pb}|\text{H}_2|\text{H}^+$ electrodes are at equilibrium at 25°C ? Take the area as 1.0 cm^2 in each case. Estimate the number of times each second a single atom on the surface takes part in a electron transfer event, assuming an electrode atom occupies about $(280 \text{ pm})^2$ of the surface.

22.24(b) How many electrons or protons are transported through the double layer in each second when the $\text{Cu}|\text{H}_2|\text{H}^+$ and $\text{Pt}|\text{Ce}^{4+}, \text{Ce}^{3+}$ electrodes are at equilibrium at 25°C ? Take the area as 1.0 cm^2 in each case. Estimate the number of times each second a single atom on the surface takes part in a electron transfer event, assuming an electrode atom occupies about $(260 \text{ pm})^2$ of the surface.

22.25(a) What is the effective resistance at 25°C of an electrode interface when the overpotential is small? Evaluate it for 1.0 cm^2 (a) $\text{Pt}|\text{H}_2|\text{H}^+$, (b) $\text{Hg}|\text{H}_2|\text{H}^+$ electrodes.

22.25(b) Evaluate the effective resistance at 25°C of an electrode interface for 1.0 cm^2 (a) $\text{Pb}|\text{H}_2|\text{H}^+$, (b) $\text{Pt}|\text{Fe}^{2+}, \text{Fe}^{3+}$ electrodes.

22.26(a) The exchange current density for H^+ discharge at zinc is about 50 pA cm^{-2} . Can zinc be deposited from a unit activity aqueous solution of a zinc salt?

22.26(b) The standard potential of the $\text{Zn}^{2+}|\text{Zn}$ electrode is -0.76 V at 25°C . The exchange current density for H^+ discharge at platinum is 0.79 mA cm^{-2} . Can zinc be plated on to platinum at that temperature? (Take unit activities.)

Problems*

Numerical problems

22.1 In the dimerization of methyl radicals at 25°C , the experimental pre-exponential factor is $2.4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. What are (a) the reactive cross-section, (b) the P factor for the reaction if the C–H bond length is 154 pm ?

22.2 Nitrogen dioxide reacts bimolecularly in the gas phase to give $2 \text{NO} + \text{O}_2$. The temperature dependence of the second-order rate constant for the rate law $\text{d}[\text{P}]/\text{d}t = k[\text{NO}_2]^2$ is given below. What are the P factor and the reactive cross-section for the reaction?

T/K	600	700	800	1000
$k_r/(\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	4.6×10^2	9.7×10^3	1.3×10^5	3.1×10^6

Take $\sigma = 0.60 \text{ nm}^2$.

22.3 The diameter of the methyl radical is about 308 pm . What is the maximum rate constant in the expression $\text{d}[\text{C}_2\text{H}_6]/\text{d}t = k_r[\text{CH}_3]^2$ for

second-order recombination of radicals at room temperature? 10 per cent of a 1.0-dm^3 sample of ethane at 298 K and 100 kPa is dissociated into methyl radicals. What is the minimum time for 90 per cent recombination?

22.4 The rates of thermolysis of a variety of *cis*- and *trans*-azoalkanes have been measured over a range of temperatures in order to settle a controversy concerning the mechanism of the reaction. In ethanol an unstable *cis*-azoalkane decomposed at a rate that was followed by observing the N_2 evolution, and this led to the rate constants listed below (P.S. Engel and D.J. Bishop, *J. Amer. Chem. Soc.* **97**, 6754 (1975)). Calculate the enthalpy, entropy, energy, and Gibbs energy of activation at -20°C .

$\theta/^\circ\text{C}$	−24.82	−20.73	−17.02	−13.00	−8.95
$10^4 \times k_r/\text{s}^{-1}$	1.22	2.31	4.39	8.50	14.3

22.5 In an experimental study of a bimolecular reaction in aqueous solution, the second-order rate constant was measured at 25°C and at a variety of ionic

* Problems denoted with the symbol ‡ were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.

strengths and the results are tabulated below. It is known that a singly charged ion is involved in the rate-determining step. What is the charge on the other ion involved?

I	0.0025	0.0037	0.0045	0.0065	0.0085
$k_r/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	1.05	1.12	1.16	1.18	1.26

22.6 The rate constant of the reaction $\text{I}^-(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{IO}^-(\text{aq})$ varies slowly with ionic strength, even though the Debye–Hückel limiting law predicts no effect. Use the following data from 25°C to find the dependence of $\log k_r$ on the ionic strength:

I	0.0207	0.0525	0.0925	0.1575
$k_r/(\text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1})$	0.663	0.670	0.679	0.694

Evaluate the limiting value of k_r at zero ionic strength. What does the result suggest for the dependence of $\log \gamma$ on ionic strength for a neutral molecule in an electrolyte solution?

22.7 The total cross-sections for reactions between alkali metal atoms and halogen molecules are given in the table below (R.D. Levine and R.B. Bernstein, *Molecular reaction dynamics*, Clarendon Press, Oxford, 72 (1974)). Assess the data in terms of the harpoon mechanism.

σ^*/nm^2	Cl_2	Br_2	I_2
Na	1.24	1.16	0.97
K	1.54	1.51	1.27
Rb	1.90	1.97	1.67
Cs	1.96	2.04	1.95

Electron affinities are approximately 1.3 eV (Cl_2), 1.2 eV (Br_2), and 1.7 eV (I_2), and ionization energies are 5.1 eV (Na), 4.3 eV (K), 4.2 eV (Rb), and 3.9 eV (Cs).

22.8† One of the most historically significant studies of chemical reaction rates was that by M. Bodenstein (*Z. physik. Chem.* 29, 295 (1899)) of the gas-phase reaction $2 \text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ and its reverse, with rate constants k_r and k'_r , respectively. The measured rate constants as a function of temperature are

T/K	647	666	683	700	716	781
$k_r/(22.4 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1})$	0.230	0.588	1.37	3.10	6.70	105.9
$k'_r/(22.4 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1})$	0.0140	0.0379	0.0659	0.172	0.375	3.58

Demonstrate that these data are consistent with the collision theory of bimolecular gas-phase reactions.

22.9 In an experiment on the $\text{Pt}|\text{H}_2|\text{H}^+$ electrode in dilute H_2SO_4 the following current densities were observed at 25°C. Evaluate α and j_0 for the electrode.

η/mV	50	100	150	200	250
$j/(\text{mA cm}^{-2})$	2.66	8.91	29.9	100	335

How would the current density at this electrode depend on the overpotential of the same set of magnitudes but of opposite sign?

22.10 The standard potentials of lead and tin are –126 mV and –136 mV, respectively, at 25°C, and the overpotentials for their deposition are close to zero. What should their relative activities be in order to ensure simultaneous deposition from a mixture?

22.11† The rate of deposition of iron, v , on the surface of an iron electrode from an aqueous solution of Fe^{2+} has been studied as a function of potential, E , relative to the standard hydrogen electrode, by J. Kanya (*J. Electroanal. Chem.* 84, 83 (1977)). The values in the table below are based on the data obtained with an electrode of surface area 9.1 cm^2 in contact with a solution of concentration $1.70 \mu\text{mol dm}^{-3}$ in Fe^{2+} . (a) Assuming unit activity coefficients, calculate the zero current potential of the Fe^{2+}/Fe cathode and the overpotential at each value of the working potential. (b) Calculate the cathodic current density, j_c , from the rate of deposition of Fe^{2+} for each value

of E . (c) Examine the extent to which the data fit eqn 22.69 and calculate the exchange current density.

$v/(\text{pmol s}^{-1})$	1.47	2.18	3.11	7.26
$-E/\text{mV}$	702	727	752	812

22.12† The thickness of the diffuse double layer according to the Gouy–Chapman model is given by eqn 18.16. Use this equation to calculate and plot the thickness as a function of concentration and electrolyte type at 25°C. For examples, choose aqueous solutions of NaCl and Na_2SO_4 ranging in concentration from 0.1 to 100 mmol dm^{-3} .

22.13† V.V. Losev and A.P. Pchel'nikov (*Soviet Electrochem.* 6, 34 (1970)) obtained the following current–voltage data for an indium anode relative to a standard hydrogen electrode at 293 K:

$-E/\text{V}$	0.388	0.365	0.350	0.335
$j/(\text{A m}^{-2})$	0	0.590	1.438	3.507

Use these data to calculate the transfer coefficient and the exchange current density. What is the cathodic current density when the potential is 0.365 V?

22.14† An early study of the hydrogen overpotential is that of H. Bowden and T. Rideal (*Proc. Roy. Soc. A* 120, 59 (1928)), who measured the overpotential for H_2 evolution with a mercury electrode in dilute aqueous solutions of H_2SO_4 at 25°C. Determine the exchange current density and transfer coefficient, α , from their data:

$j/(\text{mA m}^{-2})$	2.9	6.3	28	100	250	630	1650	3300
η/V	0.60	0.65	0.73	0.79	0.84	0.89	0.93	0.96

Explain any deviations from the result expected from eqn 22.69.

Theoretical problems

22.15 Confirm that eqn 22.26 is a solution of eqn 22.25, where $[J]$ is a solution of the same equation but with $k_r = 0$ and for the same initial conditions.

22.16 Confirm that, if the initial condition is $[J] = 0$ at $t = 0$ everywhere, and the boundary condition is $[J] = [J]_0$ at $t > 0$ at all points on a surface, then the solutions $[J]^*$ in the presence of a first-order reaction that removed J are related to those in the absence of reaction, $[J]$, by

$$[J]^* = k_r \int_0^t [J] e^{-k_r t} dt + [J] e^{-k_r t}$$

Base your answer on eqn 22.25.

22.17 Estimate the orders of magnitude of the partition functions involved in a rate expression. State the order of magnitude of q_m^T/N_A , q^R , q^V , q^E for typical molecules. Check that in the collision of two structureless molecules the order of magnitude of the pre-exponential factor is of the same order as that predicted by collision theory. Go on to estimate the P factor for a reaction in which $\text{A} + \text{B} \rightarrow \text{P}$, and A and B are nonlinear triatomic molecules.

22.18 Use the Debye–Hückel limiting law to show that changes in ionic strength can affect the rate of reaction catalysed by H^+ from the deprotonation of a weak acid. Consider the mechanism: $\text{H}^+(\text{aq}) + \text{B}(\text{aq}) \rightarrow \text{P}$, where H^+ comes from the deprotonation of the weak acid, HA . The weak acid has a fixed concentration. First show that $\log [\text{H}^+]$, derived from the ionization of HA , depends on the activity coefficients of ions and thus depends on the ionic strength. Then find the relationship between $\log(\text{rate})$ and $\log [\text{H}^+]$ to show that the rate also depends on the ionic strength.

22.19 The Eyring equation can also be applied to physical processes. As an example, consider the rate of diffusion of an atom stuck to the surface of a solid. Suppose that in order to move from one site to another it has to reach the top of the barrier where it can vibrate classically in the vertical direction

and in one horizontal direction, but vibration along the other horizontal direction takes it into the neighbouring site. Find an expression for the rate of diffusion, and evaluate it for W atoms on a tungsten surface ($E_a = 60 \text{ kJ mol}^{-1}$). Suppose that the vibration frequencies at the transition state are (a) the same as, (b) one-half the value for the adsorbed atom. What is the value of the diffusion coefficient D at 500 K? (Take the site separation as 316 pm and $\nu = 1 \times 10^{11} \text{ Hz}$.)

22.20† Show that bimolecular reactions between nonlinear molecules are much slower than between atoms even when the activation energies of both reactions are equal. Use transition state theory and make the following assumptions. (1) All vibrational partition functions are close to 1; (2) all rotational partition functions are approximately $1 \times 10^{1.5}$, which is a reasonable order of magnitude number; (3) the translational partition function for each species is 1×10^{26} .

22.21 This exercise gives some familiarity with the difficulties involved in predicting the structure of activated complexes. It also demonstrates the importance of femtosecond spectroscopy to our understanding of chemical dynamics because direct experimental observation of the activated complex removes much of the ambiguity of theoretical predictions. Consider the attack of H on D_2 , which is one step in the $H_2 + D_2$ reaction. (a) Suppose that the H approaches D_2 from the side and forms a complex in the form of an isosceles triangle. Take the H–D distance as 30 per cent greater than in H_2 (74 pm) and the D–D distance as 20 per cent greater than in H_2 . Let the critical coordinate be the antisymmetric stretching vibration in which one H–D bond stretches as the other shortens. Let all the vibrations be at about 1000 cm^{-1} . Estimate k_2 for this reaction at 400 K using the experimental activation energy of about 35 kJ mol^{-1} . (b) Now change the model of the activated complex in part (a) and make it linear. Use the same estimated molecular bond lengths and vibrational frequencies to calculate k_2 for this choice of model. (c) Clearly, there is much scope for modifying the parameters of the models of the activated complex. Use mathematical software or write and run a program that allows you to vary the structure of the complex and the parameters in a plausible way, and look for a model (or more than one model) that gives a value of k close to the experimental value, $4 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

22.22 If $\alpha = \frac{1}{2}$, an electrode interface is unable to rectify alternating current because the current density curve is symmetrical about $\eta = 0$. When $\alpha \neq \frac{1}{2}$, the magnitude of the current density depends on the sign of the overpotential, and so some degree of ‘faradaic rectification’ may be obtained. Suppose that the overpotential varies as $\eta = \eta_0 \cos \omega t$. Derive an expression for the mean flow of current (averaged over a cycle) for general α , and confirm that the mean current is zero when $\alpha = \frac{1}{2}$. In each case work in the limit of small η_0 but to second order in $\eta_0 F/RT$. Calculate the mean direct current at 25°C for a 1.0 cm^2 hydrogen–platinum electrode with $\alpha = 0.38$ when the overpotential varies between $\pm 10 \text{ mV}$ at 50 Hz.

22.23 Now suppose that the overpotential is in the high overpotential region at all times even though it is oscillating. What waveform will the current across the interface show if it varies linearly and periodically (as a sawtooth waveform) between η_- and η_+ around η_0 ? Take $\alpha = \frac{1}{2}$.

Applications: to biochemistry and environmental science

22.24† R. Atkinson (*J. Phys. Chem. Ref. Data* 26, 215 (1997)) has reviewed a large set of rate constants relevant to the atmospheric chemistry of volatile organic compounds. The recommended rate constant for the bimolecular association of O_2 with an alkyl radical R at 298 K is $4.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

for $R = C_2H_5$ and $8.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $R = \text{cyclohexyl}$. Assuming no energy barrier, compute the steric factor, P , for each reaction. (*Hint*. Obtain collision diameters from collision cross-sections of similar molecules in the *Data section*.)

22.25† The compound α -tocopherol, a form of vitamin E, is a powerful antioxidant that may help to maintain the integrity of biological membranes. R.H. Bisby and A.W. Parker (*J. Amer. Chem. Soc.* 117, 5664 (1995)) studied the reaction of photochemically excited duroquinone with the antioxidant in ethanol. Once the duroquinone was photochemically excited, a bimolecular reaction took place at a rate described as diffusion-limited. (a) Estimate the rate constant for a diffusion-limited reaction in ethanol. (b) The reported rate constant was $2.77 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; estimate the critical reaction distance if the sum of diffusion constants is $1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

22.26 The study of conditions that optimize the association of proteins in solution guides the design of protocols for formation of large crystals that are amenable to analysis by the X-ray diffraction techniques discussed in Chapter 19. It is important to characterize protein dimerization because the process is considered to be the rate-determining step in the growth of crystals of many proteins. Consider the variation with ionic strength of the rate constant of dimerization in aqueous solution of a cationic protein P:

I	0.0100	0.0150	0.0200	0.0250	0.0300	0.0350
k/k°	8.10	13.30	20.50	27.80	38.10	52.00

What can be deduced about the charge of P?

22.27 A useful strategy for the study of electron transfer in proteins consists of attaching an electroactive species to the protein’s surface and then measuring k_{et} between the attached species and an electroactive protein cofactor. J.W. Winkler and H.B. Gray (*Chem. Rev.* 92, 369 (1992)) summarize data for cytochrome *c* (*Impact* 16.1) modified by replacement of the haem iron by a zinc ion, resulting in a zinc-porphyrin (ZnP) moiety in the interior of the protein, and by attachment of a ruthenium ion complex to a surface histidine aminoacid. The edge-to-edge distance between the electroactive species was thus fixed at 1.23 nm. A variety of ruthenium ion complexes with different standard reduction potentials were used. For each ruthenium-modified protein, either the $Ru^{2+} \rightarrow ZnP^+$ or the $ZnP^+ \rightarrow Ru^{3+}$, in which the electron donor is an electronic excited state of the zinc-porphyrin formed by laser excitation, was monitored. This arrangement leads to different standard reaction Gibbs energies because the redox couples ZnP^+/ZnP and ZnP^+/ZnP^* have different standard potentials, with the electronically excited porphyrin being a more powerful reductant. Use the following data to estimate the reorganization energy for this system:

$-\Delta_r G^\circ/eV$	0.665	0.705	0.745	0.975	1.015	1.055
$k_{et}/(10^6 \text{ s}^{-1})$	0.657	1.52	1.12	8.99	5.76	10.1

22.28 The rate constant for electron transfer between a cytochrome *c* and the bacteriochlorophyll dimer of the reaction centre of the purple bacterium *Rhodobacter sphaeroides* decreases with decreasing temperature in the range 300 K to 130 K. Below 130 K, the rate constant becomes independent of temperature. Account for these results.

22.29 Calculate the thermodynamic limit to the zero-current potential of fuel cells operating on (a) hydrogen and oxygen, (b) methane and air, and (c) propane and air. Use the Gibbs energy information in the *Data section*, and take the species to be in their standard states at 25°C.