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1 Molecules and molecular structures: an overview

- 1.1 (a) Draw Lewis structures for the molecules PH_3 and PF_3 , making sure that in your structures you have accounted for all the valence electrons. Show that in each structure there is no formal charge on the phosphorus atom, and that the oxidation number of the phosphorus in PF_3 is +3.
 - (b) Draw two alternative Lewis structures for the molecule POF₃: one in which there is a double bond between the phosphorus and the oxygen, and one in which there is a P–O single bond. For each structure, determine the formal charge on both the oxygen and the phosphorus atoms. Assuming that the oxidation number of the oxygen is -2, determine the oxidation number of the phosphorus. Has the octet been expanded for phosphorus in either of your structures?
 - (c) For the hypothetical molecule PO_2F , draw three alternative Lewis structures: one with two doubly-bonded oxygen atoms, one with one doubly-bonded oxygen, and one with only single bonds to oxygen. For all three structures, determine the formal charges on the phosphorus and each of the oxygen atoms.
 - (d) The species $[PO_3]^{3-}$ is usually referred to as the phosphite anion. For this species, determine the oxidation number of the phosphorus and draw a Lewis structure, indicating any formal charges.

Protonation of this anion gives the phosphonate anion, $[HPO_3]^{2-}$, which has approximately tetrahedral coordination at phosphorus. The hydrogen is attached to the phosphorus and the three oxygen atoms occupy equivalent positions. Draw possible Lewis structures for this anion, and explain whether or not they are consistent with its known geometry. Explain how the concept of resonance can be helpful in describing the bonding on this anion.

- 1.2 (a) Determine the oxidation number of nitrogen in NO_2 .
 - (b) NO₂ is known to be a free radical (i.e. it has an unpaired electron) and to adopt a bent geometry. One possible representation of the bonding in NO₂ is shown below: indicate in the usual way the location of the electrons in this molecule, and verify that the formal charges shown are correct.



- (c) Experimental data indicates that NO₂ has a dipole moment which lies in the plane of the molecule and bisects the O–N–O angle. Explain why the structure shown above is *not* consistent with these data.
- (d) Use the concept of resonance structures to give an explanation for the direction of the observed dipole in NO_2 .
- (e) Draw two alternative Lewis structures for carbon monoxide: one in which there is a triple bond and one in which there is a double bond. Determine if there are any formal charges on the atoms. Experimentally it is found that this molecule has a small dipole moment, with the carbon being δ -. How can this observation be reconciled with your Lewis structures?

1.3 Explain how the formal charges on the oxygen and boron arise in the product **A** of reaction (a), and how the formal charges on the oxygen arise in reactant **B** and product **C** of reaction (b), shown below.



- 1.4 Assuming that there is no charge on the sulfur atom, use the approach described in section 1.1.2 on page 5 to determine the number of lone pairs on the sulfur in the following molecules: (a) SF₂, (b) SF₄, (c) SF₆, (d) SO₃.
- 1.5 Determine the oxidation state of oxygen in the following compounds: (a) Li₂O, (b) Na₂O₂, (c) KO₂, (d) MgO, (e) Ba(O₃)₂.
- 1.6 Determine the oxidation state of phosphorus in the following compounds or ions: (a) PCl₃, (b) PF₅, (c) P₂O₅, (d) PO₄³⁻.
- 1.7 Determine the oxidation state of chromium in the following compounds or ions: (a) CrF_6 , (b) $CrCl_4^-$, (c) CrO_4^{3-} , (d) $Cr_2O_7^{2-}$.
- **1.8** The boron hydride with formula B_4H_{10} is often drawn as



- (a) If each line represents a conventional bond in which two electrons are shared between two atoms, how many electrons are indicated by this structure?
- (b) Assuming that each boron contributes three electrons, and each hydrogen contributes one, how many valence electrons are there in B_4H_{10} ?
- (c) How can you reconcile your answers to (a) and (b)?
- 1.9 Use the VSEPR model to predict approximate structures for the following species:
 (i) BH₃, (ii) BH₄⁻, (iii) H₃O⁺, (iv) CH₅⁻, (v) PCl₅, (vi) PCl₄⁺, (vii) PCl₆⁻, (viii) NO₃⁻ (structure given below). (Hint: for the charged species, first work out the number of electrons in the valence shell ignoring the charge, and then reduce this total by one for a positive overall charge, or increase it by one for an overall negative charge).



1.10 ClF_3 is a highly reactive but nevertheless well-characterized volatile liquid used (among other things) to produce UF₆ in the processing of nuclear fuels. It has the following T-shaped structure



- (a) Use the VSEPR theory to show that the structure of ClF_3 can be expected to be based on a trigonal bipyramid.
- (b) The T-shaped structure can be considered to be a distorted trigonal bipyramid in which two 'equatorial' positions are occupied by lone pairs. Draw a diagram to illustrate this, and suggest why the bond angle in ClF₃ is not 90° as it would be in a regular trigonal bipyramid.
- 1.11 Explain why, at normal pressures and temperatures, MgCl₂ is a solid, SiO₂ is a solid, CO₂ is a gas and Ar is a gas.
- 1.12 What is the distinction between a *molecular* solid and an *ionic* solid? Account for the following observations:
 - (a) Solid PbBr₂ does not conduct electricity, but when molten the salt is a good conductor.
 - (b) Neither solid naphthalene nor molten naphthalene conduct electricity.



naphthalene

- (c) Metallic gold, both when solid and molten, conducts electricity.
- 1.13 As we go down Group 18, the noble gases, the atoms become more polarizable. Explain what you understand by this statement. Also explain how this trend in polarizability can be used to explain the observation that the boiling points of the liquefied noble gases increase as you go down the group.
- 1.14 Explain the following trends in the boiling points of the following two sets of hydrides:

set (a)	boiling point / °C	set (b)	boiling point / °C
H_2O	100.0	CH_4	-161.5
H_2S	-59.6	NH ₃	-33.3
H_2Se	-41.3	H_2O	100.0
H ₂ Te	-2		

1.15 What types of intermolecular forces are present in the following molecules: (a) butane C₄H₁₀;
(b) CH₃F; (c) CH₃OH; (d) CF₄?

1.16 In the gas phase, ethanoic acid is thought to exist as a dimer, held together by *two* hydrogen bonds. Suggest a structure for the dimer.

In the solid, $(COOH)_2$, forms extended chains, also held together by hydrogen bonds. Sketch a likely structure for such a chain.



oxalic acid

1.17 The following framework structures are poorly drawn or simply implausible. Point out the errors in each, and re-draw them correctly.



1.18 Find the molecular formula (i.e. $C_a H_b...$) of each of the following framework structures:



1.19 Draw framework structures of the following molecules:





1.20 Draw framework structures of the following molecules:

- 1.21 Calculate the concentration, in moles m^{-3} and molecules m^{-3} , of nitrogen gas at a pressure of 0.1 atmospheres and a temperature of 298 K. You may assume that the gas behaves ideally. (1 atmosphere is 1.013×10^5 N m⁻²)
- 1.22 What pressure will one mole of an ideal gas exert at 298 K if it is confined to a volume of (i) 1 m³, (ii) 1 dm³, and (iii) 1 cm³?
- **1.23** A container of volume 100 cm³ contains 1.0×10^{-4} moles of H₂ and 2.0×10^{-4} moles of N₂, such that the total pressure is 0.1 atmospheres. Calculate the mole fraction and partial pressure of each species. Also, calculate the temperature of the mixture.

1.24 Two containers of equal volume, and held at the same temperature, each contain the same amount in moles of an ideal gas. Explain why the pressure in each container is the same.

Suppose that one of these containers is filled with gas A and one with an equal amount in moles of gas B. Now, we connect the two containers such that the gases A and B mix. On mixing, what happens to the total pressure? How are the partial pressures of A and B related to the total pressure?

1.25 Suppose we take a container of fixed volume and maintain it at a constant temperature. In the container there is a mixture of three gases, which can be considered to be ideal. Suppose that the amount in moles of one of the gases is now increased. What happens to: (i) the total pressure and (ii) the partial pressures of each gas?

If the amount in moles of each gas is doubled, what happens to (i) the total pressure, (ii) the mole fraction of each gas?

2 Electrons in atoms

2.1 The probability of finding an electron in a small volume δV located at a particular point is given by $\psi(x, y, z)^2 \delta V$, where $\psi(x, y, z)$ is the wavefunction at that point.

For an electron in a 1*s* orbital, describe how this probability varies as the distance from the nucleus is increased. At what point is the probability (electron density) a maximum?

2.2 Explain what is meant by the *radial distribution function*. For an electron in a 1*s* orbital, how does the RDF vary with distance from the nucleus?

Explain why it is that although the 1s wavefunction is a maximum at the nucleus, the corresponding RDF goes to zero at the nucleus. Also, explain why the RDF shows a maximum, and why the RDF goes to zero for large values of the distance r.

2.3 This question requires a knowledge of calculus. The RDF for a 1s orbital is $4\pi r^2 [\psi_{1s}(r)]^2$. Given that the 1s wavefunction is $\psi_{1s}(r) = N_{1s} \exp(-r/a_0)$, show that the RDF is given by

$$P_{1s}(r) = 4N_{1s}^2 \pi r^2 \exp\left(-2r/a_0\right).$$

We can find the maximum in this RDF by differentiating it with respect to *r*, and then setting the derivative to zero. Show that the required derivative is

$$\frac{\mathrm{d}P_{1s}(r)}{\mathrm{d}r} = 8N_{1s}^2\pi r \exp\left(-2r/a_0\right) - 8N_{1s}^2\pi \frac{r^2}{a_0}\exp\left(-2r/a_0\right).$$

Further show that this differential goes to zero at $r = a_0$, and use a graphical argument to explain why this must correspond to a maximum.

For a hydrogen-like atom with nuclear charge Z, the 1s wavefunction is $\psi_{1s}(r) = N_{1s} \exp(-Zr/a_0)$. Show that the corresponding RDF has a maximum at $r = a_0/Z$.

2.4 The N shell has the principal quantum number n equal to four. Determine the quantum numbers (l and m_l) of all the possible AOs in this shell. What new feature arises in this shell that is not present in the M shell? How do the energies of these orbitals in the N shell compare with one another?

How many electrons could be accommodated in the N shell?

Orbitals for which the orbital angular momentum quantum number, l, takes the value 4 are given the letter g. In which shell would you expect g orbitals first to appear?

- 2.5 For a hydrogen atom (with Z = 1), calculate the energies, in kJ mol⁻¹, of the four lowest energy levels. Do the same for the He⁺ ion, which has Z = 2. Plot the levels of He⁺ to scale in a similar way to Fig. 2.13 on page 45, labelling each with the value of the principal quantum number *n*. Discuss the choice of energy zero you have used.
- 2.6 What do you understand by the terms *radial node* and *nodal plane*, as applied to AO wavefunctions? Illustrate your answer using the 2s and 2p AOs.

Explain why radial nodes arise from the radial part of the wavefunction, whereas nodal planes arise from the angular part of the wavefunction.

2.7 The radial part of the 3s AO wavefunction is

$$R_{3,0}(r) = N_{3,0} \left[27 - 18 \left(\frac{r}{a_0} \right) + 2 \left(\frac{r}{a_0} \right)^2 \right] \exp\left(-\frac{r}{3a_0} \right).$$

This function will go to zero, i.e. have a radial node, when the term in the large square bracket goes to zero

$$\left[27 - 18\left(\frac{r}{a_0}\right) + 2\left(\frac{r}{a_0}\right)^2\right] = 0$$

Finding out the values of *r* at which this is the case is made easier if we substitute $x = r/a_0$. Show that the above equation then becomes

$$27 - 18x + 2x^2 = 0.$$

This is a simple quadratic whose roots can be found using the standard formula. Show that these roots are x = 1.9 and x = 7.1. Hence show that there are radial nodes at $r = 1.9 a_0$ and 7.1 a_0 . Compare these answers with the plot shown in Fig. 2.28 on page 55.

Using a similar approach, determine the position of the radial node in the 3p orbital; the radial part of the wavefunction is

$$R_{3,1}(r) = N_{3,1} \left[6 \left(\frac{r}{a_0} \right) - \left(\frac{r}{a_0} \right)^2 \right] \exp\left(-\frac{r}{3a_0} \right).$$

2.8 Draw up a table showing the number of radial nodes, the number of angular nodes (nodal planes), and the total number of radial and angular nodes for 1*s*, 2*s*, 2*p*, 3*s*, 3*p* and 3*d* orbitals. Confirm that the numbers in your table are in accord with the general rules given on page 60.

Describe the nodal structures of 5s, 5p, 5d, 5f and 5g orbitals (5g has l = 4).

2.9 The contour plot shown below is of one of the 4p orbitals: positive intensity is indicated by red contours, negative by blue, and the zero contour is indicated in green.

Sketch how the wavefunction will vary along the dotted line a, and along the two circular paths b and c (for the latter two, this means making a plot of the wavefunction as a function of an *angle* which specifies how far we have moved around the circle).



- 2.10 Using the concepts of electron *screening* and *penetration*, and with reference to the relevant RDFs, explain the following observations concerning the orbital energies of 3*s* and 3*p* shown in Fig. 2.41 on page 66:
 - (a) The ground state configuration of Na is $\dots 3s^1$ and not $\dots 3p^1$.
 - (b) In Al, the 3s is lower in energy than the 3p.
 - (c) As we go along the series Na...Ar, the energy of both the 3s and the 3p orbitals falls steadily; however, the energy of the 3s falls more rapidly than does that of the 3p.

What would you expect to happen to the energies of the 3*s* and 3*p* orbitals for elements with Z > 18 i.e. along the fourth period?

2.11 Calculate the effective nuclear charges of the following orbitals for Al and Ar. Comment on the differences of Z_{eff} values seen between these two elements, and between the two different types of orbital.

element	Ζ	energy of 3s (eV)	energy of 3p (eV)
Al	13	-10.7	-5.71
Ar	18	-34.8	-16.1

2.12 The electron in hydrogen can be promoted from one orbital to another by the absorption of a photon whose energy matches the energy difference between the two orbitals. This process is described as a transition.

If the electron starts in an orbital with principal quantum number n_1 and moves to an orbital with principal quantum number n_2 ($n_2 > n_1$), show that the energy change $\Delta E(n_1 \rightarrow n_2)$ is given by

$$\Delta E(n_1 \to n_2) = E_{n_2} - E_{n_1}$$
$$= R_{\rm H} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right).$$

The energy of a photon with frequency v is hv, where h is Planck's constant (6.626 × 10⁻³⁴ J s). Show that it follows that the frequency of a photon which can cause a transition from n_1 to n_2 , $v_{n_1 \rightarrow n_2}$, is

$$\upsilon_{n_1 \to n_2} = \frac{R_{\rm H}}{h} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right).$$

Using $R_{\rm H} = 2.180 \times 10^{-18}$ J, work out the frequency (which will be in Hz), of the transitions $2 \rightarrow 3, 2 \rightarrow 4$ and $2 \rightarrow 5$.

Convert these frequencies to wavelengths using $c = v\lambda$, where c is the speed of light (2.998 × 10⁸ m s⁻¹) and λ is the wavelength in m. Give your answers in m and nm.

What region of the electromagnetic spectrum do these transitions appear in?

2.13 Using a similar approach to that in the previous question, show that for a hydrogen-like (one-electron) atom with nuclear charge Z, the frequency of the photon needed to cause a transition from an orbital with principal quantum number n_1 to one with quantum number n_2 is

$$v_{n_1 \to n_2} = \frac{Z^2 R_{\rm H}}{h} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right).$$

Super-nova remnant E0102-72 is located some 200,000 light years from the Earth, and is 20 light years across. The matter contained in the remnant is at extremely high temperatures, up to millions of degrees. At such extremes, very highly ionized atoms are found, such as O^{7+} (which is a hydrogen-like atom).

In the light from this remnant, astronomers have observed transitions attributed to this ion. The transitions are thought to be $1 \rightarrow 2$, $1 \rightarrow 3$ and $1 \rightarrow 4$. Work out the frequency (in Hz) and wavelength (in nm) of the light which would cause these transitions. What part of the electromagnetic spectrum does this appear in?

- 2.14 Explain why it is that in a hydrogen-like atom the ionization energy is exactly equal to minus the orbital energy, whereas this is only approximately true for multi-electron atoms.
- 2.15 There are five 3*d* orbitals, which can accommodate a maximum of ten electrons. The lowest energy arrangement of the electrons in these five orbitals is shown opposite for the configurations d^1 , d^2 and d^3 . Explain why these are the lowest energy arrangements, and go on to complete the figure showing the lowest energy arrangements for d^4 to d^{10} .

For each configuration, work out the number of pairs of electrons with parallel spins, and hence draw up a table similar to Table 2.2 on page 75 showing the exchange contribution to the energy of the atom, the corresponding ion, and the difference between the two.

Finally, plot the difference of these exchange energies in a similar way to Fig. 2.50 (b) on page 76. What do these data imply about the variation in ionization energies of atoms with the configurations $d^1 \dots d^{10}$?



3 Symmetry

- 3.1 CH₃F is a trigonal pyramidal molecule. It possesses a three-fold axis and three mirror planes.
 - (a) Make sketches showing the positions of these symmetry elements.
 - (b) Is the three-fold axis the principal axis of this molecule?
 - (c) Giving your reasons, classify the mirror planes as σ_v , σ_h or σ_d .
 - (d) To which point group does this molecule belong?
- **3.2** CH_2Cl_2 can be thought of as having tetrahedral coordination at carbon.
 - (a) Identify the symmetry elements which this molecule possesses and draw sketches showing their locations.
 - (b) Hence determine the point group to which this molecule belongs.
 - (c) Would your answers be altered if the Cl–C–Cl and H–C–H bond angles were not equal? Give your reasons.
- **3.3** The cyclopropenyl cation, $C_3H_3^+$, is planar with the carbon atoms, and the hydrogen atoms, being located at the vertices of an equilateral triangle.
 - (a) Identify the principal axis, and any other rotation axes.
 - (b) Identify any mirror planes, classifying them as σ_v , σ_h or σ_d .
 - (c) This molecule also possesses a three-fold axis of improper rotation; identify the position of this axis.
 - (d) To which point group does this molecule belong?
- **3.4** In a reference work the shapes of various molecules are described by giving the point groups to which they belong. Based on the information given below, sketch the shapes of the molecules.
 - (a) O_3 belongs to the point group $C_{2\nu}$.
 - (b) N₂O belongs to the point group $C_{\infty v}$.
 - (c) CS₂ belongs to the point group $D_{\infty h}$.
 - (d) $Ni(CN)_4^{2-}$ belongs to the point group D_{4h} .
 - (e) FeCl₄²⁻ belongs to the point group T_d .
 - (f) PH₃ belongs to the point group $C_{3\nu}$.
 - (g) ClF₃ belongs to the point group $C_{2\nu}$.
 - (h) $\operatorname{CrCl}_6^{3-}$ belongs to the point group O_h .
- 3.5 Use symmetry arguments to explain the following statements or answer the questions.
 - (a) In 1,2-diiodobenzene there are two different kinds of hydrogen atoms, whereas in 2iodochlorobenzene there are four different kinds of hydrogen atoms.
 - (b) In 1,4-dichlorobenzene there is only one kind of hydrogen atom.
 - (c) Spectroscopic data show that in a particular difluorinated benzene $(C_6H_4F_2)$ there is only one type of fluorine. Giving your reasons, explain which substitution pattern or patterns are consistent with these data.

- (d) Spectroscopic data show that in a particular trifluorinated benzene $(C_6H_3F_3)$ there is only one type of fluorine. Which substitution pattern is consistent with these data? Give your reasons.
- (e) For a different isomer of $C_6H_3F_3$ it is found that there are two different kinds of fluorine. Giving your reasons, explain which isomer this is.
- (f) Identify the number of different carbon environments there are in (i) naphthalene, (ii) pyrene, and (iii) coronene, whose structures are shown below. [Recall that the symmetry depends on the arrangement of the atoms, not the arrangement of any indicated bonds.]



- 3.6 Use symmetry arguments to explain the following observations or answer the questions.
 - (a) All of the Cl atoms in square-planar $PtCl_4^{2-}$ are equivalent. For each of the isomers of $PtCl_2(CN)_2^{2-}$ shown below (which are based on square-planar coordination at Pt) there is only one chlorine environment.



- (b) The shape of IF₇ can be described as a pentagonal bipyramid. How many different fluorine environments are there?
- (c) All of the boron atoms in $B_6H_6^{2-}$, in which the boron atoms are arranged at the vertices of an octahedron, are equivalent.



(d) Three possible structures for SF_4 are shown below; for each the position occupied by the lone pair is also shown. Structures 1 and 2 are based on a trigonal bipyramid, whereas structure 3 is based on a square-based pyramid. For each structure, how many different fluorine environments are there?



- 3.7 Use symmetry arguments to explain the following observations.
 - (a) NH_3 has a dipole pointing along its three-fold axis whereas BF_3 does not.
 - (b) CO_2 has no dipole, but OCS has a dipole parallel to its long axis (both molecules are linear).
 - (c) SF₆ has no dipole.
 - (d) Naphthalene (A) has no dipole, nor does the isomer of difluoronaphthalene shown in B, but the isomer C possess a dipole.



- (e) PF_5 has no dipole despite the fact that all the fluorine atoms are not equivalent.
- (f) Isomer D has no dipole, but isomer E does.



- **3.8** Use symmetry arguments to explain the following observations.
 - (a) None of CH₄, CH₃Cl, and CH₂ClF are chiral, but CHClFI is.
 - (b) No planar molecule can be chiral.
 - (c) Of the three allenes shown below, A and B are not chiral, whereas C is.



(d) Consider the transition metal complex $MA_2B_2C_2$ which has octahedral coordination about the central metal atom M, and where A, B and C are ligands. Draw the structures of all of the isomers of this complex and indicate which are chiral. [Hint: in drawing the isomers you simply need to consider arrangements in which the two A ligands are at either 90° or 180° to one another, and likewise for B and C.]

- 3.9 BeH₂ is a linear centro-symmetric molecule. It possesses a mirror plane, perpendicular to the long axis and passing through the Be; as is the usual convention, the long axis defines the z direction.
 - (a) Classify the following beryllium atomic orbitals as symmetric or anti-symmetric with respect to reflection in this mirror plane: 2s, $2p_x$, $2p_y$ and $2p_z$.
 - (b) Construct a symmetric and an anti-symmetric symmetry orbital from the two hydrogen 1*s* AOs.
 - (c) Classify the AOs in (a) and the symmetry orbitals found in (b) according to reflection in the *yz*-plane.
- **3.10** OF₂ has a similar geometry to H₂O; assume that the molecule lies in the *xz*-plane. By considering their behaviour on reflection in the *yz*-plane, construct a symmetric and an anti-symmetric symmetry orbital from the two fluorine $2p_x$ AOs.
- 3.11 In Fig. 3.30 on page 95 we classified the oxygen AOs in H_2O according to reflection in the *yz*-plane. Do the same for the other symmetry operations of this molecule i.e. the C_2 rotation and reflection in the *xz*-plane.

Likewise, classify the two symmetry orbitals shown in Fig. 3.31 on page 96 according to these two symmetry operations.

4 Electrons in molecules: diatomics

4.1 Explain how the bonding and antibonding MOs are formed in H_2^+ , and rationalize why it is that the energy of the bonding MO shows a minimum when plotted as a function of the internuclear separation *R*, whereas the energy of the antibonding MO simply increases as *R* decreases.

Construct a MO diagram for H_2^+ , and make rough sketches of the form of the MOs. Explain how symmetry labels are assigned to the two MOs.

4.2 Explain what is meant by the overlap integral between two AOs, and also explain why this quantity goes to zero for large distances between the two AOs. How would you expect the plot of S(R) to compare between two 1s AOs and two 2s AOs?

Shown below is a plot of the overlap integral between two 2*p* orbitals. The blue line is for the sideways-on overlap to give π MOs, whereas the red line is for the head-on overlap to give σ MOs. Explain the form of these two curves.



- 4.3 Use MO diagrams to rationalize why He₂ is an unknown species, but the ion He₂⁺ has been observed. Make what predictions you can about the stability of the molecules He₂²⁺ and H₂²⁻ with respect to dissociation.
- 4.4 Suppose that there is overlap between the $2p_z$ AOs from two atoms A and B, where z is the internuclear axis. Sketch the form of the MO diagram, and the form of the bonding and antibonding MOs, for the following cases: (a) A and B of very similar electronegativity; (b) A somewhat more electronegative than B; (c) A much more electronegative than B.

If the resulting bonding MO is occupied by a pair of electrons, what consequences would this have for the polarity of the A–B bond in these three cases?

4.5 Consider the overlap between a $3d_{xy}$ AO on one atom and a 2p AO on a second atom as these two approach one another along the *x*-axis. Explain, using sketches, whether or not there is overlap between the $3d_{xy}$ and each of the three 2p orbitals in turn. If there is overlap, classify the resulting MO as having σ or π symmetry.

Do the same for a $3d_{x^2-y^2}$ AO interacting with each of the 2p AOs.

4.6 Explain why the *overall* sign of the MO wavefunction is not important, whereas the relative signs of two AOs which are forming an MO is of significance.

- 4.7 In O₂ the lowest energy MO is given the label $1\sigma_g$ and the next lowest is $1\sigma_u$. Explain how these MOs are formed (i.e. from which AOs); sketch the form of the MOs. Explain why it is that although both of these MOs are occupied, they make little contribution to the bonding in O₂.
- 4.8 The dissociation energy of N_2 is 942 kJ mol⁻¹, whereas that for N_2^+ is 842 kJ mol⁻¹; the dissociation energy of O_2 is 494 kJ mol⁻¹, whereas that for O_2^+ is 642 kJ mol⁻¹. rationalize these data.
- **4.9** Sketch an MO diagram for BeH. On the basis of your diagram, would you expect this molecule to be stable with respect to dissociation into atoms? Use your MO diagram to predict any other properties you can.
- 4.10 Construct an MO diagram for the diatomic molecule CH, label the MOs, indicate which orbitals are occupied, and sketch the form of the occupied orbitals. The relevant orbital energies are: H 1s -14 eV; C 2s -19 eV; C 2p -12 eV. To a first approximation, you can ignore the interaction between the H 1s and the C 2s (why?).

What does your MO diagram predict about CH and its ion CH+?

- 4.11 Explain what you understand by the statement that CN⁻ is *isoelectronic* with CO. Construct an approximate MO diagram for CN⁻, indicate which MOs are occupied and explain what the diagram predicts about this molecule.
- 4.12 We argued that in H_2 the atoms are held together as a result of the build-up of electron density along the internuclear axis. However, in LiF there is practically no such build up. What, then, holds the atoms in LiF together, and in what way is this different to H_2 ?

5 Electrons in molecules: polyatomics

5.1 Consider a hypothetical molecule in which four hydrogen atoms lie in a row. Like H_3^+ , this molecule has a mirror plane down the middle. As shown opposite, atoms 2 and 3, and atoms 1 and 4 are swapped by the mirror plane. We therefore need to consider the AOs on atoms 2 and 3 together, and the AOs on atoms 1 and 4 together.



Draw sketches of the symmetric and antisymmetric combinations of AOs on atoms 2 and 3 (i.e. the symmetry orbitals), and then do the same for the AOs on atoms 1 and 4. Using the rule that only AOs of the same symmetry overlap, sketch the form of the four MOs, two symmetric and two antisymmetric, which are formed from the overlap of the SOs.

Arrange these MOs in order of increasing energy by looking at the number of nodes in the MOs. What does your MO diagram predict about the hypothetical molecule H_4 ?

5.2 Construct an MO diagram for a hypothetical linear water molecule, H–O–H, using a similar approach to that used for FHF⁻; take the *z*-axis to be along the axis of the molecule. Sketch the form of the MOs, and indicate which will be occupied.

[Hints: The orbitals can be classified according to a mirror plane, as we did in FHF⁻. The two hydrogen 1s form a symmetric and an antisymmetric SO, and the oxygen 2s and $2p_z$ can be classified individually. The oxygen $2p_x$ and $2p_y$ have the wrong symmetry to overlap with the hydrogen 1s (why?), and so remain nonbonding.]

Compare your MO diagram with that for 'bent' water. Using these two diagrams, rationalize why it is that water adopts a bent, rather than a linear, geometry.

5.3 Using appropriate HAOs, described the bonding in each of the following molecules, being sure to specify the form of each occupied MO, and also making sure that you have accounted for all the electrons. Identify the HOMO and the LUMO for the first three molecules.



5.4 Using a similar approach to that used in section 5.5 on page 159, construct an MO diagram for F_2 assuming that (i) the two fluorine atoms are *sp* hybridized and (ii) the two fluorine atoms are *sp*³ hybridized. State which orbitals are occupied and compare the resulting descriptions of the bonding with that from the full MO picture (Fig. 4.27 on page 122).

Use a similar approach to construct an MO diagram for CO using *sp* hybrids on both atoms; remember to place the oxygen AOs and HAOs somewhat lower in energy than the corresponding orbitals on carbon. What does your diagram predict about the form of the HOMO and the LUMO? Compare your predictions about the MOs with the computed orbitals shown in Fig. 4.41 on page 137.

- 5.5 The MO diagram for the linear form of H_3^+ can be constructed by realizing that it is just three 1s orbitals in a row. The resulting MOs have the same form as the π MOs in the allyl cation, except that they are composed of 1s AOs. Compare the MOs deduced using this approach to those found in section 5.1.1 on page 143 using symmetry arguments.
- 5.6 Using the graphical method described in section 5.8.1 on page 168, deduce the form of the π MOs of hexatriene (CH₂=CH–CH=CH–CH=CH₂). Which MOs are occupied? Identify the contribution (in terms of bonding or antibonding) that each occupied MO makes to the π bonding between the end two carbons (numbered 1 and 2). Do the same for the bonding between carbons 2 and 3, and between 3 and 4. Based on your results, which of these bonds has the greatest net bonding interaction, and which has the least?
- 5.7 Using the graphical method described in section 5.8.1 on page 168, deduce the form of the π MOs of the cation (CH₂=CH–CH=CH–CH₂). Which MOs are occupied? Adding one electron to this species gives a radical, and adding a further electron gives an anion. Explain what effect you would expect adding one or two extra electrons to have on the strength of the π bonding.
- **5.8** The azide ion, N_3^- , has a symmetrical linear structure. Describe the bonding in this ion by using *sp* hybrids on each atom, and by forming delocalized π MOs from the 2*p* orbitals which point perpendicular to the long axis (the *z*-axis) of the molecule. Note that there will be two separate π systems: one formed form the 2*p_x*, and one from the 2*p_y* AOs. Identify the HOMO and the LUMO.

$$\overset{\odot}{\mathsf{N}} \overset{\oplus}{=} \overset{\odot}{\mathsf{N}} \overset{\odot}{=} \overset{\odot}{\mathsf{N}}$$

Compare your MO picture with the bonding shown in the localized structure of azide, shown opposite.

The molecules CO_2 and NO_2^+ are both symmetrical and linear, and can be described as being *isoelectronic* with N_3^- . What do you understand by this term? How does your MO description of the bonding in the azide ion need to be modified to describe CO_2 and NO_2^+ ?

5.9 Using appropriate HAOs, describe and compare the bonding in the following three molecules.



5.10 In the cyclopropenyl cation (shown below) a π system is formed from the overlap of an out-of-plane $2p_z$ AO from each carbon. The MOs formed from these AOs have exactly the same form as the MOs for triangular H₃⁺ found in section 5.1.2 on page 144, except that they are formed from $2p_z$ AOs, rather than 1s AOs.

Carefully count up how many electrons there are in this molecule, and hence determine which of the π MOs are occupied. Compare the form of the occupied π MOs with those for the allyl cation, commenting on any relevant points of difference.



6 Bonding in solids

- 6.1 In Fig. 6.1 on page 183 are shown the MOs (or COs) formed from a chain of *s* orbitals. We can just as well form such COs from chains of 2p AOs. Assuming that the chain is aligned along the *z*-axis, sketch the form of the *lowest* and *highest* energy COs for a chain composed of: (a) $2p_x$ AOs, and (b) $2p_z$ AOs. Comment on any differences between the COs you have drawn.
- **6.2** Use the idea of overlapping bands to rationalize why both lithium and beryllium are metallic conductors, and why the enthalpy of vaporization of beryllium (found to be 324 kJ mol⁻¹) is significantly greater than that of lithium (found to be 159 kJ mol⁻¹).
- 6.3 The bond length on the discrete (gaseous) Li₂ molecule is 267 pm, and the bond dissociation energy is 105 kJ mol⁻¹ (i.e. 52.5 kJ is required to create one mole of Li atoms). For metallic lithium, the Li–Li spacing is 304 pm, and the enthalpy of vaporization is 159 kJ mol⁻¹(i.e. 159 kJ is required to create one mole of Li atoms). Discuss these data in the light of the different type of bonding in Li₂(g) and Li(m).
- 6.4 What is the difference between a metallic conductor and a semiconductor, and how can this difference be explained using band theory? Explain why diamond is an insulator, whereas silicon is a semiconductor.

If a small fraction of the Si atoms in solid silicon are replaced by phosphorus atoms, it is observed that the conductivity of the material increases significantly. Rationalize this observation (hint: how many electrons does a P atom have compared to a Si atom?).

6.5 What do you understand by the statement 'BN is isoelectronic with C_2 '?

Solid boron nitride (BN) can exist in two forms. The α -form consists of hexagonal layers, is a soft material, and is an electrical insulator with a band gap of around 5.2 eV. The β -form is a very hard, abrasive material, which is also an insulator. By comparison with the allotropes of carbon, propose a structure for the β -form of BN, and explain why the α -form is an insulator.

6.6 Graphite can be 'doped' by exposing the material to potassium vapour. In the resulting materials the potassium atoms are found to fit *between* the layers of carbon atoms in the original structure, and it is also found that doping increases the electrical conductivity greatly. Use band theory to explain why doping with potassium increases the conductivity (hint: the outer electron from a K atom is easily removed: where might it be transferred to?).

Similarly, doping with bromine vapour leads to the incorporation of Br atoms between the layers, again accompanied by an increase in the conductivity. Explain why this is so.

6.7 Use the standard enthalpy changes given for the following processes to compute the lattice enthalpy of MgBr₂(s):

$$\begin{array}{rcl} Mg(s) & \longrightarrow & Mg(g) & 147 \ kJ \ mol^{-1} \\ & Br_2(l) & \longrightarrow & 2 \ Br(g) & 224 \ kJ \ mol^{-1} \\ & Mg(g) & \longrightarrow & Mg^+(g) & 738 \ kJ \ mol^{-1} \\ & Mg^+(g) & \longrightarrow & Mg^{2+}(g) & 1451 \ kJ \ mol^{-1} \\ & Br(g) & \longrightarrow & Br^-(g) & - 325 \ kJ \ mol^{-1} \\ & Mg(s) + Br_2(l) & \longrightarrow & MgBr_2(s) & - 524 \ kJ \ mol^{-1} \end{array}$$

6.8 (Requires a knowledge of elementary calculus) In section 6.2.1 on page 191 it was shown that the energy of a chain of ions with alternating charges is given by

$$E = -N_{\rm A} \mathcal{A} \frac{z^2 e^2}{4\pi\varepsilon_0 r} + \frac{N_{\rm A} C}{r^n}.$$

The value of r at which this energy is a minimum, the equilibrium separation r_e , is found by computing the derivative with respect to r, and then setting this derivative equal to zero:

$$\frac{\mathrm{d}E}{\mathrm{d}r} = 0$$

Assuming that all of the other parameters do not depend on r (i.e. are constants), find the derivative and, by setting it equal to zero, show that the constant C is given by:

$$C = \frac{\mathcal{A}z^2 e^2 r^{n-1}}{4\pi\varepsilon_0 n}.$$

Substitute this expression for *C* into the original expression for the energy *E* and hence, after some tidying up, obtain Eq. 6.2 on page 193.

6.9 Use the Kapustinskii equation, Eq. 6.5 on page 197, along with the radii listed in Table 6.3 on page 196 to estimate the lattice enthalpy of MgBr₂. Compare your answer to the value obtained in question 6.7.

Calculate the lattice enthalpy using the full expression given in Eq. 6.4 on page 195 using the following values for the parameters: $r_e = 270.7 \text{ pm}$, $\mathcal{A} = 2.355 \text{ and } n = 9$ (recall that $e = 1.602 \times 10^{-19} \text{ C}$ and $\varepsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$). You need to be careful with units: r_e must be in m, and the energy will come out in J mol⁻¹.

6.10 (a) The discrete diatomic molecule MgO is known in the gas phase and has a bond length of 175 pm. If we *assume* that the this molecule consists of Mg²⁺ and O²⁻ ions held together by an electrostatic interaction then we can work out the energy change for

$$Mg^{2+}(g) + O^{2-}(g) \longrightarrow Mg^{2+}O^{2-}(g)$$

by using Eq. 6.2 on page 193 with $\mathcal{A} = 1$:

$$E_{\rm dimer} = -N_{\rm A} \frac{z^2 e^2}{4\pi\varepsilon_0 r_{\rm e}} \left(1 - \frac{1}{n}\right).$$

Taking n = 7 and z = 2, and being careful with the units, compute E_{dimer} in kJ mol⁻¹. Hence, given the following standard enthalpy changes

$$\begin{array}{rcl} Mg(g) &\longrightarrow & Mg^{2+}(g) & 2188 \ \text{kJ mol}^{-1} \\ O(g) &\longrightarrow & O^{2-}(g) & 703 \ \text{kJ mol}^{-1}, \end{array}$$

determine the enthalpy change for

$$Mg(g) + O(g) \longrightarrow Mg^{2+}O^{2-}(g).$$

(b) Solid MgO is a crystalline solid with an Mg–O spacing of 210.2 pm. Compute its lattice enthalpy using Eq. 6.4 on page 195 taking $\mathcal{A} = 1.7476$ and n = 7. Hence determine the enthalpy change for

$$Mg(g) + O(g) \longrightarrow MgO(s).$$

(c) Compare and comment on your answers to (a) and (b).

7 Thermodynamics and the Second Law

The gas constant, *R*, has the value 8.3145 J K⁻¹ mol⁻¹. 1 bar is 10⁵ N m⁻², and 1 atmosphere is 1.01325×10^5 N m⁻².

- 7.1 Following the discussion on page 206, devise some more arrangements of the 14 molecules amongst the given energy levels such that the total energy is 10 units. For each distribution, compute the value of *W*. Were you able to find a distribution with a value of *W* greater than distribution (a) from Fig. 7.3 on page 207?
- 7.2 Imagine that we have two large copper blocks, A and B, which are isolated from the surroundings. Block A is at a temperature of 250 K, and block B is at a temperature of 300 K. As the blocks are large, we can assume that small amounts of heat flowing into or out of them is reversible, and that such a process will not change the temperature of the block. It therefore follows that for an amount of heat q the entropy change of the block is q/T, where T is the temperature of the block.

Compute the entropy change of each block when 10 J of heat flows: (a) from block A to block B; (b) from block B to block A. Using these results, compute the entropy change of the Universe in each case, and hence determine which direction of heat flow is spontaneous.

7.3 Solid elemental tin can exist as two allotropes, called β -tin and α -tin (sometimes these are called white and grey tin, respectively). For the interconversion process

$$\operatorname{Sn}(\beta) \longrightarrow \operatorname{Sn}(\alpha)$$

the enthalpy change is -2.1 kJ mol^{-1} , and the entropy change is $-7.1 \text{ J K}^{-1} \text{ mol}^{-1}$, both at 298 K. For the purposes of this question you may assume that these values are independent of temperature.

By computing the entropy change of the Universe for the above process, determine which allotrope is the stable form at: (a) -10 °C; (b) +40 °C. At what temperature will the two allotropes be in equilibrium with one another?

Calculate ΔG for the above process at the two temperatures, and comment on what the resulting values tell you about which allotrope is the stable form.

7.4 Solid elemental sulfur exists in two allotropes, α -sulfur (rhombic) and β -sulfur (monoclinic). The molar entropies of the two allotropes are 31.8 J K⁻¹ mol⁻¹ for α -sulfur, and 32.6 J K⁻¹ mol⁻¹ for β -sulfur (at 298 K). The enthalpy change for the conversion of α -sulfur to β -sulfur is 330 J mol⁻¹.

Determine the temperature at which the two allotropes are in equilibrium, and the allotrope which is favoured at temperatures higher than this.

7.5 Explain why it is that an endothermic process can be spontaneous provided (a) it is accompanied by an increase in the entropy of the system, and (b) the temperature exceeds a particular value.

7.6 This question and the one which follows concern the equilibrium

$$CO(g) + 2 H_2(g) \rightleftharpoons CH_3OH(g)$$

which we are going to investigate as a viable commercial method for the production of methanol. The following data are provided (all at 298 K)

	CO(g)	$H_2(g)$	CH ₃ OH(g)
$\Delta_{\rm f} H^\circ$ / kJ mol ⁻¹	-110.53		-200.66
$S_{\rm m}^{\circ}$ / J ${\rm K}^{-1}$ mol $^{-1}$	197.67	130.68	239.81

Using these data, determine $\Delta_r H^\circ$, $\Delta_r S^\circ$, $\Delta_r G^\circ$ and hence *K*, all at 298 K. On the basis of your answer, comment on the viability of the reaction as a method for the production of methanol.

- 7.7 In practice, it is found that the reaction in the previous question only proceeds at a viable rate at 600 K. Assuming that the values of $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are the same at 600 K as they are at 298 K, find the value of the equilibrium constant at 600 K. Qualitatively, is your answer in accord with Le Chatelier's principle?
- **7.8** Consider the equilibrium in which solid calcium carbonate decomposes to the oxide plus carbon dioxide

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g).$$

Write down an expression for the equilibrium constant of this reaction in terms of the partial pressure of CO_2 .

The standard enthalpies of formation of CaCO₃(s), CO₂(g) and CaO(s) are -1207.6 kJ mol⁻¹, -393.5 kJ mol⁻¹ and -634.9 kJ mol⁻¹ respectively, and the standard entropies are 91.7 J K⁻¹ mol⁻¹, 213.8 J K⁻¹ mol⁻¹ and 38.1 J K⁻¹ mol⁻¹ (all at 298 K). Assuming that these values are independent of temperature, compute $\Delta_r H^\circ$, $\Delta_r S^\circ$ and $\Delta_r G^\circ$ at 800 K; hence find the equilibrium pressure of carbon dioxide at this temperature.

7.9 The following data are all at 298 K

reaction	$\Delta_{\rm r} H^{\circ}$ / kJ mol ⁻¹	$\Delta_{\rm r} S^{\circ}$ / J K ⁻¹ mol ⁻¹
$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$	-110.53	89.36
$Pb(s) + \frac{1}{2}O_2(g) \longrightarrow PbO(s)$	-218.99	-100.9

Assuming that these values are independent of temperature, compute $\Delta_r G^\circ$ for the reduction of PbO by carbon

$$PbO(s) + C(s) \rightleftharpoons CO(g) + Pb(s)$$

at 298 K and at 700 K. Also, compute the temperature at which $\Delta_r G^\circ$ is zero, and comment on the significance of this value.

7.10 Using the approach described in section 7.15 on page 250, complete the following table for the equilibrium $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

line	CO(g)	$2H_2(g)$	\rightleftharpoons	$CH_3OH(g)$
1	n_0	$2n_0$		0
2	$n_0(1-\alpha)$			
3				

Line 1 is the initial amount in moles, line 2 is the amount in moles after a fraction α of the CO has reacted, and line 3 gives the mole fractions.

Hence show that the equilibrium constant is given by

$$K = \frac{\alpha (3 - 2\alpha)^2}{4(1 - \alpha)^3} \frac{(p^{\circ})^2}{p_{\rm eq}^2},$$

where p_{eq} is the equilibrium pressure.

If it can be assumed that the equilibrium constant is such that $\alpha \ll 1$, show that the equilibrium constant can be approximated as

$$K = \frac{9\,\alpha(p^\circ)^2}{4p_{\rm eq}^2},$$

hence obtain an expression for α in terms of K and p_{eq} .

Using your value of *K* from exercise 7.7, find α at 600 K for the case where the total pressure is (a) 1 bar and (b) 50 bar. Comment on your answers in the light of Le Chatelier's principle. Would it be advantageous to run the reaction at high pressure?

7.11 At high temperatures molecular iodine dissociates to iodine atoms

$$I_2(g) \rightleftharpoons 2 I(g).$$

At 298 K, the standard enthalpies of formation of $I_2(g)$ and I(g) are 62.44 kJ mol⁻¹ and 106.84 kJ mol⁻¹, respectively, and the standard molar entropies are 260.69 J K⁻¹ mol⁻¹ and 180.79 J K⁻¹ mol⁻¹, respectively. Assuming that these values are independent of temperature, compute $\Delta_r H^\circ$, $\Delta_r S^\circ$ and $\Delta_r G^\circ$ for the dissociation reaction at 600 K, and hence find the value of the equilibrium constant.

0.008 moles of I₂ are allowed to come to equilibrium in a vessel of volume 1 dm³ at a temperature of 600 K. Using Eq. 7.34 on page 252 determine the degree of dissociation α at this temperature, and hence the amount in moles of iodine atoms present.

7.12 Hydrogen cyanide, HCN, has a pK_a of 9.21 at 298 K. Compute the pH of a 0.1 mol dm⁻³ solution of HCN. Also, find the ratio of the concentrations of CN⁻(aq) to HCN(aq) in such a solution.

Methanoic acid has a p K_a of 3.75 at 298 K. If we prepared an equimolar mixture of hydrogen cyanide and methanoic acid in water, which out of the two conjugate bases CN⁻ and HCO₂⁻ would you expect to be present at the higher concentration? Give reasons for your answer.

7.13 Imagine preparing a solution of a weak acid AH and its sodium salt NaA. The acid dissociates according to the usual equilibrium

$$AH(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq),$$

and we can assume that the sodium salt dissociates completely in water. Under these conditions, explain why it is possible to write the acid dissociation constant as

$$K_{\rm a} = \frac{[\rm H_3O^+] [\rm NaA]_{\rm init}}{[\rm AH]_{\rm init}},$$

where [NaA]_{init} is the initial concentration of NaA in the solution, and [AH]_{init} is the initial concentration of AH used to make up the solution.

Hence show that the pH of the solution is given by

$$pH = pK_a + \log \frac{[NaA]_{init}}{[AH]_{init}}.$$

Propanoic acid has a pK_a of 4.87. Compute the pH of a solution with initial concentrations of 0.1 mol dm⁻³ propanoic acid and 0.1 mol dm⁻³ sodium propionate.

Such a solution is called a *buffer* as it has the property that its pH is largely unaltered by the addition of small amounts of H_3O^+ or OH^- ions. Explain, in qualitative terms, why the presence of a reservoir of A^- ions and undissociated AH leads to this buffering action.

7.14 Use the following data (all at 298 K) to calculate $\Delta_r H^\circ$, $\Delta_r S^\circ$ and $\Delta_r G^\circ$ for the dissolution of BaSO₄(s) at 298 K:

$$\begin{array}{ll} \mbox{reaction} & \Delta_{\rm r} H^{\circ} \, / \, \mbox{kJ mol}^{-1} & \Delta_{\rm r} S^{\circ} \, / \, \mbox{J K}^{-1} \, \mbox{mol}^{-1} \\ \mbox{BaSO}_4({\rm s}) \to \mbox{Ba}^{2+}({\rm g}) \, + \, \mbox{SO}_4^{2-}({\rm g}) & 2469 & 297 \\ \mbox{Ba}^{2+}({\rm g}) \to \mbox{Ba}^{2+}({\rm aq}) & -1346 & -202.5 \\ \mbox{SO}_4^{2-}({\rm g}) \to \mbox{SO}_4^{2-}({\rm aq}) & -1099 & -183 \end{array}$$

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

To what do you attribute the insolubility of BaSO₄?

8 Trends in bonding

- 8.1 Explain the following features and trends of the orbital energies shown in Fig. 8.2 on page 260.
 - (a) In going across the second period from Li to Ne the energies of both the 2s and 2p AOs fall, but the 2s AO falls more steeply than the 2p.
 - (b) On going from Ne to Na there is a large decrease in the energy of the 2p AO.
 - (c) The energies of the 2*s* AO in Li, the 3*s* AO in Na and the 4*s* AO in K show a gentle upward trend but in going from Li to Na, and from Na to K the nuclear charge increases by eight.
 - (d) On going from Sc to Zn the energy of the 4*s* AO decreases rather little, but the energy of the 3*d* AO shows a greater fall in energy.
- 8.2 The atomic radii of the lanthanide elements (Ce–Lu) are remarkably similar, varying only by a few pm across all fourteen elements. Use Slater's rules (page 262) to determine the effective nuclear charge experienced by the outer electrons (the 6s) of these elements, and hence explain why the atomic radii vary so little.
- 8.3 Explain why there is a general increase in atomic radii on moving from the first row transition metals (those in period 4) to the second row (those in period 5), but there is very little change on moving to the third row (those in period 6).
- 8.4 Rationalize the trends in the atomic radii of the Group 2 elements given in the table (the radius given for element 120 is based on a calculation, rather than experiment).

element	Be	Mg	Ca	Sr	Ba	Ra	element 120
radius / pm	112	160	197	215	222	215	200

- 8.5 When metallic gold is exposed a caesium vapour a solid compound with formula CsAu is formed; the solid is a poor conductor of electricity, but the conductivity rises sharply when the solid is molten. Discuss the likely nature of the bonding in this compound. Would you expect to be able to form a similar compound from the reaction of silver with caesium?
- **8.6** Explain the following trends in the bond strengths (in kJ mol⁻¹) of the Group 1 and Group 11 diatomics.

molecule	bond strength	molecule	bond strength
K ₂	50	Cu ₂	177
Rb_2	47	Ag ₂	160
Cs ₂	43	Au ₂	225

- 8.7 (a) Construct an MO diagram for Be_2 and use it to explain why, although the bond order is zero, *s*-*p* mixing results in the the molecule having a weak bond.
 - (b) Explain the following observations: (i) the bond strength of Li₂ is 100 kJ mol⁻¹, a value much greater than that for Be₂; (ii) the enthalpy of vaporization of solid beryllium is greater than that for solid Li.
 - (c) Rationalize the following bond strengths of the Group 12 homonuclear diatomics:

molecule	bond strength / kJ mol $^{-1}$
Zn_2	29
Cd_2	7
Hg ₂	≈ 0

- (d) Suggest why metallic mercury has the lowest enthalpy of vaporization of any metal, and hence why it is a liquid at room temperature.
- 8.8 The common oxidation states of mercury are +1 and +2. While Hg^{2+} ions are found in solution, mercury(I) exists in solution as Hg_2^{2+} . The Hg–Hg bond length in mercury(I) salts is considerably less than the Hg–Hg distance in Hg(l).
 - (a) By considering the 6s orbitals only, draw a simple MO diagram to explain the bonding in Hg_2^{2+} .
 - (b) Would you expect mercury(I) salts to be paramagnetic?
 - (c) Identify the species present in the ionic compound $Hg_3(AlCl_4)_2$, and describe the bonding in each. [Hint: consider the ions present in the compound.]
- **8.9** The following table gives the bond strengths $(kJ mol^{-1})$ for the homonuclear diatomics of the *p*-block.

group	13	14	15	16	17
	B ₂	C ₂	N_2	O ₂	F_2
	297	607	945	498	159
	Al_2	Si ₂	P_2	S_2	Cl_2
	133	327	490	425	243
	Ga ₂	Ge ₂	As ₂	Se ₂	Br ₂
	112	264	382	333	193
	In ₂	Sn ₂	Sb ₂	Te ₂	I_2
	100	187	299	260	151
	Tl_2	Pb ₂	Bi ₂	Po ₂	At_2
	64	87	200	187	80

Rationalize the trends in the bond strengths for both crossing the periods and descending the groups. Your answer should include a consideration of the bond orders present in each group.

Why are the bond strengths in Groups 16 and 17 generally greater than those in Groups 14 and 13 respectively? Explain any exceptions to this trend.

9 Bonding between the elements

9.1 (a) Discuss the factors which lead to the following trend in bond energies

diatomic	F ₂	Cl_2	Br_2	ClF
bond energy / kJ mol ⁻¹	158	242	193	297

(b) Discuss the factors which lead to the following trend in bond lengths

bond	C-Cl	Si-Cl	Ge-Cl	Sn-Cl	
bond length / Å	1.76	2.08	2.13	2.20	

9.2 Discuss the following observations.

Solid carbon dioxide sublimes at temperatures above -78 °C to give a gas containing discrete CO₂ molecules.

Solid silicon dioxide has a giant covalent structure. It melts at around 1500 °C, and finally boils at temperatures over 2800 °C; discrete SiO₂ molecules can be detected in the gas phase.

If CO₂ is subject to extremely high pressures a solid material is produced which appears to have a giant covalent structure in which there are C–O single bonds.

9.3 (a) Using the data on orbital energies given below, place the following compounds on the van Arkel diagram: CaCl₂, TiB₂, S₄N₄ and AlN.

element	В	С	Ν	Al	S	Cl	Ca	Ti
minus valence orbital energy / eV	11.8	15.2	18.8	9.05	15.8	18.2	5.34	8.44

- (b) The following descriptions refer to the properties of the compounds listed above, but not necessarily in the same order.
 - W brown solid, melting point 2980 °C, good conductor
 - X orange crystals, mp 170 °C, soluble in organic solvents
 - Y white solid, mp 1418 °C, insulator, moderately soluble in water
 - Z white solid, mp > 2400 °C, band gap 6 eV, insulator.

With the aid of the van Arkel diagram, and from your general knowledge, deduce which compound corresponds to which letter, giving brief reasons for your answers.

- 9.4 Pure calcium carbide, CaC_2 , is a colourless solid (melting point 2300 °C) which does not conduct electricity in the solid state. The structure of CaC_2 is essentially an NaCl-type lattice with alternating Ca^{2+} ions and C_2^{2-} ions. The C-C bond length in these ions is 119.1 pm.
 - (a) Use the van Arkel diagram to predict the sort of bonding you might expect to find in calcium carbide (the necessary orbital energies are given in the previous question). Are the properties given above consistent with the position of CaC_2 in the van Arkel diagram?
 - (b) Construct an MO diagram for C_2 and use it to explain why the C–C bond length in CaC_2 is considerably shorter than that in gaseous C_2 (131.2 pm).
 - (c) Lanthanum carbide, LaC₂, is thought to contain the La³⁺ ion and the C_2^{3-} ion; the C–C bond length is this ion is 130.3 pm. Use your MO diagram to explain why the C–C bond length in LaC₂ is greater than that in CaC₂.

9.5 At room temperature *white phosphorus* is an insulating solid. It boils at 280 °C to give a vapour which is a mixture of P_4 and P_2 molecules. If the vapour is condensed, white phosphorus reforms. The P–P bond length in P_2 is 1.90 Å, and in P_4 it is 2.21 Å.

If white phosphorus is held at elevated temperatures for an extended period, various other solid allotropes are formed, none of which boil under 600 °C. One of these allotropes, *black phosphorus*, is a semiconductor.

The α allotropes of arsenic, antimony and bismuth all have similar structures to that of black phosphorus.

- (a) Sketch the structures of P_4 and P_2 , and explain their relative bond lengths.
- (b) How would you expect the equilibrium between P_4 and P_2 to vary with temperature?
- (c) Suggest the common structure adopted by black phosphorus and the α allotropes of the other Group 15 elements.
- (d) Explain the differences in the physical properties of the black and white allotropes of phosphorus.
- (e) Rationalize the trends in the bond lengths and bond angles observed in the solid form of the Group 15 elements

allotrope	black P	α-As	α -Sb	α-Bi
bond length / Å	2.23	2.52	2.91	3.07
bond angle / degree	98.2	96.7	96.6	95.5

9.6 (a) The Si–Si bond lengths in $(R_2Si)_2$ and the *cyclic* compound $(R_2Si)_3$ are 2.14 Å and 2.40 Å, respectively. Draw the structures of these two compounds and comment on the Si–Si bond orders in each.



- (b) Suggest why naturally occurring carbon may be found in either of two allotropes, whereas silicon exists in only one allotropic form in which the Si–Si bond length is 2.35 Å.
- (c) The standard enthalpies of sublimation of graphite, diamond and silicon are 715 kJ mol⁻¹, 710 kJ mol⁻¹ and 456 kJ mol⁻¹, respectively. Comment on these values.
- (d) Explain why silicon is a semiconductor whereas diamond is an electrical insulator.
- (e) Explain why heating silicon with small quantities of arsenic leads to a new material with higher electrical conductivity then pure silicon.
- 9.7 At high temperatures, calcium metal reacts with silicon to give a salt with empirical formula CaSi₂, and with carbon to give a salt with empirical formula CaC₂. X-ray crystallography reveals that the structures of these two salts are very different: CaC₂ contains discrete C_2^{2-1} ions, whereas in CaSi₂ the silicon atoms form sheets of (Si⁻)_n with each silicon having three Si–Si single bonds.
 - (a) Which element occurs in a form which is isoelectronic and isostructural with the C_2^{2-} anion, and which element occurs in a form which is isoelectronic and isostructural with the $(Si^-)_n$ sheets?
 - (b) Why is there such a difference between the structures of the carbon and silicon anions?
 - (c) Calcium and silicon can also react to give a compound with empirical formula CaSi, whose structure is found to contain helical chains of Si atoms. How may the structure of these chains be rationalized?

9.8 (a) In the anion Ph_3C^- the Ph–C bonds have a trigonal planar arrangement about the carbon, with the Ph–C–Ph bond angle being 120°. In contrast, in the anion Ph_3Pb^- the Ph–Pb bonds have a trigonal pyramidal arrangement about the Pb, with a Ph–Pb–Ph bond angle of 91°. Comment on the reasons why these two ions have such different structures.



- (b) From your answer to (a), explain why Ph_3C^- is a far stronger base than Ph_3Pb^- .
- **9.9** Discuss the likely reasons for the observation that in going from Sc to Mn the maximum oxidation state shown by successive elements increases steadily, but as we carry on from Fe to Zn there is a steady decrease in the maximum oxidation state for successive elements.

10 Describing reactions using orbitals

10.1 By following the implications of the curly arrows, determine the products of the following reactions



10.2 Draw the appropriate curly arrows for the following reactions (if your arrow originates from a lone pair, indicate this)



10.3 Explain why it is likely that the most favourable interaction between two molecules will be between the HOMO of one and the LUMO of the other.

Identify the HOMO in each of these molecules and hence suggest the position at which each would be most easily protonated. Draw a curly arrow mechanism for the protonation in each case.



- 10.4 Under normal conditions pure BF₃ is a gas, but it can be purchased from chemical suppliers as a solution in ethoxyethane (diethyl ether, Et₂O). Describe the interaction between BF₃ and the solvent, and draw a curly arrow mechanism for the interaction you suggest. Do you think that BH₃ might also be transported in this way?
- 10.5 At high temperatures in the gas phase aluminium trichloride exists as discrete AlCl₃ molecules which have a trigonal planar structure. At lower temperatures, a dimer Al₂Cl₆ is formed, and this species is also found in molten aluminium trichloride. The structure of the dimer is illustrated below (any formal charges are not shown)



Identify the HOMO and the LUMO in an AlCl₃ molecule and hence explain how a reaction between two such molecules can give rise to a dimer with the structure shown. Assign any formal charges required, and explain why the dimerization must be an exothermic process.

10.6 Protonation of cyclohexene gives and ion A which reacts with water to give a species B



Identify the HOMO in cyclohexene and hence determine the structure of A; draw a curly arrow mechanism for its formation. Consider the possible HOMO/LUMO interactions between A and H_2O , and hence predict the structure of B, drawing a curly arrow mechanism for its formation.

- 10.7 (a) Assuming the C and N to be sp hybridized, draw up a description of the bonding in CN^- and hence identify the HOMO.
 - (b) By considering the likely orbital interactions, predict the initial product of the reaction between CN⁻ and methanal. Draw a curly arrow mechanism for your proposed reaction.
- 10.8 Cyanides (nitriles) R-C≡N react hardly at all with H₂O, but under acid conditions their reactivity is greatly enhanced. By considering the orbitals involved, explain why protonation of a nitrile enhances its reactivity towards nucleophiles. In your answer be sure to specify the site of protonation, and give a curly arrow mechanism for the initial reaction of the protonated nitrile with H₂O.
- 10.9 Compound (a) is readily available and is stable under normal conditions, whereas compound (b) is not listed by any chemical supplier. Why is this?



11 Organic chemistry 1: functional groups

11.1 Identify the functional groups present in the following molecules.



11.2 Copy the structures of each of the following molecules and identify the functional group level of each of the carbon atoms in them.



11.3 Draw the structures of the products formed in the following hydrolysis reactions.



11.4 The drug *Fenipentol*, shown below, is synthesized by the reaction between butylmagnesium bromide and an aldehyde. Draw the structure of the aldehyde and give the mechanism for the reaction.



11.5 A synthesis of the anti-inflammatory drug *Felbinac* is shown below. Suggest a structure for the intermediate A and give a mechanism for its formation. Give a mechanism for the hydrolysis of A to Felbinac.



11.6 Consider the following scheme for the synthesis of the drug *Cicletanine*, which is used as a diuretic and antihypertensive.



- (a) Give the reagents needed to form acetal A in step 1 and draw a mechanism for this step.
- (b) What sort of reaction is step 2: a reduction; an oxidation; or a nucleophilic substitution?
- (c) Give the reagent needed for step 3 and draw a mechanism for this step.
- (d) Steps 4 and 5 occur under the same conditions. What conditions are needed for the hydrolysis of acetal D? Give a mechanism for this step.
- (e) What sort of reaction is step 5: a reduction; an oxidation; or a nucleophilic substitution?
- 11.7 The synthesis of the antihistimine drug *Bamipine* is given below.



- (a) What sort of reaction is step 1: a reduction; an oxidation; or a nucleophilic substitution?
- (b) What is the role of the NaNH $_2$ in step 2? Draw mechanisms for the reactions in step 2.
- (c) The imine A is formed by the reaction of $PhNH_2$ with another reagent. Identify this reagent, and give a mechanism for its reaction with $PhNH_2$ to form A.
11.8 A synthesis of the antiparkinsonian drug *Pridinol* is outlined below.



- (a) At which *two* sites could bromoester A react with a nucleophile? Name the key orbitals involved in each case.
- (b) Suggest a reagent X to form B from A and give a mechanism for the reaction. Explain why X reacts in the manner shown, rather than at the alternative site identified in (a).
- (c) Intermediate **B** reacts with excess phenylmagnesium bromide to give Pridinol. Suggest a structure for Pridinol and give a mechanism for its formation.
- 11.9 Part of the synthesis of the antiasthmatic drug *Fenspiride* is shown below. Identify the structure of the intermediate **B** and give a mechanism for its formation. Give a mechanism for the reduction of **B** to **C**.



The drug Fenspiride is prepared from intermediate C by reacting it with the base NaOEt and compound X. X is one of the compounds shown in the box below. By considering the functional group levels, suggest which one of the compounds D–H is X and give a mechanism for the formation of Fenspiride.



11.10 A synthesis of the sedative *Ethinamate* is shown below. Suggest a structure for the intermediate A and draw a mechanism for its formation. Give mechanisms for the formation of Ethinamate from A.



11.11 A synthesis of the mite and spider killer *Chlorobenzilate* is shown below. When the Grignard reagent **A** is added slowly to a solution of diethyl oxalate **B** at low temperatures, the intermediate **C** is first formed, but this reacts with further Grignard reagent to form, after work-up in aqueous acid, Chlorobenzilate. Suggest a structure for the intermediate **C** and give a mechanism for its formation. Give a mechanism for the reaction of the intermediate **C** with the Grignard reagent **A** and explain why the addition of the second Grignard reagent occurs at the position it does.



11.12 Explain the following. When sodium borohydride is added to a solution of an ester, as shown in (a), no reduction takes place. However, on addition of aluminium trichloride, as shown in (b), the reduction readily takes place.





11.13 A synthesis of the muscle relaxant Nefopam is shown below.

- (a) Which of the carbonyls in compound A is reduced by the borohydride? Draw a mechanism for this reduction and for the subsequent formation of B.
- (b) Suggest a suitable reagent for the conversion of **B** to **C** and draw a mechanism for this step.
- (c) Give a mechanism for the reduction of C to D.
- (d) The cyclyzation of intermediate E to give F is an example of an intramolecular nucleophilic substitution reaction. Will this proceed via an S_N 1-like mechanism or an S_N 2- like mechanism? Explain your answer.
- (e) Draw a mechanism for the reduction of F and the subsequent formation of Nefopam which takes place in acid.
- (f) Explain why $NaBH_4$ is the reducing agent of choice for the first step, but $LiAlH_4$ for the later two reductions.

12 The rates of reactions

12.1 The thermal decomposition of N_2O_5 in the gas phase has the overall reaction

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$
.

Using the approach described in section 12.1.1 on page 409, write down the value of the stoichiometric coefficients of the reactant and each product. Then, write down the expression for the rate of reaction in terms of the slope of a plot of $[N_2O_5]$ against time, $[NO_2]$ against time, and $[O_2]$ against time.

12.2 By writing the units of concentration as 'conc' and the units of time as 'time', determine the units of the rate constants in the following rate laws

rate =
$$k_1 [N_2O_5]$$
 rate = $k_2 [PhCH_2Br] [DABCO]$
rate = $k_3 [RH] [Cl_2]^{\frac{1}{2}}$ rate = $k_4 [CH_3CHO]^{\frac{3}{2}}$
rate = $k_5 \frac{[O_3]^2}{[O_2]}$ rate = k_6 .

12.3 The thermal decomposition of N_2O_5 in the gas phase is found to be first order in $[N_2O_5]$. The first order rate constant, k_{1st} , has been measured as a function of temperature as follows

 $\begin{vmatrix} T / K \\ k_{1st} / s^{-1} \end{vmatrix} \begin{array}{c} 349 \\ 0.0068 \\ 0.041 \\ 0.13 \\ 0.50 \end{vmatrix}$

Make an Arrhenius plot of these data, and hence determine a value for the activation energy and the pre-exponential factor; state the units of each quantity.

12.4 Methanoic acid is oxidized in acid solution by Br₂ according to the following stoichiometric equation

 $\text{HCOOH} + \text{Br}_2 + 2\text{H}_2\text{O} \longrightarrow \text{CO}_2 + 2\text{Br}^- + 2\text{H}_3\text{O}^+.$

It is found that the rate of reaction depends on the concentration of HCOOH and Br_2 , and is also influenced by the concentration of added H_3O^+ . If H_3O^+ and HCOOH are in excess, then it is found that the reaction is first order in [Br_2]. The following rate law was therefore proposed

rate =
$$k_{obs}[Br_2][HCOOH]^a[H_3O^+]^b$$

where *a* and *b* are the orders with respect to HCOOH and H_3O^+ , respectively.

If H₃O⁺ and HCOOH are in excess the rate law can be written

rate =
$$k_{1st}[Br_2]$$
,

where k_{1st} is a pseudo first-order rate constant.

- (a) Write down an expression for k_{1st} .
- (b) The following values of k_{1st} were measured for different excess concentrations of HCOOH and H₃O⁺:

[HCOOH] / mol dm ^{-3}	0.10	0.10	0.12	0.22
$[H_3O^+] / mol dm^{-3}$	0.05	0.12	0.15	0.15
$k_{1 \text{st}} / \text{s}^{-1}$	7.00×10^{-3}	2.92×10^{-3}	2.80×10^{-3}	5.13×10^{-3}

By comparing the data in the first two columns, determined the value of *b*. Similarly, determine the value of *a* by comparing the data in the third and fourth columns.

- (c) Use all of the data in the table to determine an average value of k_{obs} ; state the units of this rate constant.
- 12.5 Consider the following two energy profiles for the reaction scheme (all reactions are first order)



In each case, discuss whether or not the pre-equilibrium and/or the steady-state approaches can be used to analyse the overall kinetics. Using the appropriate approximation(s) in each case, obtain expressions for the rate of formation of C, identify the rate-limiting step, and mark the apparent activation energy on the energy profiles.

12.6 Consider the following reaction scheme, in which all of the reactions are first order and reversible. $k_1 k_2$

A
$$\underset{k_1}{\overset{k_1}{\leftarrow}}$$
 B $\underset{k_2}{\overset{k_2}{\leftarrow}}$ C.

By equating the rates of formation and loss of B, show that the steady-state concentration of B is given by

$$[\mathbf{B}]_{\rm SS} = \frac{k_1[\mathbf{A}] + k_{-2}[\mathbf{C}]}{k_2 + k_{-1}}$$

Hence show that the overall rate of change of the concentration of C is given by

rate of change of [C] =
$$\frac{k_1k_2[A] - k_{-1}k_{-2}[C]}{k_2 + k_{-1}}$$
.

Under what conditions will this steady-state analysis be valid? Draw an energy profile for such a situation, marking on it all of the activation energies.

12.7 The reaction (in solution) between Br_2 and dicyanomethane, $CH_2(CN)_2$, has the overall stoichiometry.

$$CH_2(CN)_2 + Br_2 \longrightarrow CHBr(CN)_2 + Br^- + H^+.$$

The following mechanism, involving the intermediate CH(CN)₂⁻, is proposed

$$\begin{array}{rcl} CH_2(CN)_2 & \xrightarrow{k_1} & CH(CN)_2^- + H^+ \\ CH(CN)_2^- + H^+ & \xrightarrow{k_{-1}} & CH_2(CN)_2 \\ CH(CN)_2^- + Br_2 & \xrightarrow{k_2} & CH(CN)_2Br + Br^- \end{array}$$

By putting the intermediate in the steady state, show that

rate of formation of CH(CN)₂Br =
$$\frac{k_1k_2[CH_2(CN)_2][Br_2]}{k_{-1}[H^+] + k_2[Br_2]}$$
.

Under what conditions will this analysis be valid?

What simplification of the expression for the rate law occurs if: (a) the rate of reaction 2 is much greater than that of reaction -1; (b) the rate of reaction -1 is much greater than that of reaction 2? In each case, identify the rate-limiting step and the apparent activation energy.

12.8 In aqueous solution the oxidation of Fe^{II} by Pb^{IV} is though to proceed via the intermediate species Pb^{III} according to the following mechanism

$$\begin{array}{ccc} \operatorname{Fe}^{\mathrm{II}} + \operatorname{Pb}^{\mathrm{IV}} & \xrightarrow{k_{1}} & \operatorname{Fe}^{\mathrm{III}} + \operatorname{Pb}^{\mathrm{III}} \\ \operatorname{Fe}^{\mathrm{III}} + \operatorname{Pb}^{\mathrm{III}} & \xrightarrow{k_{-1}} & \operatorname{Fe}^{\mathrm{II}} + \operatorname{Pb}^{\mathrm{IV}} \\ \operatorname{Fe}^{\mathrm{II}} + \operatorname{Pb}^{\mathrm{III}} & \xrightarrow{k_{2}} & \operatorname{Fe}^{\mathrm{III}} + \operatorname{Pb}^{\mathrm{II}}. \end{array}$$

Assuming that Pb^{III} can be placed in the steady state, determine the overall rate law for the rate of change of the concentration of Fe^{III} .

12.9 Under acid conditions and in aqueous solution, *t*-butanol undergoes a substitution reaction with iodide to give *t*-butyl iodide



Experimentally the rate law for this reaction is found to be first order in the concentration of the *t*-butanol and also first order in H_3O^+ , but not to have a dependence on the concentration of the iodide. The fact that the rate depends on the concentration of the acid is a clue that protonation is involved at some stage. A possible mechanism is



The reason for proposing the initial protonation as the first step is that the dissociation of ROH_2^+ to give R^+ and H_2O is thought to be considerably faster than the dissociation of ROH to give R^+ and OH^- .

(a) Assuming that ROH and ROH_2^+ are in equilibrium, show that

$$[ROH_2^+] = K_{eq}[ROH][H_3O^+].$$
(12.1)

(b) Apply the steady-state approximation to R^+ and hence shown that

$$[\mathbf{R}^+]_{\rm SS} = \frac{k_1 K_{\rm eq} [\rm ROH] [\rm H_3O^+]}{k_{-1} + k_2 [\rm I^-]}$$

You will need to use the expression for $[ROH_2^+]$ from Eq. 12.1 on page 41.

(c) The rate of formation of the alkyl iodide is simply $k_2[R^+][I^-]$. Using you expression for $[R^+]$, show that

rate of formation of RI =
$$\frac{k_1 k_2 K_{eq} [ROH] [H_3 O^+] [I^-]}{k_{-1} + k_2 [I^-]}$$
.

If it can be assumed that the rate at which R^+ reacts with iodide is much faster than the rate at which the carbenium ion reacts with H_2O , show that the rate of formation of RI can be approximated by

rate of formation of
$$RI = k_1 K_{eq} [ROH] [H_3 O^+]$$
.

- (d) Give an interpretation of this rate law, identifying the rate-limiting step.
- 12.10 The destruction of ozone by Cl atoms in the stratosphere can be modelled using the following four reactions

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

propagation $Cl + O_3 \xrightarrow{k_2} ClO + O_2$
 $ClO + O_3 \xrightarrow{k_3} Cl + 2O_2$
termination $Cl + Cl \xrightarrow{k_4} Cl_2.$

- (a) Write down an expression equating the rate of formation and loss of Cl; do the same for ClO.
- (b) Compare these two equations carefully, and hence deduce that, in the steady state,

$$[\mathrm{Cl}] = \sqrt{\frac{k_1[\mathrm{Cl}_2]}{k_4}}.$$

(c) Using your equation equating the rate of formation and loss of ClO, together with the above expression for [Cl], to show that

$$[\text{CIO}] = \frac{k_2}{k_3} \sqrt{\frac{k_1[\text{Cl}_2]}{k_4}}.$$

(d) Hence show that the rate of loss of ozone is given by

rate of loss of ozone =
$$2k_2[O_3] \sqrt{\frac{k_1[Cl_2]}{k_4}}$$
.

- (e) Explain why this final expression does not include the rate constant k_3 . Also, discuss the origin of the term in the square root.
- 12.11 This question concerned the mechanism of the $H_2 + Br_2$ reaction discussed in section 12.9.1 on page 432. In that section it was assumed that the concentration of HBr was low, so that the inhibition step (step 4) could be omitted. This question explores the effect of including this step.

Taking into account *all five* steps in the mechanism, show that equating the rate of formation and loss of Br gives

$$2k_1[Br_2] + k_3[H][Br_2] + k_4[H][HBr] = k_2[Br][H_2] + 2k_5[Br]^2.$$

Further, by equating the rate of formation and loss of H show that

$$k_2[Br][H_2] = k_3[H][Br_2] + k_4[H][HBr].$$
 (12.2)

By adding together these two equations show that

$$[Br] = \left(\frac{k_1}{k_5}\right)^{\frac{1}{2}} [Br_2]^{\frac{1}{2}}.$$

Substitute this expression for [Br] into Eq. 12.2 and rearrange the result to obtain an expression for [H].

The rate of formation of HBr is

rate of formation of HBr = $k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr]$.

Use Eq. 12.2 to show that this can be rewritten

rate of formation of HBr = $2k_3$ [H][Br₂],

and then substitute your expression for [H] into this to obtain, after some rearrangement

rate of formation of HBr =
$$\frac{2k_2 \left(\frac{k_1}{k_5}\right)^{\frac{1}{2}} [H_2][Br_2]^{\frac{3}{2}}}{[Br_2] + \left(\frac{k_4}{k_3}\right)[HBr]}$$
.

Compare this rate law with the experimentally determined form.

12.12 It is possible that the gas phase reaction between NO and O_2 to give NO_2

$$2NO + O_2 \longrightarrow 2NO_2$$

proceeds via the following mechanism involving the intermediate N2O2

$$\begin{array}{rcl} 2\text{NO} & \stackrel{k_1}{\longrightarrow} & \text{N}_2\text{O}_2\\ \text{N}_2\text{O}_2 & \stackrel{k_{-1}}{\longrightarrow} & 2\text{NO}\\ \text{N}_2\text{O}_2 + \text{O}_2 & \stackrel{k_2}{\longrightarrow} & 2\text{NO}_2. \end{array}$$

Show how this mechanism can be consistent with the experimentally observed rate law

rate of formation of NO₂ = $k_{obs}[O_2][NO]^2$,

and give an expression for k_{obs} .

13 Spectroscopy

The following nuclei all have spin $I = \frac{1}{2}$: ¹H, ¹³C, ¹⁹F and ³¹P. Of these nuclei, all but ¹³C have 100% natural abundance. Unless otherwise stated, you may assume that all ¹³C spectra have been recorded with broadband proton decoupling.

13.1 The carbonyl stretching frequency for the amide 1 is 1670 cm⁻¹, which is significantly lower than the value for a ketone. For the amide 2 the stretching frequency is 1720 cm⁻¹. Account for these differences.



- 13.2 The carboxylate anion, RCO₂, shows two absorptions in the C=X region, one at around 1575 cm⁻¹ and one at around 1430 cm⁻¹. The C=O vibrational frequency for a typical carboxylic acid, RCOOH, is 1725 cm⁻¹; the vibrational frequency of a C-O single bond is around 1100 cm⁻¹. Discuss these data.
- 13.3 (a) The relative molecular mass of a compound X has been determined by high resolution mass spectrometry to be 68.0261. Using the accurate relative atomic masses below, determine the formula of compound X.

¹H: 1.0078 ¹²C: 12.0000 ¹⁶O: 15.9949

(b) The IR spectrum of compound X is shown below. Use the information from this spectrum, along with your answer to (a), to determine the structure of X; give reasons for your answer. [Hint: you will need to measure carefully the carbonyl frequency to distinguish between different possible structures.]



13.4 Predict how many lines you would expect to see in the broadband proton-decoupled ¹³C NMR spectra of the following molecules, giving brief reasons for your answers in each case (a) benzene, (b) anthracene, (c) 1,4-dinitrobenzene, (d) 1-chloro-4-bromobenzene, (e) 1-chloro-2-nitrobenzene, (f) Et₂O, (g) EtOMe, (h) CH₃(CH₂)₄COEt.



13.5 Sketch the ¹³C NMR spectra that you expect from the following molecules. You should indicate on you spectrum which carbon is responsible for which line in the spectrum. (You cannot give precise values of the shifts, but you can predict the region of the spectrum in which each carbon will give a line, and for similar carbons you can make a reasonable guess as to what order the shifts will come in).



Compound (d) is *mescaline*, an hallucinogenic drug first isolated from certain mushrooms.

13.6 How can APT NMR spectra be used distinguish between the following hydrocarbons?



13.7 How could the following six isomers be distinguished using ¹³C NMR?



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13.8 For organic molecules, 'reduction' involves adding H_2 across double bonds. Reduction of the following molecule gave two products A and B, both with molecular formula $C_6H_{12}O$.



From the following spectroscopic data, identify these two products and explain how the data is consistent with your proposals for the structures of **A** and **B**:

Product A: ¹³C NMR: 137, 115, 85, 36 and 17 ppm; IR: 3400 and 1650 cm⁻¹. Product B: ¹³C NMR: 213, 38, 31, 17 and 8 ppm; IR: 1710 cm⁻¹.

- 13.9 (a) Discuss the ¹³C chemical shifts observed in the following compounds: methyl lithium: -15 ppm propene: 134, 116 and 20 ppm allyl lithium (LiCH₂CH=CH₂): 143 and 51 ppm.
 - (b) Under acidic conditions 1 gives a very reactive species 2, whose ¹³C NMR spectrum can be recorded at low temperatures



The following peaks were observed in the ¹³C NMR spectra of 1 and 2: 1: 131, 129, 66, 32, 25 and 19 ppm 2: 224, 142, 37 and 18 ppm. Suggest a structure for 2 and assign the spectra of both 1 and 2.

13.10 Cyanogen reacts with morpholine to give a compound A, the spectroscopic data for which are given below. Identify A, giving your reasons.



¹³C NMR: peaks at 45.6, 66.2, 110.6 and 142.1 ppm Significant IR absorptions at 3290, 2234 and 1620 cm⁻¹

- 13.11 Compound A has the formula $C_7H_7NO_3$ and may be reduced to give compound B with the formula C_7H_9NO . The ¹³C NMR and the IR spectra for A and B are shown in Fig. 13.1 and Fig. 13.2, shown on the next pages. The aromatic region of the ¹H NMR spectrum of A shows two triplets and two doublets. Deduce the structures of A and B and, as far as possible, assign the spectra.
- 13.12 The ¹⁹F NMR spectrum of IF₅ consists of a doublet (that is two lines with intensity ratio 1:1) and a quintet (that is five lines with intensity ratios 1:4:6:4:1). Suggest a structure for IF₅ that is consistent with this spectrum, explaining how you arrive at your result. [No splittings are seen due to coupling to the iodine].



- 13.13 Explain why the broadband proton-decoupled ¹³C spectrum of CH_2Cl_2 consists of a single line, whereas that of CD_2Cl_2 consists of a 1:2:3:2:1 quintet. Predict the form of the ¹³C spectrum of d₆-DMSO (i.e. CD_3SOCD_3).
- 13.14 ¹¹B has spin $\frac{3}{2}$ and relaxes sufficiently slowly that couplings to it can be seen. Explain what you would expect to see in the proton NMR spectrum of diborane, B₂H₆, whose structure is shown in Fig. 1.8 on page 18. (You may assume that all the B atoms are ¹¹B, and can ignore any couplings between the protons.)
- 13.15 Explain why the ¹²⁹Xe NMR spectrum of XeF⁺ is a doublet with J = 7600 Hz, but the ¹⁹F spectrum *appears* to be a triplet with J = 3800 Hz. [¹⁹F has spin $\frac{1}{2}$ and 100% natural abundance; ¹²⁹Xe has spin $\frac{1}{2}$ and 26% natural abundance].
- 13.16 Rhodium and carbon monoxide combine to form a cluster compound with formula $Rh_4(CO)_{12}$ whose structure, 1, is shown below. Note that in this structure the four rhodium atoms are placed at the corners of a tetrahedron.





Fig. 13.2 IR spectra of compounds A and B from question 13.11.

- (a) Identify the number of chemically distinct carbon atoms in 1 and hence predict the form of its ¹³C NMR spectrum. Explain your reasoning carefully. [¹⁰³Rh is spin-half and has a natural abundance of 100%].
- (b) Predict the form of the ¹⁰³Rh NMR spectrum of 1. Explain your reasoning carefully.

13.17 (a) State the expected structures of BF₃, BCl₃ and BBr₃.

(b) The ¹⁹F NMR spectrum of BF₃ shows a 1:1:1:1 quartet. The ¹⁹F spectrum of a mixture of BF₃ and BCl₃ shows *three* 1:1:1:1 quartets, likewise the spectrum from a mixture of BF₃ and BBr₃ also shows *three* 1:1:1:1 quartets. The ¹⁹F spectrum of a mixture of BF₃, BCl₃ and BBr₃ shows *six* 1:1:1:1 quartets. The chemical shifts at which each of these quartets is centred are given in the table

mixture	shift (ppm)					
BF ₃ only	0					
BF ₃ and BCl ₃	0	51.5	99.0			
BF ₃ and BBr ₃	0	68.4	130.4			
BF ₃ , BCl ₃ and BBr ₃	0	51.5	68.4	99.0	114.8	130.4

Assuming that only the isotope ¹¹B, which has spin $I = \frac{3}{2}$, is present: (i) identify the species responsible for each quartet and (ii) rationalise the *relative* chemical shifts.

(c) The mass spectrum of BCl₃ is shown below. Explain the spectrum as fully as possible assuming the following isotopic abundances: ¹⁰B 20%, ¹¹B 80%, ³⁵Cl 75%, ³⁷Cl 25%.



- (d) The IR spectrum of BF₃ shows a single absorption in the B–F region of the spectrum at 692 cm^{-1} . The addition of one equivalent of Et₂O causes this peak to shift to 665 cm^{-1} and a second absorption to appear at 770 cm⁻¹. Explain these observations.
- 13.18 Shown below is a portion of the ¹H NMR spectrum of bromoethane as measured on a 400 MHz spectrometer where 1 ppm \equiv 400 Hz. In order to show the small peaks, the spectrum has been vertically expanded and the strong peaks cropped. Explain the appearance of the spectrum as fully as possible and determine (in Hz) the ¹J_{C-H} coupling constants and the ³J_{H-H} coupling constant.



13.19 (a) The proton-decoupled ¹³C NMR spectrum of ethanoyl fluoride (acetyl fluoride) consists of a doublet with a coupling constant of 354.3 Hz and centred at 160.8 ppm, and a doublet with coupling constant 58.3 Hz centred at 18.7 ppm. The IR spectrum includes a strong absorption at 1848 cm⁻¹. Assign the ¹³C and IR spectra.



(b) At low temperatures in an inert solvent, ethanoyl fluoride reacts with Lewis acids such as BF_3 , PF_5 or SbF_5 to yield a salt X^+Y^- in which the identity of Y^- depends on the particular Lewis acid used.

The ¹³C NMR of the salt shows just two singlets at 7.5 ppm and 150.3 ppm. The IR spectrum no longer has an absorption at 1848 cm⁻¹, but now shows a strong absorption at 2297 cm⁻¹.

Suggest a structure for the salt formed between ethanoyl fluoride and BF_3 , and explain how your suggestion is consistent with the given spectroscopic data.

(c) Describe the appearance of the 31 P NMR spectrum of the salt formed when ethanoyl fluoride reacts with PF₅.

13.20 Given overleaf are details of the ¹H and ¹³C NMR spectra of *five* isomers with the formula C_5H_8O . *Each isomer contains a carbonyl group*.

The second column gives details of the ¹H spectrum in an abbreviated form: '2.1, 3H, singlet' means that at a shift of 2.1 ppm there is a *singlet* which the integral indicates is from *three* protons. Similarly '2.32, 2H, doublet of doublets' means that at a shift of 2.32 ppm there is a *doublet of doublets* which the integral indicates is from *two* protons. If a multiplet is too difficult to interpret, it is simply described as a 'complex multiplet'.

The third column gives the number of peaks in the ¹³C spectrum; apart from one of the peaks corresponding to a carbonyl carbon, the shifts are not particularly useful, and so are not given. The fourth column gives details of the APT spectrum (page 486) which indicates whether there are an odd or even number of protons attached to a particular carbon.

Your task is to identify the structures A–G. You may find it useful to adopt the following strategy:

- (a) Draw out all the isomers of $C_5H_{10}O$ which contain a carbonyl group. [Hint: there are seven in all].
- (b) Identify the number of different environments for all the hydrogen atoms in each structure.
- (c) Using the data about the integrals given in the table, work out (in as far as you can) which structure corresponds to which spectrum.
- (d) The ¹³C spectra may also be helpful in sorting out any ambiguities or in confirming your assignment. Identify the number of different carbon atoms in each structure, and check that this matches your proposed structure. Also, check that the APT data are consistent with your answers.
- (e) (More difficult) once you are confident of your assignments, try to explain the form of the proton multiplets in terms of the expected couplings.

Struc.	¹ H spectrum	¹³ C spectrum	APT
A	2.1, 3H, singlet 2.38, 2H, triplet 1.58, 2H, sextet 0.9, 3H, triplet	5	carbonyl down 2 up 2 down
В	9.8, 1H, triplet2.32, 2H, doublet of doublets2.23, 1H, complex multiplet1.0, 6H, doublet	4	carbonyl up 2 up 1 down
С	9.78, 1H, triplet 2.45, 2H, triplet of doublets 1.64, 2H, quintet 1.38, 2H, sextet 0.95, 3H, triplet	5	carbonyl up 1 up 3 down
D	2.43, 4H, quartet 1.05, 6H, triplet	3	carbonyl down 1 up 1 down
E	9.64, 1H, doublet 2.29, 1H, sextet of doublets 1.11, 3H, doublet 1.4-1.8, 2H, complex multiplet 0.97, 3H, triplet	5	carbonyl up 3 up 1 down
F	2.14, 3H, singlet 2.59, 1H, septet 1.1, 6H, doublet	4	carbonyl down 3 up 0 down
G	9.5, 1H, singlet 1.1, 9H, singlet	3	carbonyl up 1 up 1 down

13.21 Phosphine, PH₃, is a colourless, toxic gas. It reacts with aqueous acid HA and methanal (formaldehyde, CH_2O) to give a salt, X^+A^- . Figure 13.3 on the next page shows various spectra recorded for the species X^+ .

The (low resolution) positive-ion electrospray mass spectrum of X^+ shows a main peak at 155, along with three fragments each showing a successive loss of mass 30.

For the ¹H and ³¹P NMR spectra the shifts (in ppm) are some peaks are indicated; note also that the conversion from ppm to Hz is given for each spectrum. The only feature in the *proton decoupled* ¹³C NMR spectrum (not shown) is a doublet, centred at 48.7 ppm, and with a splitting of 50 Hz.

- (a) Explain why it is that the ³¹P NMR spectrum of phosphine consists of a 1:3:3:1 quartet, whereas the ¹H NMR spectrum consists of a 1:1 doublet. [³¹P, $I = \frac{1}{2}$, abundance 100 %]
- (b) By considering the mass spectrum and *all* of the NMR data, suggest a structure for the X⁺. Be sure to explain how each spectrum is consistent with your structure and include the actual values for any coupling constants as determined from the spectra. [You may find it helpful to think about the reaction, which starts with a nucleophilic addition to a double bond.]



Fig. 13.3 Mass spectrum, 1 H and 31 P NMR spectra of species X⁺ from question 13.21.

14 Organic chemistry 2: three-dimensional shapes

14.1 Describe the relationship between the following pairs of structures (e.g. whether they are enantiomers, diastereomers etc.)



14.2 Redraw each of the following structures in the ways described in Box 14.2 on page 509, indicating the direction in which your views are taken. Describe the relationship between the substituents (other than hydrogen) on the two carbons.



- 14.3 (a) Sketch (i) a graph of the energy of BrCH₂CH₂Br as a function of the dihedral angle between the two C-Br bonds, and (ii) a similar graph for BrCH₂CH₃ as a function of the dihedral angle between the C-Br bond and one of the C-H bonds in the methyl group. Comment on the form of the two graphs.
 - (b) According to the Boltzmann distribution, if conformation A is higher in energy than conformation B by an amount ΔE the ratio r of the populations of the conformations is given by

$$r = \frac{\text{population of A}}{\text{population of B}}$$
$$= \exp\left(\frac{-\Delta E}{RT}\right),$$

where *R* is the gas constant (8.3145 J K⁻¹ mol⁻¹) and *T* is the absolute temperature. Use this relationship to calculate the ratio of the populations of the *gauche* and *anti* conformers of butane, the energy profile for which is shown in Fig. 14.9 on page 510, at 298 K and at 398 K.

(c) If the number of molecules in conformer A is N_A and the number in conformer B is N_B , then it follows that $r = N_A/N_B$. The *fraction* of molecules which are in conformer A is given by $N_A/(N_A + N_B)$. Show that

$$\frac{N_{\rm A}}{N_{\rm A}+N_{\rm B}}=\frac{r}{1+r}.$$

Hence work out the percentage of butane in the *gauche* and *anti* conformers at 298 K and at 398 K.

14.4 Using the CIP convention (Box 14.3 on page 515) assign E/Z labels to the double bonds in the following molecules.



14.5 Using the CIP convention, assign *R/S* labels to the chiral centre or centres in the following molecules.



14.6 For both of the following compounds draw all possible stereoisomers, indicating which are enantiomers and which are diastereomers (use wedged and dashed bonds to differentiate the individual isomers). For which of these compounds does a *meso* isomer exist?



14.7 Inositol, (a), exists as nine stereoisomers, some of which are shown below.



- (a) Using symmetry arguments, explain why isomer (b) is achiral, and why isomer (c) is chiral.
- (b) Draw out the structures of all nine stereoisomers (using wedged and dashed bonds), identifying which are chiral.
- (c) Draw isomer (d) with the ring in the chair conformation, being careful to place the OH groups in the correct 'up' and 'down' positions. Explain why the structure you have drawn is chiral, and consider what effect a ring flip would have on this structure.
- (d) Using your answer to (d), explain why it has not been possible to isolate the enantiomers of isomer (d).
- 14.8 Explain why the presence of a bulky substituent, such as *t*-Bu, results in a cyclohexane ring being 'locked' in a particular conformation. Draw the lowest energy conformations of (a) and (b), making it clear whether the Cl is axial or equatorial.



14.9 In the low-temperature spectrum of bromocyclohexane shown in Fig. 14.40 on page 533 the integral of the peak at 20.3 ppm was found to be 0.215 (arbitrary units) and that of the peak at 27.1 ppm was found to be 0.998 (same arbitrary units). Assuming that the integral is proportional to concentration, find the equilibrium constant for the axial \rightleftharpoons equatorial equilibrium. Hence find $\Delta_r G^\circ$ for the process and the *A*-value. Compare your value with those in Table 14.2 on page 534. [Be sure to use the correct temperature.]

15 Organic chemistry 3: reactions of π systems

15.1 Compounds A and B both react in aqueous ethanol to give isobutene and t-butyl alcohol. A and B react at different rates, but give exactly the same proportions of the two products. What does this suggest about the mechanism for the reactions?



15.2 Both the *cis* and *trans* bromoalkenes shown below react with NaOH to form the alkyne, but the *cis* isomer reacts 2.1×10^5 times faster than the *trans* isomer. Explain why this is so.



15.3 When 1,2-dimethylcyclohexene, A, is treated with dilute acid, diastereoisomers B and C are formed in approximately equal proportions (together with their enantiomers). No matter how long the mixture is left standing, only around 10% of A is found to have reacted. With the aid of a suitable mechanism, account for these observations.



15.4 2-Bromoethyl nitrate, shown below, may be obtained in good yield by bubbling ethene gas through an aqueous solution of bromine and sodium nitrate. Give a mechanism for this reaction.



15.5 The diastereoisomers *cis*- and *trans*-but-2-ene both give 2,3-dibromobutane on reaction with bromine. However, one alkene gives only the achiral *meso* form of 2,3-dibromobutane, whilst the other gives only a racemic mixture of the optically active diastereomer. With the aid of clear mechanisms, explain these observations.

15.6 Compound **A**, shown below, may be prepared either from cyclohexene via an epoxide, or by the hydroboration of 1-methylcyclohexene. Give mechanisms for each of these reactions and account for the observed stereochemistry.



15.7 In the presence of a trace of acid or base, the optically active ketone shown below readily forms a racemic mixture. With the aid of appropriate mechanisms, explain how this occurs.



15.8 A synthesis of the drug Amobarbital (also called amylobarbitone) is shown below.



- (a) The sodium ethoxide can react with the diethyl malonate either as a nucleophile, or as a base. Give the mechanisms for each of these reactions.
- (b) Identify the intermediates A and B, and give mechanisms for their formation.
- (c) Intermediate B reacts with urea and NaOEt to form amobarbital. What is the role of the NaOEt? Give a mechanism for the formation of amobarbital.
- 15.9 Both 5-androstene-3,17-dione, **A**, and 4-androstene-3,17-dione, **B**, may be deprotonated in hydroxide to give a common anion, X^- . The p K_a of **A** to form the anion is 12.7, whereas the p K_a of **B** is 16.1.



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- (a) Identify the acidic proton in A and in B which must be lost to form the common anion X^- . Give a mechanism in each case.
- (b) Suggest why the pK_a of **A** is lower than that of **B**, and why both are lower than the pK_a of acetone (around 20).
- (c) Give expressions for $K_a(A)$ and $K_a(B)$, the acidity constants for A and B, and calculate the values of these equilibrium constants from the given pK_a values.
- (d) Write an expression for the equilibrium constant for $A \rightleftharpoons B$ in terms of $K_a(A)$ and $K_a(B)$, and calculate its value. Comment on your answer.
- 15.10 In the presence of a catalytic amount of acid or base, 4-methylcyclopent-2-enone, A, isomerizes to 3-methylcyclopent-2-enone, B. Give a mechanism for this reaction. Why is B favoured at equilibrium rather than A?



15.11 A synthesis of the drug *Normethadone* is shown below. Give the mechanisms for all the reactions involved in the synthesis.



15.12 A synthesis of the bronchodilator *Clenbuterol* is shown below.



- (a) Identify the intermediates A–D.
- (b) Give a mechanism for each step of the reaction scheme, except for the catalytic reduction of **B** to **C**.
- (c) How do the two substituents on the benzene ring affect the reaction with chlorine in the formation of D from C?

16 Main-group chemistry

- 16.1 (a) Discuss why it is that in the gas phase BCl₃ exists as a discrete molecule, whereas AlCl₃ forms dimers (illustrated in Fig. 16.16 on page 617).
 - (b) Explain why B_2H_6 is sometimes described as an 'electron deficient' molecule.
 - (c) Assuming that the Al is sp^3 hybridized, draw up a description of the bonding in the Al₂Cl₆ dimer. Is this molecule electron deficient?
- 16.2 Comment on and rationalize the following observations
 - (a) BF_3 is a gas, whereas the other Group 13 trifluorides are all high-melting solids.
 - (b) BF_3 and AlF_3 both readily act as Lewis acids toward F^- ions to give $[BF_4]^-$ and $[AlF_4]^-$; however, TlF_3 does not form an analogous adduct with F^- .
 - (c) GaF and InF are known as unstable gaseous species, but GaI and InI are known as stable solids; all of the thallium(I) halides are known, including TlF.
- 16.3 (a) Rationalize the trend in the pK_a values of the following three aquo ions

$$[K(H_2O)_6]^+ pK_a = 14.5 [Ca(H_2O)_6]^{2+} pK_a = 12.8 [Ga(H_2O)_6]^{3+} pK_a = 2.6$$

- (b) Use these pK_a values to discuss: (i) the nature of the metal-containing species which would be present in aqueous solutions of these ions, (ii) what would happen if such solutions were made progressively more basic.
- 16.4 One of the pieces of evidence that mercury(I) salts contain the species [Hg₂]²⁺, rather than a simple Hg⁺ ion, is that these salts are not paramagnetic (i.e. there are no unpaired electrons). Explain why it is that Hg⁺ is paramagnetic whereas [Hg₂]²⁺ is not. [Hint: draw up a simple MO diagram for [Hg₂]²⁺, considering only the 6s electrons].
- 16.5 Comment on the following
 - (a) AlF_3 is a high melting point solid, whereas SiF_4 is a gas at room temperature.
 - (b) Silicon has fluorides with four, five and six-fold coordination: SiF₄, [SiF₅]⁻ and [SiF₆]²⁻, but for carbon only the four-coordinate fluoride CF₄ is known. However, the gas phase species [CH₅]⁺ has been detected.
 - (c) The Si–F bond lengths in SiF₄, $[SiF_5]^-$ and $[SiF_6]^{2-}$ are 154 pm, 159 pm, and 169 pm, respectively.
- 16.6 The strength if the N≡N triple bond is 946 kJ mol⁻¹, whereas that of P≡P is 490 kJ mol⁻¹; N–N and P–P single bonds have bond strengths in the range 160 kJ mol⁻¹ to 200 kJ mol⁻¹, depending on the compound. Discuss these data and the consequences they have for the kinds of compounds formed by nitrogen and phosphorus.
- 16.7 If PCl₅ reacts with an excess of water the ultimate product is phosphoric(V) acid, H₃PO₄. However, if equimolar amounts of PCl₅ and water react the compound POCl₃ is formed. Describe the likely steps by which these two products might be formed, and explain why limiting the amount of water gives a different product.

16.8 Determine the oxidation state of the sulfur in the following compounds or ions

(a) Na_2S (b) SF_2 (c) S_2F_2 (d) $[SO_3]^{2-}$ (sulfite) (d) $[SSO_3]^{2-}$ (thiosulfate).

- 16.9 Discuss the following
 - (a) The reaction of sulfur with F_2 gives SF_4 and SF_6 , but its reaction with Cl_2 gives SCl_2 and S_2Cl_2 ; there is no evidence for SCl_4 and SCl_6 .
 - (b) The ¹⁹F spectrum of SF₆ consists of a single line, whereas that of SF₄ consists of two 1:2:1 triplets (³²S has spin zero). [Hint: use VSEPR to predict the structures.]
 - (c) SO₂ exists as a discrete molecule in which the sulfur is two-fold coordinate; solid SeO₂(s) contains chains of the form -O-SeO-O-SeO- in which the Se is three-fold coordinate; TeO₂(s) has a layered structure in which the Te is four-fold coordinate; PbO₂(s) has a three-dimensional structure similar to the fluorite lattice in which the Pb is eight-fold coordinate.
- 16.10 Use VSEPR to predict the shapes of the following molecules or ions, and predict the form of the ¹⁹F NMR spectrum in each case (ignore any coupling to iodine)

(a) $[IF_2]^+$ (b) $[IF_2]^-$ (c) IF_3 (d) IF_5 (e) IF_7 .

Discuss the reasons why it is that IF_4 has not been prepared but $[IF_4]^-$ is well known.

- 16.11 Explain the following observations
 - (a) Liquid HF and liquid BF₃ are both very poor conductors of electricity, but a 1:1 mixture of the two liquids is a good conductor.
 - (b) BF_3 is more resistant to hydrolysis than is BCl_3 .
 - (c) PF_5 is molecular in the solid state, whereas PBr_5 forms an ionic lattice containing $[PBr_4]^+$ and Br^- ions.
 - (d) The equilibrium constants for the formation of the adducts A increase as X is changed from F to Cl and then to Br.



16.12 On careful hydrolysis of PF₃ an intermediate compound X is obtained. Accurate mass spectrometry of X gives a parent ion peak at 83.9976. The ³¹P NMR spectrum shows a doublet of doublets with coupling constants 1079 Hz and 756 Hz. The ¹H NMR spectrum shows a very broad peak, and a doublet of doublets with coupling constants 756 Hz and 60 Hz.

Suggest a structure for compound X that is consistent with these data, and predict the form of its 19 F NMR spectrum.

[Relative atomic masses: ³¹P 30.9938;¹⁹F 18.9984; ¹H 1.0078; ¹⁶O 15.9949. ³¹P, ¹⁹F and ¹H all have spin $I = \frac{1}{2}$]

16.13 The superoxides of Group 1 metals tend to decompose to the peroxide according to the following reaction

$$2MO_2(s) \longrightarrow M_2O_2(s) + O_2(g).$$

The energetics of this reaction can be analysed using the following Hess's Law cycle



 $\Delta_r H^\circ$ for step 1 is *minus twice* the lattice enthalpy of MO₂(s), $\Delta_r H^\circ$ for step 2 is twice the enthalpy of dissociation of the superoxide anion to the peroxide anion, and $\Delta_r H^\circ$ for step 3 is the lattice enthalpy of M₂O₂(s). Our aim is to use this cycle to work out the value of $\Delta_r H^\circ$ for step 4, the decomposition of the superoxide.

- (a) Use the Kapustinskii equation, Eq. 6.5 on page 197, to write down expressions the lattice enthalpies needed for steps 1 and 3. Write the radius of the cation as r_+ , and assume that of both of the anions O_2^- and O_2^{2-} have the same radius r_- (this is a fair assumption for this rather crude calculation).
- (b) $\Delta_r H^\circ$ for step 2 does not change with the metal, so we can simply assume a value, which we will call *C*. Use this value and your answer to (a) to obtain an expression for $\Delta_r H^\circ$ of step 4.
- (c) Carefully explain why your expression predicts that as r_+ increases, the value of $\Delta_r H^\circ$ for step 4 increases. Use this result to rationalize why LiO₂ is not known, but RbO₂ is easily formed.
- (d) (Requires calculus) Differentiate your expression for $\Delta_r H^\circ$ of step 4 with respect to r_+ , assuming that r_- is constant. Argue that the derivative is positive, and hence leads to the same prediction as in (c) as to the way $\Delta_r H^\circ$ changes with r_+ .
- (e) Rather than considering $\Delta_r H^\circ$ for step 4, we ought really to consider $\Delta_r G^\circ$ i.e. an entropy term should be included. Discuss whether or not the conclusions of this discussion are likely to be affected by the inclusion of such an entropy term.
- 16.14 The polyanion I_3^- forms ionic compounds with Group 1 metals, but these compounds tend to decompose to the iodide and iodine according to the following reaction

$$MI_3(s) \longrightarrow MI(s) + I_2(s).$$

Analyse this decomposition using a Hess's Law cycle similar to that in the previous question. Use estimates of the lattice energy to show that this reaction becomes less favoured as the radius of the cation increases. (You should assume that the radius of the I_3^- anion is significantly greater than that of the I^- anion).

16.15 No compounds in which a Group 2 metal is in the oxidation state +1 are known, and it is speculated that this is because such compounds would disproportionate according to

$$2MgCl(s) \longrightarrow Mg(s) + MgCl_2(s),$$

where we have taken MgCl as an example. It is possible to estimate a value for $\Delta_r H^\circ$ for this reaction using the following Hess's Law cycle



 $\Delta_r H^\circ$ for step 1 is *twice minus* the lattice enthalpy of MgCl, $\Delta_r H^\circ$ for step 2 is *minus* the enthalpy of ionization for Mg(g) \rightarrow Mg⁺(g), $\Delta_r H^\circ$ for step 3 is the enthalpy of ionization for Mg⁺(g) \rightarrow Mg²⁺(g), $\Delta_r H^\circ$ for step 4 is *minus* the enthalpy of atomization of Mg(s), and $\Delta_r H^\circ$ for step 5 is the lattice enthalpy of MgCl₂.

- (a) Use the Kapustinskii equation, Eq. 6.5 on page 197, to estimate the lattice enthalpies of MgCl and MgCl₂, taking the radius of Mg⁺ as 100 pm (a guess based on the radius of Na⁺), that of Mg²⁺ as 68 pm, and that of Cl⁻ as 182 pm.
- (b) Given that $\Delta_r H^{\circ}$ for atomization of Mg(s) is 148 kJ mol⁻¹, $\Delta_r H^{\circ}$ for Mg(g) \rightarrow Mg⁺(g) is 737 kJ mol⁻¹, and $\Delta_r H^{\circ}$ for Mg⁺(g) \rightarrow Mg²⁺(g) is 1447 kJ mol⁻¹, estimate $\Delta_r H^{\circ}$ for step 6, the disproportionation of MgCl.
- (c) Explain why $\Delta_r S^\circ$ for step 6 is expected to be small.
- (d) Do your calculations support the contention that MgCl is unstable with respect to disproportionation? Explain *in words* the origin of this instability.
- 16.16 High oxidation state metal halides are often unstable with respect to dissociation into a lower oxidation state halide plus the elemental halogen. For example, MX_4 may decompose to MX_2

$$MX_4(s) \longrightarrow MX_2(s) + X_2(g),$$

where M is a metal and X is one of the halogens. This reaction can be analysed using the following Hess's Law cycle



Given the following data, discuss why it is that the higher oxidation state (MX_4) tends to be more stable for the fluoride than the other halides. A quantitative answer is not expected.

	F	Cl	Br	Ι	
electron affinity / kJ mol ⁻¹	328	349	325	295	
$\Delta_{\rm r} H^{\circ}({\rm X}_2({\rm g}) \rightarrow 2{\rm X}({\rm g})) \ / \ {\rm kJ \ mol^{-1}}$	158	243	193	151	
$r(X^{-}) / pm$	133	182	198	220	

The definition of the electron affinity is given in section 8.4.2 on page 275. 16.17 The table below gives the values of $\Delta_r H^\circ$ (in kJ mol⁻¹) for the processes indicated for the cases where M is K or Ca

process	Κ	Ca
$M(s) \to M(g)$	90	193
$M(g) \to M^{2+}(g)$	3470	1735
$\mathrm{M}^{2+}(\mathrm{g}) + 2\mathrm{Cl}^{-}(\mathrm{g}) \to \mathrm{M}\mathrm{Cl}_2(\mathrm{s})$	-2210	-2226

 $\Delta_r H^\circ$ for $Cl_2(g) \rightarrow 2Cl(g)$ is 242 kJ mol⁻¹, and the electron affinity of Cl is 349 kJ mol⁻¹.

Use these data to calculate $\Delta_f H^\circ$ for KCl₂(s) and CaCl₂(s), and hence predict which of these compounds you would expect to form. What is the principle origin of the difference between the values for these two compounds?

17 Transition metals

17.1 (a) Using Slater's rules (page 262), determine the effective nuclear charge experienced by the 4s and 3d electrons in the metals of the first transition series (use the electronic configurations given in Fig. 17.1 on page 626). Compute the energies of the 4s and 3d orbitals using

$$E_n = -\frac{Z_{\rm eff}^2 R_{\rm H}}{n^2}$$

where $R_{\rm H} = 13.6$ eV and *n* is the principal quantum number. On the same graph, plot these energies against atomic number.

- (b) Comment on the trends that you see in your graph, and compare it with the data given in Fig. 17.2 on page 627.
- (c) Repeat the calculations for the ion M⁺, assuming that a 4s electron has been ionized. Comment on how the orbital energies for M⁺ compare with those for M. According to your calculations, which electron will be the easiest to ionize to give M²⁺?
- 17.2 Explain or rationalize the following.
 - (a) The ground-state electronic configuration of potassium is $[Ar] 4s^1$ and not $[Ar] 3d^1$.
 - (b) In titanium (Ti) the 3*d* AO is lower in energy than the 4*s*, yet the ground-state electronic configuration of Ti is $4s^2 3d^2$ and not $3d^4$.
 - (c) The ground-state configuration of copper (Cu) is $4s^1 3d^{10}$ rather than $4s^2 3d^9$.
 - (d) Across the first transition series, the energy of the 4s orbital falls more slowly than does the energy of the 3d.
- 17.3 Throughout this question assume that the exchange interaction contributes an energy of -K per pair of parallel spins (see section 2.7.3 on page 73).
 - (a) Show that the exchange contribution to the energy of the configuration $4s^2 3d^3$ is -6K, and that the contribution for the configuration $4s^1 3d^4$ is -10K.
 - (b) Work out the exchange contribution to the configurations $4s^2 3d^4$, $4s^1 3d^5$, $4s^2 3d^5$ and $4s^1 3d^6$
 - (c) By considering the *change* in the exchange contribution on going from $4s^2 3d^n$ to $4s^1 3d^{n+1}$, rationalize the ground-state configurations adopted by V, Cr and Mn.
- 17.4 (a) What do you understand by the *chelate effect*?
 - (b) For the following reaction

$$[\operatorname{Ni}(\operatorname{NH}_3)_6]^{2+} + 3 \operatorname{en} \longrightarrow [\operatorname{Ni}(\operatorname{en})_3]^{2+} + 6 \operatorname{NH}_3$$

it is found that $\Delta_r H^\circ = -12.1 \text{ kJ mol}^{-1}$ and $\Delta_r S^\circ = 185 \text{ J K}^{-1} \text{ mol}^{-1}$ in aqueous solution at 298 K. Compute the value of $\Delta_r G^\circ$ and hence the value of the equilibrium constant. Does the entropy term make a significant contribution to the value of $\Delta_r G^\circ$?

(c) Discuss the trend in the values of the equilibrium constant for the following reactions (all in aqueous solution)

$$[Co(H_2O)_6]^{2+} + 6 NH_3 \longrightarrow [Co(NH_3)_6]^{2+} + 6 H_2O \qquad lg K = 5.2$$

$$[Co(H_2O)_6]^{2+} + 3 en \longrightarrow [Co(en)_3]^{2+} + 6 H_2O \qquad lg K = 13.9$$

$$[Co(H_2O)_6]^{2+} + (6-en) \longrightarrow [Co(6-en)]^{2+} + 6 H_2O \qquad lg K = 15.8$$

(6-en) is a hexadentate ligand which coordinates through nitrogen.

- 17.5 (a) Draw two isomers of the octahedral complex $[Co(NH_3)_4Cl_2]^+$. Are either of these isomers optically active?
 - (b) Draw all the possible isomers of the octahedral complex $[Co(en)_2(NH_3)Cl]^{2+}$. Which of these are optically active?
 - (c) Draw all the possible isomers of the hypothetical octahedral complex MA₂B₂C₂, where A, B and C are three different monodentate ligands. Which, if any, of these isomers are optically active?
- 17.6 When carbon monoxide acts as a ligand to a transition metal it invariably bonds through the carbon and not through the oxygen. Discuss why this is so.
- 17.7 Using the same approach as in section 17.4 on page 639, show that for the d^6 configuration the high-spin arrangement is preferred when

$$2\Delta_{\rm o} - 10K < -6K.$$

Similarly, show that for the d^7 configuration the high-spin arrangement is preferred when $\Delta_0 < 2K$.

17.8 For paramagnetic first-row transition metal complexes the *magnetic moment* μ , in units of the *Bohr magneton* (B.M.), is reasonably well approximated by the spin-only formula

magnetic moment in B.M. = $\sqrt{n(n+2)}$

where n is the number of unpaired electrons. Use this expression to draw up a table of the expected magnetic moments for between one and five unpaired electrons. Then draw up a second table showing the expected magnetic moments for high-spin and for low-spin octahedral complexes with between one and nine d electrons.

Use the following experimentally measured magnetic moments to determine whether the given octahedral complex is high or low spin. [Be aware that the spin-only formula is not expected to give precise agreement with experimental data.]

complex	μ / B.M.	complex	μ / B.M.	In the complex
$[Co(NO_2)_6]^{4-}$	1.9	$[Cr(H_2O)_6]^{3+}$	3.8	$[Co(NO_2)_6]^{4-}$
$[Cr(H_2O)_6]^{2+}$	4.8	$[Mn(H_2O)_6]^{2+}$	5.9	the ligands are
$[Fe(CN)_{6}]^{3-}$	2.3	$[Fe(H_2O)_6]^{2+}$	5.3	[1002] .

17.9 Using the approach described in section 17.6.1 on page 644, compute the change in energy due to the occupation of the $1e_g$, $1t_{2g}$ and $2e_g$ MOs as a function of the number of *d* electrons assuming that a *low-spin* configuration is adopted.

Plot a graph of this energy in the same form as Fig. 17.22 on page 645, and use it to predict how you would expect the energy of a low-spin complex to vary with the number of d electrons.

17.10 This question is about how the energy difference between a square planar and tetrahedral ML_4 complex varies with the number of *d* electrons. Shown below are partial MO diagrams for the two geometries: *only* those MOs which have a contribution from the metal orbitals are shown. Note that MO3, MO6 and MO8 are triply degenerate; MO7 is doubly degenerate.



A simplified MO treatment shows that the amount by which each MO is shifted in energy on forming the complex can be expressed in terms of a single energy parameter e_{σ} . For example, MO1 is shifted down in energy by $3e_{\sigma}$, whereas MO8 is shifted up in energy by $\frac{4}{3}e_{\sigma}$. MO3 and MO7 are nonbonding and so do not change energy.

In the square-planar geometry MO1 and MO2 are occupied by two electrons each, contributing an total energy change of $2 \times (-3e_{\sigma}) + 2 \times (-e_{\sigma}) = -8e_{\sigma}$. Similarly in the tetrahedral geometry the triply degenerate MO6 is occupied by six electrons, contributing an total energy change of $6 \times (-\frac{4}{3}e_{\sigma}) = -8e_{\sigma}$ i.e. exactly the same amount. In comparing the two geometries, we can therefore ignore these filled orbitals.

The electrons originating from the metal 3d AOs can fill MO3, MO4 and MO5 in the square-planar case, and MO7 and MO8 in the tetrahedral case. The precise details of which orbitals are occupied will determine the relative energy of the two possible geometries for ML₄.

Consider the case of four *d* electrons. Assuming a high-spin configuration, in the squareplanar complex three electrons will occupy the three degenerate orbitals MO3, which contribute nothing to the energy change, and one will occupy MO4, which contributes $+e_{\sigma}$. The energy change is thus $+e_{\sigma}$. In the tetrahedral case, two electrons occupy MO7 and two occupy MO8, so the energy change is $2 \times 0 + 2 \times (+\frac{4}{3}e_{\sigma}) = 2.67 e_{\sigma}$. It is clear that the square-planar geometry is preferred since the energy increase due to the *d* electrons is smaller than that for the tetrahedral case.

- (a) Repeat this calculation for between one and ten d electrons (assuming a high-spin configuration), and hence identify those configurations for which the square-planar geometry is preferred.
- (b) Now consider the case where the square-planar complex is low spin (meaning that MO5 is not occupied until *both* MO3 *and* MO4 are full) but the tetrahedral complex is still high spin. Again identify those configurations for which the square-planar geometry is preferred.
- (c) In the light of your calculations, comment on the fact that square-planar complexes are most commonly found for metals with d^8 configurations in conjunction with ligands which give rise to large splitting of the *d* orbitals.

17.11 Count the number of valence electrons associated with each metal atom in the following complexes (perform the count using the scheme in Box 17.1 on page 651 and then using the scheme in Box 17.2 on page 652).



- 17.12 Determine the number of carbon monoxide ligands which need to be attached to each transition metal atom from the first row in order that the eighteen-electron rule is obeyed by a complex $M(CO)_n$ or $[M(CO)_n]^+$.
- 17.13 (a) Comment on the fact that no mono-nuclear neutral cobalt carbonyl $Co(CO)_n$ has been detected, but the anion $[Co(CO)_4]^-$ is known.
 - (b) Reaction of cobalt with carbon monoxide gives the species $Co_2(CO)_8$ which is thought to exist in two structural isomers. The IR spectrum of isomer A shows a number of bands between 2000 cm⁻¹ and 2100 cm⁻¹; the spectrum of isomer B shows bands in this same region as well as bands at around 1850 cm⁻¹.

Explain what you can deduce from the IR spectrum about the bonding of the CO groups in these two carbonyl complexes, and hence suggest possible structures for A and B. You should ensure that your structures are consistent with the eighteen-electron rule.

- (c) The carbonyl complex $Co_4(CO)_{12}$ is also formed quite readily. Suggest a structure for this in which the eighteen-electron rule is obeyed [hint: start with a tetrahedron of cobalt atoms].
- 17.14 Discuss the following observations. MnO is a basic oxide, dissolving in aqueous acid to give the species $[Mn(H_2O)_6]^{2+}$. Similarly, Mn_2O_3 is also basic, dissolving in acid to give the aquated ion $[Mn(H_2O)_6]^{3+}$ which tends to be unstable with respect to disproportionation. MnO_2 is an amphoteric oxide; it dissolves in alkali to give the anion $[MnO_3]^{2-}$, but even in strongly acidic solutions there is no evidence for a simple aquo ion ' $[Mn(H_2O)_6]^{4+}$ '. Mn_2O_7 readily dissolves in and reacts with water to give strongly acidic solutions containing $[MnO_4]^{-}$.
- 17.15 Discuss the following observations. Even in the most acidic solutions there is no evidence for the Ti(IV) species $[Ti(H_2O)_6]^{4+1}$. However, the species $[Ti(H_2O)_5(OH)]^{3+}$, $[Ti(H_2O)_4(OH)_2]^{2+}$ and $[Ti(H_2O)_3(OH)_3]^+$ have all been characterized. Some workers have also suggested the existence of the species $[TiO]^{2+}$ (with associated waters of solvation), but the evidence is not compelling (discuss how this species might be formed). In contrast, there is ample evidence for the existence of the vanadium(IV) species $[VO]^{2+}$. In this ion, the V–O bond length is around 160 pm, indicative of multiple bonding between these atoms.

18 Quantum mechanics and spectroscopy

Physical constants: $h = 6.626 \times 10^{-34}$ J s, $k_{\rm B} = 1.381 \times 10^{-23}$ J K⁻¹, $N_{\rm A} = 6.022 \times 10^{23}$ mol⁻¹, $c = 2.998 \times 10^8$ m s⁻¹, mass unit (u) = 1.6605 × 10⁻²⁷ kg.

- 18.1 Show that $\phi_1(x) = A \sin(Bx)$ and $\phi_2(x) = C \cos(Bx)$ are both eigenfunctions of the operator d^2/dx^2 , and find the corresponding eigenvalue in each case. Do different values of A and C give different eigenfunctions? Are these two eigenfunctions degenerate?
- 18.2 State the *Born interpretation* of the wavefunction and use is to explain whether or not the following (one-dimensional) functions are likely to be acceptable wavefunctions. (The dashed lines in (c) imply that the sine function continues indefinitely to positive and negative x.)



18.3 Imagine a free particle, moving in one dimension, which has total energy E and experiences a fixed potential energy V_0 . Explain why it is that in classical mechanics the potential energy cannot exceed the total energy.

Without going into mathematical details, describe the behaviour of a typical eigenfunction of the hamiltonian (the operator for energy) for the classical case where $E > V_0$, and for the non-classical case where $E < V_0$. What happens to the eigenfunction when the potential V_0 becomes very large?

18.4 Consider a particle which experiences the potential shown below in red. The potential is zero in the region (a), equal to V_0 in the region (b), and zero again in the region (c). Also shown in blue is a typical eigenfunction ψ of the hamiltonian; rationalize the behaviour of this eigenfunction. What will happen to ψ as V_0 is increased, and as V_0 is decreased?



- 18.5 (a) Write down the hamiltonian for a particle of mass *m* experiencing a potential $V_0 = 0$ and moving in one dimension. Show that $\psi(x) = A \cos(kx)$ is an eigenfunction of this hamiltonian, and give an expression for the energy (the eigenvalue) in terms of *k*.
 - (b) Explain the boundary conditions which are imposed on the wavefunction by a potential which is zero between x = 0 and x = L, and infinite elsewhere.
 - (c) Discuss whether or not $\psi(x) = A \cos(kx)$ satisfies these boundary conditions.

- 18.6 With reference to the wavefunctions and energy levels for the particle in a (one-dimensional) box, explain what you understand by the terms (a) quantum number, (b) normalized, (c) orthogonal, and (d) zero-point energy.
- 18.7 Why do the number of nodes in a wavefunction increase as its energy increases?
- 18.8 (a) With reference to the case of a particle in a two-dimensional square well (described in section 18.4 on page 681), explain what you understand by a *degenerate* energy level.
 - (b) Calculate the energies (expressed as multiples of $(\hbar^2 \pi^2)/(2mL^2)$), for all of the levels with n_x in the range 1 to 4, and for n_y in the range 1 to 4. Arrange these in order of increasing total energy. Why are some of the levels degenerate, while others are not?
- 18.9 In the case of an harmonic oscillator with potential $V(x) = \frac{1}{2}k_f x^2$, what do you understand by the 'classical' and 'non-classical' regions of the oscillation? How does the behaviour of the wavefunction differ between the two regions?
- 18.10 In the IR spectrum of ¹H³⁵Cl there is a strong absorption centred at 2885 cm⁻¹. Assuming that the vibrational energy levels can be approximated by those of the harmonic oscillator, use this observation to (a) determine the frequency of the oscillation (in Hz and in rad s⁻¹), (b) determine the force constant of the bond. (¹H = 1.0078 mass units and ³⁵Cl = 34.9689 mass units).
- 18.11 The 'energy in wavenumbers' of the energy levels of a Morse oscillator are given by Eq. 18.29 on page 699

$$\tilde{E}_{\upsilon} = \left(\upsilon + \frac{1}{2}\right)\tilde{\omega}_{\rm e} - \left(\upsilon + \frac{1}{2}\right)^2\tilde{\omega}_{\rm e}x_{\rm e},$$

- (a) Using these energies, show that the wavenumber of the $0 \rightarrow 1$ and $0 \rightarrow 2$ transitions are given by $\tilde{\omega}_e 2\tilde{\omega}_e x_e$ and $2\tilde{\omega}_e 6\tilde{\omega}_e x_e$, respectively.
- (b) In the spectrum of ${}^{1}\text{H}{}^{35}\text{Cl}$ there is a strong absorption centred at 2885 cm⁻¹, and a weaker absorption centred at 5665 cm⁻¹. Use these data to find values for $\tilde{\omega}_{e}$ and $\tilde{\omega}_{e}x_{e}$ (in cm⁻¹), explaining your method.
- (c) Convert the values of $\tilde{\omega}_e$ and $\tilde{\omega}_e x_e$ from cm⁻¹ to rad s⁻¹. Hence determine the values of the Morse parameters *a* and *D*_e.
- 18.12 Using the expression for the energy levels of the Morse oscillator (in cm⁻¹) given in the previous question, show that the value of the vibrational quantum number at which dissociation occurs, v_{max} , is given by

$$\upsilon_{\max} = \frac{1}{2x_{\rm e}} - \frac{1}{2}.$$

Hence show that the dissociation energy, expressed in wavenumbers, is

$$\tilde{D}_{\rm e} = \frac{(\tilde{\omega}_{\rm e})^2}{4\tilde{\omega}_{\rm e} x_{\rm e}}.$$

Using the values of $\tilde{\omega}_e$ and $\tilde{\omega}_e x_e$ from the previous question, determine \tilde{D}_e (in wavenumbers). Convert your answer to joules and confirm that it is the same as you obtained in the previous question.

18.13 Illustrated below are five of the normal modes of ethyne (acetylene, HCCH). At its equilibrium geometry this molecule has no dipole moment, but for some of the normal modes the distortion during the vibration induces a dipole. Determine which of the normal modes are IR active and explain why modes 4 and 5 are each doubly degenerate.



- 18.14 In a Raman scattering experiment on ${}^{1}\text{H}_{2}$ using a green argon ion laser (which emits at a frequency of 20492 cm⁻¹) very strong scattering of light at 20492 cm⁻¹ was seen, along with much weaker scattering at 16333 cm⁻¹. Explain the origin of the scattered light at these two different frequencies. Hence determine the vibrational frequency of ${}^{1}\text{H}_{2}$ and the corresponding force constant (use the harmonic oscillator energy levels; ${}^{1}\text{H} = 1.0078$ mass units).
- 18.15 The microwave (rotational) spectrum of ${}^{12}C{}^{16}O$ consists of a series of lines spaced by 115.3 GHz (1 GHz = 10⁹ Hz). Assuming that the rotational energy levels of this molecule can be approximated by those of the rigid rotor, use these data to determine a value for the rotational constant *B*, the moment of inertia *I*, and hence the bond length *R*. Be careful to work in SI units throughout. (${}^{12}C = 12.000$ mass units and ${}^{16}O = 15.995$ mass units.)
- 18.16 Using the same approach as is described in section 18.13 on page 713, show that the frequencies of the lines in the P branch of the vibration-rotation spectrum of a diatomic are given by

$$\tilde{\nu}_{\rm P}(J^{\prime\prime}) = \tilde{\omega} - 2\tilde{B}J^{\prime\prime}.$$

What range of values can the quantum number J'' take in this expression?

- 18.17 In the IR spectrum of ${}^{12}C^{16}O$ there is a strong band at around 2157 cm⁻¹ which, on closer inspection, shows P/R branch structure. The spacing between successive lines in the two branches is roughly constant at 3.85 cm⁻¹. Use these data to estimate the bond length in ${}^{12}C^{16}O$, explaining any approximations you find it necessary to make. (${}^{12}C = 12.000$ mass units and ${}^{16}O = 15.995$ mass units.)
- 18.18 Why is it that although the rotational level with J = 0 has the lowest energy, the first line in the R branch (R_0) is not the most intense?
- 18.19 Verify that the wavelengths quoted in Table 18.2 on page 718 are correct.

18.20 A very simple model for the electronic structure of a conjugated polyene

is to assume that the π electrons move in a one-dimensional box of length Na, where N is the number of conjugated double bonds and a is the typical length of such a bond. Given that the energy levels of a particle in a box are

$$E_n = \frac{n^2 h^2}{8mL^2}$$
 $n = 1, 2, ...,$

the energy levels available to the π electrons are therefore

$$E_n = \frac{n^2 h^2}{8m_e N^2 a^2}$$
 $n = 1, 2, ...,$

where $m_{\rm e}$ is the mass of the electron (9.11 × 10⁻³¹ kg).

- (a) Given that N conjugated π bonds contribute 2N π electrons, and that two electrons occupy each energy level, explain why the highest occupied level has n = N, and the lowest unoccupied level has n = N + 1.
- (b) Show that the energy of the photon needed to cause a transition between the highest occupied and lowest unoccupied levels is given by

$$E_{\rm photon} = \frac{(2N+1)h^2}{8m_{\rm e}N^2a^2},$$

and hence that the corresponding wavelength of the light that will cause this transition is $2 - \frac{1}{2}$

$$\lambda = \frac{8m_{\rm e}cN^2a^2}{(2N+1)h}.$$

(c) Explain why this expression for λ predicts that as the number of conjugated double bonds increases the wavelength of the absorption also increases. Taking the value of the length *a* to be 220 pm, find the value of λ for N = 6. What region of the spectrum does this correspond to?
19 Chemical thermodynamics

The gas constant, *R*, has the value 8.3145 J K⁻¹ mol⁻¹; 1 bar is 10^5 N m⁻²; 1 atmosphere is 1.01325×10^5 N m⁻²; 1 Torr is 133.3 N m⁻².

- 19.1 4×10^{-3} moles of an ideal gas are held inside a cylinder by a piston such that the volume of the gas is 10 cm³; the whole assembly is held in a thermostat at 298 K. Calculate the pressure of the gas in N m⁻². [Note that the SI unit of volume is m³.]
 - (a) Assume that the external pressure is fixed at 1 bar. Explain why the piston moves out when it is released, and why it eventually comes to a stop. What will the pressure of the gas inside the cylinder be when the piston finally stops?
 - (b) Calculate the volume of the gas inside the cylinder when the piston has come to rest, and hence the work for this irreversible expansion.
 - (c) State the change in the internal energy, ΔU , of the gas when it undergoes this isothermal expansion. Hence, using the First Law, calculate the heat associated with the expansion, explaining its sign.
 - (d) Calculate the work associated with reversible isothermal expansion between the same initial and final states as the irreversible expansion described above; hence find the heat. Comment on these values in relation to those for the irreversible expansion.
 - (e) Determine the enthalpy change of the gas in (i) the reversible and (ii) the irreversible expansion.
- 19.2 A sample of methane gas of mass 4.50 g has volume 12.7 dm³ at 310 K. It expands isothermally against a constant external pressure of 200 Torr until its volume has increased by 3.3 dm³. Assuming methane to be a perfect gas, calculate the work and heat associated with the process, along with the change in the internal energy and enthalpy of the gas. [1 Torr = 133.3 N m⁻².]

Calculate these same quantities if the expansion is carried out reversibly.

19.3 For the A \rightleftharpoons B equilibrium, sketch a graph showing how the molar Gibbs energy of a mixture of A and B varies as the composition varies from pure reactant A to pure product B for the following cases: (a) $G_{m,A}^{\circ} = G_{m,B}^{\circ}$, (b) $G_{m,A}^{\circ} < G_{m,B}^{\circ}$. On your graph indicate the equilibrium composition.

Explain why it is that if the proportions of A and B are not at their equilibrium values, there is always a spontaneous process which will result in the composition moving to its equilibrium value, but that once this point is reached, no further change is possible.

19.4 Consider the equilibrium

$$2A(g) \rightleftharpoons B(g)$$
.

Using the approach illustrated in section 19.6.3 on page 748, show that for this reaction at equilibrium we have

$$\Delta_{\rm r}G^\circ = -RT \ln K$$
 where $K = \frac{p_{\rm B,eq}/p^\circ}{(p_{\rm A,eq}/p^\circ)^2}$,

and

$$\Delta_{\rm r}G^\circ = G^\circ_{\rm m,B} - 2G^\circ_{\rm m,A}.$$

19.5 This question and the two which follow concern the equilibrium

$$CO(g) + 2 H_2(g) \rightleftharpoons CH_3OH(g)$$

which we are going to investigate as a viable commercial method for the production of methanol. The following data are provided (all at 298 K)

	CO(g)	$H_2(g)$	$CH_3OH(g)$
$\Delta_{\rm f} H^\circ$ / kJ mol ⁻¹	-110.53		-200.66
$S_{\rm m}^{\circ}$ / J ${\rm K}^{-1}$ mol $^{-1}$	197.67	130.68	239.81
$C_{p,\mathrm{m}}^{\circ}$ / J K ⁻¹ mol ⁻¹	29.14	28.82	43.89

Using these data, determine $\Delta_r H^\circ$, $\Delta_r S^\circ$, $\Delta_r G^\circ$ and hence *K*, all at 298 K. On the basis of your answer, comment on the viability of the reaction as a method for the production of methanol.

- 19.6 In practice, it is found that the reaction in the previous question only proceeds at a viable rate at 600 K. Assuming that the values of $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are the same at 600 K as they are at 298 K, find the value of the equilibrium constant at 600 K. Qualitatively, is your answer in accord with Le Chatelier's principle?
- 19.7 Using the approach described in section 19.8.1 on page 752 and section 19.8.2 on page 753, together with the data given in question 19.5, find the value of $\Delta_r C_p^{\circ}$ and hence the values of $\Delta_r H^{\circ}$ and $\Delta_r S^{\circ}$ at 600 K for the equilibrium

$$CO(g) + 2 H_2(g) \rightleftharpoons CH_3OH(g).$$

Hence compute $\Delta_r G^\circ$ and *K* at 600 K. How do your values compare with those found in exercise 17.5?

19.8 Consider the equilibrium in which solid calcium carbonate decomposes to the oxide plus carbon dioxide

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g).$$

Using the approach illustrated in section 19.7.1 on page 750, show that

$$\Delta_{\rm r}G^\circ = -RT\ln K$$

where p_{CO_2} is the equilibrium pressure of CO₂ and

$$\Delta_{\mathrm{r}}G^{\circ} = G^{\circ}_{\mathrm{m}}(\mathrm{CaO}) + G^{\circ}_{\mathrm{m}}(\mathrm{CO}_2) - G^{\circ}_{\mathrm{m}}(\mathrm{CaCO}_3) \quad \mathrm{and} \quad K = \frac{p_{\mathrm{CO}_2}}{p^{\circ}}.$$

The standard enthalpies of formation of CaCO₃(s), CO₂(g) and CaO(s) are -1207.6 kJ mol⁻¹, -393.5 kJ mol⁻¹ and -634.9 kJ mol⁻¹ respectively, and the standard entropies are 91.7 J K⁻¹ mol⁻¹, 213.8 J K⁻¹ mol⁻¹ and 38.1 J K⁻¹ mol⁻¹ (all at 298 K). Assuming that these values are independent of temperature, compute $\Delta_r H^\circ$, $\Delta_r S^\circ$ and $\Delta_r G^\circ$ at 800 K; hence find the equilibrium pressure of carbon dioxide at this temperature.

19.9 Thermodynamic data, at 298 K, for the reagents and products of the gas phase reaction

$$2HNO_2(g) \rightleftharpoons H_2O(g) + NO(g) + NO_2(g)$$

are given below.

	$\Delta_{\rm f} H^\circ$ / kJ mol ⁻¹	$S_{\rm m}^{\circ}$ / J K ⁻¹ mol ⁻¹	$C_{p,\mathrm{m}}^{\circ}$ / J K ⁻¹ mol ⁻¹
$HNO_2(g)$	-79.5	254.0	45.6
$H_2O(g)$	-241.8	188.7	33.6
NO(g)	90.2	210.7	29.8
$NO_2(g)$	33.2	240.0	37.2

Calculate $\Delta_r H^\circ$, $\Delta_r S^\circ$ and $\Delta_r G^\circ$ at 298 K. Assuming that the values of $\Delta_r H^\circ$ and $\Delta_r S^\circ$ at 548 K are the same as those at 298 K, calculate $\Delta_r G^\circ$ at 548 K.

Calculate $\Delta_r C_p^{\circ}$ and, using this value, compute $\Delta_r H^{\circ}$, $\Delta_r S^{\circ}$ and $\Delta_r G^{\circ}$ at 548 K. Compare the two values of $\Delta_r G^{\circ}$ you have obtained, and comment on what is the major source of the temperature variation of $\Delta_r G^{\circ}$ for this reaction. Calculate *K* for the reaction at 298 K and at 548 K.

- 19.10 The standard molar entropy of N₂ gas at 298 K is 191.6 J K⁻¹ mol⁻¹, and its standard molar constant pressure heat capacity, $C_{p,m}^{\circ}$, at the same temperature is 29.70 J K⁻¹ mol⁻¹.
 - (a) Using Eq. 19.46 on page 754, find the standard molar entropy of N_2 at 398 K.
 - (b) A better approximation than assuming that $C_{p,m}^{\circ}$ is constant is to use a parametrized form which includes a temperature dependence. For example

$$C_{p,\mathrm{m}}^{\circ}(T) = A + BT.$$

Using this expression for $C_{p,m}^{\circ}$, show that integrating Eq. 19.45 on page 754 between T_1 and T_2 gives the following

$$S_{\rm m}^{\circ}(T_2) = S_{\rm m}^{\circ}(T_1) + A \ln\left(\frac{T_2}{T_1}\right) + B[T_2 - T_1]$$

- (c) For N₂ $A = 28.58 \text{ J K}^{-1} \text{ mol}^{-1}$ and $B = 3.77 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}$. Using these values in the expression above, calculate the entropy at 398 K. Comment on the difference between your answer and that obtained in (a).
- 19.11 The equilibrium constant, *K*, for the reaction

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

has been measured at a series of temperatures around 700 K as follows

By plotting a graph of $\ln K$ against 1/T, obtain a value for $\Delta_r H^\circ$ for the above reaction; explain any approximations you have to make. Use your graph to find a value of $\Delta_r G^\circ$ at 700 K, and hence find a value for $\Delta_r S^\circ$ at the same temperature.

19.12 Using the approach illustrated in section 19.9 on page 755 show that the equilibrium constants at T_1 and T_2 are related according to

$$\ln (K(T_2)) - \ln (K(T_1)) = -\frac{\Delta_r H^{\circ}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right].$$

What assumptions are made in deriving this equation?

For the reaction

 $CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$

K is 1.038×10^5 at 298 K and 1.094×10^4 at 350 K. Use the expression above to calculate a value for $\Delta_r H^\circ$. Determine $\Delta_r G^\circ$ at 298 K, and use this value to find $\Delta_r S^\circ$ at this temperature.

19.13 Ketene O=C=CH₂ is a reactive gas which can be prepared by the thermal decomposition of propanone (acetone) vapour

$$CH_3COCH_3(g) \rightleftharpoons O=C=CH_2(g) + CH_4(g)$$

Using the approach described in section 7.15 on page 250, complete the following table:

line	propanone	\rightleftharpoons	ketene	CH ₄
1	n_0		0	0
2	$n_0(1-\alpha)$			
3				

Line 1 gives the initial amount in moles, line 2 gives the amounts in moles at equilibrium, and line 3 gives the mole fractions; α is the fraction of propanone which has decomposed. Show that the equilibrium constant can be written

$$K = \frac{\alpha^2}{(1-\alpha)(1+\alpha)} \frac{p_{\rm eq}}{p^\circ},$$

where p_{eq} is the pressure of the equilibrium mixture. Using this expression, find the value of *K* which corresponds to 90% decomposition of propanone at a total pressure of 1.2 bar.

At 298 K, $\Delta_r G^\circ$ for this reaction is 42 kJ mol⁻¹, and $\Delta_r H^\circ$ is 81 kJ mol⁻¹. Find the value of the equilibrium constant at 298 K and then, using the relationship below, find the temperature at which there is 90% decomposition of propanone at a total pressure of 1.2 bar.

$$\ln(K(T_2)) - \ln(K(T_1)) = -\frac{\Delta_{\rm r} H^{\circ}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

20 Chemical kinetics

Physical constants: $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$, $k_{\text{B}} = 1.381 \times 10^{-23} \text{ J K}^{-1}$, $h = 6.626 \times 10^{-34} \text{ J s}$, $N_{\text{A}} = 6.022 \times 10^{23} \text{ mol}^{-1}$, $F = 96,485 \text{ C mol}^{-1}$, mass unit (*u*) = 1.6605 × 10^{-27} kg, 1 $\tau = 133.3 \text{ N m}^{-2}$, 0 °C = 273.15 K.

Many of these questions involve manipulating tables of data and plotting graphs; you will find it convenient to do this using a spreadsheet package, such as EXCEL.

20.1 The alkaline hydrolysis of ethyl ethanoate in aqueous solution is first order in ester and OH⁻, and so second order overall

$$\frac{\mathrm{d[OH^{-}]}}{\mathrm{d}t} = -k_{2\mathrm{nd}}[\mathrm{ester}][\mathrm{OH^{-}}].$$

In an experiment to verify this rate law, a reaction mixture was prepared in which the initial concentration of ester and OH^- were both 0.025 mol dm⁻³. At intervals after the reaction was initiated, a 10 cm³ aliquot of the reaction mixture was withdrawn and mixed with 10 cm³ of 0.05 mol dm⁻³ HCl(aq). This amount of acid is sufficient to neutralize any unreacted OH^- , thus quenching the reaction. The remaining acid was then titrated with 0.02 mol dm⁻³ NaOH(aq) to the end point in the usual way. This method gave the following data at 0 °C

<i>t</i> / s	vol. of titre / cm ³	n _{titre} / mol	n _{aliquot} / mol	[OH ⁻] / mol dm ⁻³
120	13.4	2.68×10^{-4}	2.32×10^{-4}	0.0232
300	14.3			
600	15.6			
900	16.4			
1200	17.4			
1500	18.1			
1800	18.5			

Complete the table in the following way (to help you, the first line has been completed).

- (a) Work out the amount in moles of OH^- in the volume of NaOH solution added in the titration. Enter this in the column headed n_{titre} .
- (b) Work out the amount in moles of H^+ in the acid used to quench the reaction mixture, and hence the amount in moles of *unreacted* OH⁻ in the aliquot: this is n_{aliquot} .
- (c) Finally, work out the concentration of OH⁻ in the aliquot, and enter this into the final column.

Since the initial concentrations of OH⁻ and ester are equal, the rate law can be simplified to $d[OH^-]/dt = -k_{2nd}[OH^-]^2$. It therefore follows that a plot of $1/[OH^-]$ against *t* should be a straight line.

Make such a plot and use it to estimate a value for the second-order rate constant, stating the units of your result. (These are real data, and so some scatter is to be expected).

Test the data to see if they fit a first-order rate law (i.e. plot $\ln [OH^-]$ against *t*).

20.2 The same reaction as in 20.1 can be studied by measuring the conductance as a function of time. Although the number of ions do not change in the course of the reaction, the identity of the ions does, with OH^- ions being gradually replaced by ethanoate ions. The latter are less effective at passing a current, so the conductance *decreases* as the reaction proceeds. If the conductance at time t is G(t), and at long times (when the reaction has gone to completion) the conductance is G(t).

completion) the conductance is G_{∞} , then it can be shown that the concentration of OH⁻ is proportional to the difference ($G(t) - G_{\infty}$).

A reaction mixture was prepared in which the initial concentration of ethyl ethanoate was 0.25 mol dm^{-3} , and that of NaOH was $0.0025 \text{ mol dm}^{-3}$. The ester is thus in excess so the rate law becomes

$$\frac{\mathrm{d}[\mathrm{OH}^-]}{\mathrm{d}t} = -k_{1\mathrm{st}}[\mathrm{OH}^-],$$

where the pseudo first-order rate constant k_{1st} is given by k_{2nd} [ester]. For a first-order process we expect a plot of $\ln [OH^-]$ against *t* to be a straight line with slope $-k_{1st}$. As was explained in section 20.2.1 on page 770, for such a first-order process we can also plot the log of any quantity which is *proportional* to concentration. In this case we can therefore plot $\ln (G(t) - G_{\infty})$ against time.

The following data were obtained at 0 °C

t / s	60	120	180	240	300	360	420	480
G / arb. units	85.5	75.0	65.9	60.3	56.6	52.7	51.0	48.9

At long times the conductance was measured as 45.0. Use these data to plot a suitable graph from which you can determine the pseudo first-order rate constant, and hence determine the second-order rate constant.

20.3 The reaction between propanone and bromine in aqueous acid conditions was studied by measuring the absorbance at 400 nm due to Br_2 . The initial concentrations of propanone and acid were both 0.50 mol dm⁻³, with both reagents being in excess compared to the bromine.

The following data of absorbance at 400 nm as a function of time were obtained at 298 K

<i>t</i> / s	0	60	120	180	240	300	360	420
abs.	0.995	0.964	0.903	0.830	0.772	0.739	0.679	0.605

The path length provided by the cuvette was 1 cm, and the extinction coefficient of Br_2 at 400 nm is 168 mol⁻¹ dm³ cm⁻¹.

- (a) Convert the absorbance data to concentrations, and then plot concentration as a function of time. You should find that the graph is a straight line, implying that the reaction is zero-order in bromine.
- (b) Determine a value for the (pseudo) zero-order rate constant, stating its units.
- (c) Assuming that the reaction is first order in both propanone and acid, determine the second-order rate constant for the overall reaction, stating its units.
- **20.4** The gas-phase reaction between NO and O_2

$$2NO + O_2 \longrightarrow 2NO_2$$

is thought to have the following rate law, which is overall third order

$$\frac{\mathrm{d}[\mathrm{O}_2]}{\mathrm{d}t} = -k_{\mathrm{3rd}}[\mathrm{O}_2][\mathrm{NO}]^2.$$

If the initial concentration of NO is twice the initial concentration of O_2 , then this ratio will persist as the reaction proceeds, in which case the rate law simplifies to

$$\frac{d[O_2]}{dt} = -k'_{3rd}[O_2]^3,$$

where $k'_{3rd} = 4k_{3rd}$.

(a) Integrate this rate law to show that the concentration of O_2 varies with time in the following way

$$\frac{1}{[O_2]^2} = \frac{1}{[O_2]_0^2} + 2k'_{3\mathrm{rd}}t,$$

where $[O_2]_0$ is the concentration of O_2 at time zero.

For a gas phase reaction, the partial pressure can be used as a measure of the concentration. As was shown in section 20.1.4 on page 765, for this reaction under the initial conditions described above, the partial pressure of O₂ is given by $p_{\text{tot}} - \frac{2}{3}p_{\text{tot,init}}$, where p_{tot} is the total pressure, and $p_{\text{tot,init}}$ is its initial value.

The following data were obtained at 298 K for a mixture of NO and O₂ in the ratio 2:1

<i>t</i> / s	60	120	180	240	300	360	420	480	
$p_{ m tot}$ / $ au$	84.0	79.6	77.5	76.2	75.3	74.6	74.0	73.7	

The pressure is given in units of Torr (τ), where 1 τ = 133.3 N m⁻². The initial pressure was 100.1 τ.

- (b) By plotting a suitable graph, show that these data are consistent with the overall third-order rate law given above, and obtain a value of the rate constant, stating its units. [You can either use the pressure directly as a unit of concentration or convert the pressures to concentrations in mol dm⁻³ using the ideal gas law.]
- 20.5 The oxidation of methanoic acid by bromine

$$HCOOH + Br_2 + 2H_2O \longrightarrow CO_2 + 2Br^- + 2H_3O^+,$$

can be studied by setting up the reaction in an electrochemical cell, as illustrated in Fig. 20.3 on page 767. If it is arranged that in the reaction mixture the bromide ion is in excess, the potential (voltage) E generated by the cell is given by

$$E = C - \frac{RT}{2F} \ln [\mathrm{Br}_2],$$

where F is the Faraday constant (96,485 C mol⁻¹) and C is a constant. The consumption of bromine can therefore be followed by measuring the potential as a function of time. The rate law of this reaction is thought to be first order in bromine. An experiment was

designed to investigate the order with respect to methanoic acid (a) and acid (b)

rate =
$$k[Br_2][HCOOH]^a[H_3O^+]^b$$
.

The reaction mixture is set up so that HCOOH and H_3O^+ are in excess, making the rate law pseudo first order

rate =
$$k_{1st}[Br_2]$$
 $k_{1st} = k[HCOOH]^a[H_3O^+]^b$.

The above expression for the cell potential can be rearranged to

$$\ln\left[\mathrm{Br}_{2}\right] = \frac{2FC}{RT} - \frac{2FE}{RT}$$

(a) For a first-order process a plot of $\ln [Br_2]$ against time will have slope $-k_{1st}$. Show that it therefore follows that a plot of E against time will have slope $(k_{1st}RT)/(2F)$.

The following data were obtained at 25 °C for a reaction mixture with the following initial concentrations: $[Br_2] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[HCOOH] = 0.10 \text{ mol dm}^{-3}$, $[H_3O^+]$ $= 0.05 \text{ mol } dm^{-3}$

time / s	0	60	120	180	240	300	360
<i>E /</i> V	-0.772	-0.766	-0.761	-0.757	-0.752	-0.745	-0.741

(b) Plot these data as described above, and hence obtain a value of the first-order rate constant.

Similar experiments, with different initial (excess) concentrations of methanoic acid and acid gave the following data (the value indicated by the * is obtained from the graph above)

run	1	2	3	4	5	6
$[HCOOH] / mol dm^{-3}$	0.10	0.10	0.10	0.12	0.16	0.22
$[H_3O^+]$ / mol dm ⁻³	0.05	0.12	0.25	0.15	0.15	0.15
$10^3 \times k_{1st} / s^{-1}$	*	2.77	1.33	2.66	3.55	4.88

Runs 1, 2 and 3 have the same (excess) concentration of methanoic acid, but different Note that (excess) concentrations of acid. Runs 4, 5 and 6 have the same (excess) concentration of $10^3 \times k_{1st} = 2.77$ acid, but different (excess) concentrations of methanoic acid.

Taking logarithms of the expression for k_{1st} gives

$$\ln k_{1st} = \ln k + a \ln [\text{HCOOH}] + b \ln [\text{H}_3\text{O}^+].$$

- (c) For runs 1, 2 and 3 plot $\ln k_{1st}$ against $\ln [H_3O^+]$ and hence obtain a value for the order *b* from the slope of the graph.
- (d) Similarly, use the data from runs 4, 5 and 6 to obtain a value for the order *a*. Comment on what your values for these orders imply about the mechanism for this reaction.
- **20.6** Aqueous Fe³⁺ reacts with thiocyanate (SCN⁻) to give a complex which absorbs strongly at 460 nm

$$\operatorname{Fe}(\operatorname{H}_2\operatorname{O})_6^{3+} + \operatorname{SCN}^- \longrightarrow \operatorname{Fe}(\operatorname{H}_2\operatorname{O})_5(\operatorname{SCN})^{2+} + \operatorname{H}_2\operatorname{O}.$$

The reaction is thought to be first order in each reactant

rate =
$$k_{2nd}$$
[Fe(H₂O)₆³⁺][SCN⁻].

The reaction was followed using a flow system in which a solution containing Fe³⁺ (concentration 2.0×10^{-4} mol dm⁻³) was flowed together with a solution of SCN⁻ (concentration 0.2 or 0.3 mol dm⁻³, in excess over the Fe³⁺). The concentration of the complex was monitored at various distances down the flow tube by measuring the absorbance at 460 nm, giving the following data (at 298 K) for two different concentrations of SCN⁻. The flow rate was 10 m s⁻¹.

distance / cm	10	20	30	40	50
absorbance ([SCN ⁻] = $0.2 \text{ mol } \text{dm}^{-3}$)	0.253	0.438	0.576	0.667	0.750
absorbance ([SCN ⁻] = $0.3 \text{ mol } \text{dm}^{-3}$)	0.344	0.569	0.708	0.802	0.842

Since the thiocyanate is in excess, the reaction is pseudo first order in Fe^{3+} and so, as shown on page 772, the time dependence of the concentration of the *product* (i.e. the complex, denoted B) is given by

$$\ln ([B]_{\infty} - [B](t)) - \ln ([B]_{\infty}) = -k_{1st}t,$$

where $[B]_{\infty}$ is the concentration of B at long time i.e. when the reaction has gone to completion.

(a) Assuming that the absorbance at time t, A(t), is proportional to the concentration of B, show that

$$\ln\left(\frac{A_{\infty}-A(t)}{A_{\infty}}\right) = -k_{1\rm st}t,$$

where A_{∞} is the absorbance when the reaction has gone to completion.

- (b) In this experiment the absorbance at long reaction times was 0.94. Determine the value of the pseudo first-order rate constant (by plotting a suitable graph) for the two different excess concentrations of thiocyanate.
- (c) Hence, determine the value of the second-order rate constant.

[Note that you will have to convert the distances to times, using velocity = distance / time.]

20.7 The rate of the gas phase reaction between the hydroxyl radical and HCl gas

$$OH + HCl \longrightarrow H_2O + Cl$$

has been studied by a combination of flash photolysis and laser induced fluorescence. In this technique, the OH radicals were generated by applying a pulse of UV light from a laser to a small amount of water vapour. Subsequently, the concentration of the OH radicals was monitored by using a laser to promote them to an excited electronic state, and then measuring the intensity of the fluorescence (i.e. the light emitted) from these excited molecules. The intensity of the fluorescence, $I_{\rm F}$, is proportional to the concentration of OH radicals.

The following data were obtained at 300 K and at 220 K for the indicated concentrations of HCl; the fluorescence intensity I_F is given in arbitrary units.

<i>t</i> / μs	0	100	200	300
$I_{\rm F}$ ([HCl] = 5 × 10 ¹⁵ molec. cm ⁻³ , T = 300 K)	100	69.5	48.3	33.6
$I_{\rm F}$ ([HCl] = 1 × 10 ¹⁶ molec. cm ⁻³ , T = 300 K)	100	48.3	23.3	11.3
$I_{\rm F}$ ([HCl] = 1 × 10 ¹⁶ molec. cm ⁻³ , T = 220 K)	100	64.7	41.9	27.1

- (a) By plotting a graph, show that in each case the decay of OH follows a first-order process, and hence determine the first-order rate constant.
- (b) By comparing the two data sets at 300 K, show that the rate law is first order in HCl, and hence determine the overall second-order rate constant at this temperature. Also determine the second-order rate constant at 220 K. Be sure to state the units of each rate constant.
- (c) Using the values of the rate constant at these different temperatures, determine the activation energy and pre-exponential factor for the reaction.

[Data kindly provided by Dr David Husain, Dept. of Chemistry, Cambridge.]

20.8 The gas phase decomposition of ethanal

 $CH_3CHO \longrightarrow CH_4 + CO$

has the rate law

$$\frac{\mathrm{d}[\mathrm{CH}_{3}\mathrm{CHO}]}{\mathrm{d}t} = -k \left[\mathrm{CH}_{3}\mathrm{CHO}\right]^{\frac{3}{2}}.$$

- (a) Integrate this rate law and hence obtain an expression for how the concentration of ethanal varies with time (assume that the concentration of ethanal at time zero is [CH₃CHO]₀).
- (b) Determine the form a plot which would be expected to give a straight line for data which follows this rate law. How is the rate constant related to the slope of this plot?
- (c) Find an expression for the half life of the reaction.
- 20.9 (a) Using the data in Table 20.1 on page 781, determine the collision cross section for an encounter between NO and Cl₂. Take the masses of N, O and Cl as 14, 16 and 35.5 mass units, respectively.
 - (b) Following the approach used in Example 20.3 on page 781, use simple collision theory to determine the value of the pre-exponential factor for the reaction between NO and Cl₂ at 298 K.

20.10 Rate constants for the following reaction (in solution)

 $RBr + Cl^{-} \longrightarrow RCl + Br^{-}$ (R = *n*Bu)

as a function of temperature are given in the following table. Use a graphical method to determine the enthalpy and entropy of activation.

$$\begin{bmatrix} T / ^{\circ}C \\ 10^{5} \times k_{2nd} / mol^{-1} dm^{3} s^{-1} \end{bmatrix} \begin{bmatrix} 25.0 & 34.6 & 44.5 & 55.2 & 64.8 \\ 6.45 & 16.4 & 41.0 & 106 & 215 \end{bmatrix}$$

Is your value of $\Delta_r S^{\circ,\ddagger}$ consistent with the reaction proceeding via a mechanism in which RBr and Cl⁻ come together in the rate-limiting step?

20.11 Explain why it is that whereas the bimolecular gas phase Diels-Alder reaction

has $\Delta_r S^{\circ,\ddagger} = -150 \text{ J K}^{-1} \text{ mol}^{-1}$, the solution phase bimolecular reaction

$$Cr(H_2O)_6^{3+} + CNS^- \longrightarrow Cr(H_2O)_5(CNS)^{2+} + H_2O$$

has $\Delta_r S^{\circ,\ddagger} = +125 \text{ J K}^{-1} \text{ mol}^{-1}$.

21 Electrochemistry

Physical constants: $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$, $F = 96,485 \text{ C mol}^{-1}$.

21.1 For each of the following cells: (a) write the cell using the notation described in section 21.1.2 on page 794, (b) determine the conventional cell reaction, stating the number of electrons involved, (c) write down the Nernst equation for the cell, (d) using the data in Table 21.1 on page 805 determine the standard cell potential, (e) hence determine the spontaneous cell reaction when all of the species are present in their standard states.

In the following table it can be assumed that: (i) all ions are in aqueous solution; (ii) H_2O is in its liquid form; (iii) O_2 , H_2 , and Cl_2 are gases; (iv) the solutions in the right- and left-hand sides are separated by a salt bridge; (v) an inert platinum electrode can be used as required.

	left-hand half-cell reaction	right-hand half-cell reaction
1	$\mathrm{H^{+}} + e^{-} \rightarrow \frac{1}{2}\mathrm{H}_{2}$	$\mathrm{Cu}^+ + e^- \rightarrow \mathrm{Cu}(\mathrm{m})$
2	$\mathrm{H^{+}} + e^{-} \rightarrow \frac{1}{2}\mathrm{H_{2}}$	$\mathrm{Fe}^{2+} + 2e^- \rightarrow \mathrm{Fe}(\mathrm{m})$
3	$\mathrm{Fe}^{2+} + 2e^- \rightarrow \mathrm{Fe}(\mathrm{m})$	$\mathrm{H^{+}} + e^{-} \rightarrow \frac{1}{2}\mathrm{H_{2}}$
4	$\mathrm{Mn}^{2+} + 2e^- \rightarrow \mathrm{Mn}(\mathrm{m})$	$Au^{3+} + 3e^- \rightarrow Au(m)$
5	$AgCl(s) + e^{-} \rightarrow Ag(m) + Cl^{-}$	$\mathrm{H^{+}} + e^{-} \rightarrow \frac{1}{2}\mathrm{H_{2}}$
6	$AgI(s) + e^- \rightarrow Ag(m) + I^-$	$\operatorname{Zn}^{2+} + 2e^{-} \to \operatorname{Zn}(m)$
7	$AgCl(s) + e^{-} \rightarrow Ag(m) + Cl^{-}$	$\mathrm{Hg}_{2}\mathrm{Cl}_{2}(\mathrm{s})+2e^{-}\rightarrow2\mathrm{Hg}(\mathrm{l})+2\mathrm{Cl}^{-}$
8	$2\mathrm{H}_{2}\mathrm{O}+2e^{-}\rightarrow\mathrm{H}_{2}+2\mathrm{OH}^{-}$	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
9	$\mathrm{O}_2 + 4\mathrm{H}^+ + 4e^- \rightarrow 2\mathrm{H}_2\mathrm{O}$	$\mathrm{MnO_4^-} + 8\mathrm{H^+} + 5e^- \rightarrow \mathrm{Mn^{2+}} + 4\mathrm{H_2O}$
10	$2\mathrm{H}_{2}\mathrm{O}+2e^{-}\rightarrow\mathrm{H}_{2}+2\mathrm{OH}^{-}$	$PbO(s) + H_2O + 2e^- \rightarrow Pb(m) + 2OH^-$

- 21.2 For each of the following cells: (a) write down the right- and left-hand half-cell reactions (as reductions); (b) determine the conventional cell reaction, stating the number of electrons involved, (c) write down the Nernst equation for the cell, (d) using the data in Table 21.1 on page 805 determine the standard cell potential, (e) hence for cells 1–9 hence determine the spontaneous cell reaction when all of the species are present in their standard states.
 - $1 \qquad Zn(m) \,|\, Zn^{2+}(aq) \,\|\, Mg^{2+}(aq) \,|\, Mg(m)$
 - $2 \qquad Pt(m) \,|\, H_2(g) \,|\, H^+(aq) \,\|\, Fe^{3+}(aq) \,|\, Fe(m)$
 - $3 \qquad Pt(m) \,|\, Sn^{4+}(aq), Sn^{2+}(aq) \,\|\, Cu^{2+}(aq) \,|\, Cu(m)$
 - $4 \qquad Ag(m), AgI(s) \,|\, HI(aq) \,|\, H_2(g) \,|\, Pt(m)$
 - $5 \qquad Pt(m) \,|\, H_2(g) \,|\, H^+(aq) \,|\, O_2(g) \,|\, Pt(m)$
 - $6 \qquad Pt(m) \,|\, H_2(g) \,|\, OH^-(aq) \,|\, O_2(g) \,|\, Pt(m)$
 - $7 \qquad Ag(m), AgBr(s) \,|\, Br^-(aq), Br_2(aq) \,|\, Pt(m)$
 - 8 $Pb(m), PbO(s) | OH^{-}(aq) | H_{2}(g) | Pt(m)$
 - $9 \qquad Pt(m) \,|\, Cr_2O_2^{2-}(aq), Cr^{3+}(aq), H^+(aq) \,\|\, Cl^-(aq) \,|\, AgCl(s), Ag(m)$
 - 10 $\operatorname{Ag}(m), \operatorname{AgCl}(s) | \operatorname{Cl}^{-}(\operatorname{aq}, [\operatorname{Cl}^{-}] = c_{L}) || \operatorname{Cl}^{-}(\operatorname{aq}, [\operatorname{Cl}^{-}] = c_{R}) | \operatorname{AgCl}(s), \operatorname{Ag}(m)$

- 21.3 Devise cells which have the following conventional cell reactions. In each case: (a) write the cell in the way described in section 21.1.2 on page 794; (b) write the right- and left-hand side half-cell reactions (as reductions); (c) determine the cell potential when all of the species are present in their standard states; (d) hence determine the direction of the spontaneous cell reaction when all of the species are present in their standard states.
 - 1 $Zn(m) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(m)$
 - 2 $2Ag(m) + Sn^{4+}(aq) \longrightarrow Sn^{2+}(aq) + 2Ag^{+}(aq)$
 - 3 $\operatorname{AgCl}(m) + \frac{1}{2}H_2(g) \longrightarrow H^+(aq) + \operatorname{Cl}^-(aq) + \operatorname{Ag}(m)$
 - 4 $H^+(aq) + Cl^-(aq) + Ag(m) \longrightarrow AgCl(m) + \frac{1}{2}H_2(g)$
 - 5 $2AgCl(m) + H_2(g) \longrightarrow 2H^+(aq) + 2Cl^-(aq) + 2Ag(m)$
 - $6 \qquad 2AgCl(m) + 2Hg(l) \longrightarrow Hg_2Cl_2(m) + 2Ag(m)$
 - $7 \qquad O_2(g) + 4H^+(aq) + 4Cl^-(aq) + 4Ag(m) \longrightarrow 2H_2O(l) + 4AgCl(m)$
 - 8 $H_2O(l) + Pb(m) \longrightarrow H_2(g) + PbO(s)$
 - 9 $AgBr(m) \longrightarrow Ag^{+}(aq) + Br^{-}(aq)$
 - 10 $Al(m) + 3Ce^{4+}(aq) \longrightarrow Al^{3+}(aq) + 3Ce^{3+}(aq)$
- **21.4** Consider the following cell (at 298 K)

$$\operatorname{Fe}(m) | \operatorname{Fe}^{2+}(\operatorname{aq}, [\operatorname{Fe}^{2+}] = c_1) || \operatorname{Cd}^{2+}(\operatorname{aq}, [\operatorname{Cd}^{2+}] = c_2) | \operatorname{Cd}(m)|$$

- (a) Determine the conventional cell reaction and hence write down the Nernst equation for the cell in terms of the concentrations c_1 and c_2 .
- (b) Determine the cell potential when all of the species are present in their standard states (i.e. $c_1 = c_2 = 1 \text{ mol dm}^{-3}$), and hence state the spontaneous cell reaction.
- (c) By considering the Nernst equation, determine the value of the ratio c_1/c_2 which will reduce the cell potential to zero.
- (d) Hence state what range of values of c_1/c_2 will lead to the spontaneous cell reaction being the *opposite* of that determined in (b).
- 21.5 Use the data in Table 21.1 on page 805 to determine whether or not the following processes are thermodynamically feasible when all of the species are present in their standard states and at 298 K (all ions are in aqueous solution).
 - (a) The oxidation of Cu(m) to Cu^{2+} by Fe^{3+} (assume that the Fe^{3+} is reduced to Fe^{2+})
 - (b) The oxidation of Fe^{2+} to Fe^{3+} by $Cl_2(g)$
 - (c) The oxidation of $H_2O(l)$ to $O_2(g)$ by Fe^{3+} (under acidic conditions)
 - (d) The reduction of Cu^{2+} to Cu^+ by Ag(m)
 - (e) The reduction of Fe^{3+} to Fe(m) by Zn(m)
 - (f) The reduction of Mn^{2+} to Mn(m) by Tl.

- **21.6** The potential produced by the hydrogen electrode is dependent on concentration of $H^+(aq)$ and the partial pressure of H_2 .
 - (a) Given that the half-cell reaction is

$$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$$
 $E^{\circ}(H^+/H_2) = 0.00 V,$

write down the Nernst equation for the half-cell potential.

(b) Assuming that the partial pressure of H_2 is 1 bar (i.e. the standard pressure) show that the half-cell potential is given by

$$E = \frac{RT}{F} \ln \left[\mathbf{H}^+ \right].$$

(c) Hence show that the half-cell potential is related to the pH in the following way [hint $\ln x \equiv \ln 10 \times \log x$]

$$E = -\ln 10 \times \frac{RT}{F} \times \text{pH}.$$

- (d) Does it become easier or more difficult for a reducing agent to reduce H⁺ to H₂ as the pH increases?
- 21.7 (a) Devise a cell whose conventional cell reaction is

$$\operatorname{AgCl}(s) \longrightarrow \operatorname{Ag}^+(aq) + \operatorname{Cl}^-(aq).$$

- (b) Using tabulated data, determine the standard potential of this cell at 298 K and hence find $\Delta_r G_{cell}^{\circ}$.
- (c) Hence determine the solubility product of AgCl, and the concentration of dissolved Ag⁺ ions in a saturated solution of AgCl.
- 21.8 In this question we will use data on cell potentials to compute some thermodynamic parameters for Mg²⁺ in a way very similar to that illustrated in section 21.9.2 on page 817 for Ag⁺. The cell we need to consider in this case is the following

RHS:
$$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$$

LHS: $Mg^{2+}(aq) + 2e^- \longrightarrow Mg(m).$

At 298 K the standard potential for this cell is +2.360 V, and the temperature dependence of the standard cell potential is $dE^{\circ}/dT = -1.99 \times 10^{-4} \text{ V K}^{-1}$.

- (a) Determine the conventional cell reaction.
- (b) Determine $\Delta_r G_{cell}^{\circ}$, $\Delta_r S_{cell}^{\circ}$ and $\Delta_r H_{cell}^{\circ}$ (all at 298 K) for this reaction.
- (c) Hence, assuming the usual conventions that $\Delta_f G^{\circ}(H^+(aq)) = 0$, $\Delta_f H^{\circ}(H^+(aq)) = 0$ and $\Delta_f S^{\circ}(H^+(aq)) = 0$, find the standard Gibbs energy, enthalpy and entropy of formation of Mg²⁺(aq).
- (d) Dissect the conventional cell reaction found in (a) into a Hess's Law cycle of the same form as that in Fig. 21.12 on page 819. [continued over]

(e) Use the following data, along with your value of $\Delta_f H^{\circ}(Mg^{2+}(aq))$, to determine the *absolute* enthalpy of hydration of Mg^{2+} , $\Delta H^{\circ}_{hvd}(Mg^{2+})$:

$\mathrm{H}^{+}(\mathrm{g}) \rightarrow \mathrm{H}^{+}(\mathrm{aq})$	$\Delta_{\rm r} H^{\circ}$ = -1110 kJ mol ⁻¹
$Mg(m) \rightarrow Mg(g)$	$\Delta_{\rm r} H^{\circ}$ = 147.1 kJ mol ⁻¹
$H(g) \rightarrow H^+(g)$	$\Delta_{\rm r} H^{\circ}$ = 1312 kJ mol ⁻¹
$Mg(g) \rightarrow Mg^{2+}(g)$	$\Delta_{\rm r} H^{\circ}$ = 1450.7 kJ mol ⁻¹
$H_2(g) \rightarrow 2H(g)$	$\Delta_{\rm r} H^\circ$ = 456 kJ mol ⁻¹ .

[Be very careful to make sure that you use the $\Delta_r H^\circ$ value for the *direction* of reaction specified in the Hess's Law cycle.]

21.9 Use the following data to construct an oxidation state diagram for cobalt. Comment on any features of interest which are revealed by your diagram.

half-cell reaction	E°/V (298K)
$\operatorname{Co}^{2+}(\operatorname{aq}) + 2e^{-} \to \operatorname{Co}(\operatorname{m})$	-0.282
$\mathrm{Co}^{3+}(\mathrm{aq}) + e^- \rightarrow \mathrm{Co}^{2+}(\mathrm{aq})$	+1.92
$\mathrm{CoO}_2(\mathrm{s}) + 4\mathrm{H}^+ + e^- \rightarrow \mathrm{Co}^{3+}(\mathrm{aq}) + 2\mathrm{H}_2\mathrm{O}(\mathrm{l})$	+1.4

21.10 Before an ion-selective electrode can be used to make measurements, the potential it generates (when forming a cell with a suitable external reference electrode) needs to be calibrated as a function of the concentration of the ions. This is normally done by measuring the potential for a series of solutions of known concentration and then constructing a calibration curve. For the greatest accuracy, it is best to calibrate the electrode over the range of concentrations likely to be encountered in the measurements.

Low concentrations of ions are usually specified in parts per million (ppm) by weight. For example, if a solution contains 5 ppm of fluoride it means that

$$\frac{\text{mass of } F^-}{\text{mass of solvent}} = 5 \times 10^{-6}.$$

It follows that 1 dm³ of water, which would weigh 1000 g, will contain 5.0×10^{-3} g of F⁻. Given that the RMM of F is 18.998, this corresponds to a concentration of 2.63 × 10^{-4} mol dm⁻³. For these very dilute solutions, the concentration expressed in ppm is directly proportional to the concentration in mol dm⁻³.

Measurements on a series of solutions of known concentration gave the following data

The expected variation of the cell potential with concentration is of the form

$$E = A + B \ln [F^-],$$

where *A* and *B* are constants; in this expression, $[F^-]$ can be expressed in ppm. By plotting a suitable straight-line graph, show that these data fit this equation; determine the values of *A* and *B*.

The electrode was then used to measure the fluoride concentration in drinking water. Over a series of measurements the average potential was found to be 0.255 V, with a spread of measurements between 0.254 V and 0.256 V. Determine the concentration (in ppm) of F^- in the water, and the likely error on the measurement.

21.11 Manufacturers of glass electrodes, used to measure pH, warn customers that the accuracy of the results may be reduced if the Na⁺ concentration in the solution under test is high. Why is this?

21.12 A *concentration cell* is one in which the RHS and LHS electrodes are identical with the only difference between them being the concentration (or pressure) of the species involved. An example of such a cell is once constructed from two AgCl/Cl⁻ electrodes

 $Ag(m), AgCl(s) | Cl^{-}(aq, [Cl^{-}]_{L}) || Cl^{-}(aq, [Cl^{-}]_{R}) | AgCl(s), Ag(m),$

in which the concentration of Cl^- in the left-hand half-cell is $[Cl^-]_L$, and that on the right is $[Cl^-]_R$. In writing the half-cell reactions for such a cell, we need to be careful to keep track of which side of the cell the Cl^- is in. The half cell reactions are therefore written

 $\begin{array}{rcl} RHS: & AgCl(s) + e^- & \longrightarrow & Ag(m) + Cl^-(aq)_R \\ LHS: & AgCl(s) + e^- & \longrightarrow & Ag(m) + Cl^-(aq)_L. \end{array}$

Note the subscripts 'R' and 'L' indicating which half-cell the Cl⁻ belongs to.

(a) Determine the conventional cell reaction, and hence show that the cell potential is given by

$$E = \frac{RT}{F} \ln \frac{[\mathrm{Cl}^-]_{\mathrm{L}}}{[\mathrm{Cl}^-]_{\mathrm{R}}}.$$

- (b) Why does the standard half cell potential of the AgCl/Cl⁻ couple *not* appear in the expression for the cell potential?
- (c) Determine the direction of the spontaneous cell reaction when $[Cl^-]_R > [Cl^-]_L$ and when $[Cl^-]_L > [Cl^-]_R$. Rationalize your conclusions.
- (d) From the above expression for the cell potential, compute dE/dT [Hint: all but one of the terms on the right do not depend on *T*]. Hence find $\Delta_r S_{cell}$ and $\Delta_r H_{cell}$. Comment on the results you obtain.
- **21.13** The potential of the following cell was measured at temperatures of 278, 298 and 318 K as +0.0389, +0.0458 and +0.0527 V respectively

 $Ag(m), AgCl(s) | KCl(aq, 0.1 mol dm^{-3}) | Hg_2Cl_2(s) | Hg(l)$

- (a) Write down the half cell reactions of the two electrodes and hence determine the conventional cell reaction. Also, write down the Nernst equation for the cell, and comment on why the cell potential does not depend on the concentration of Cl⁻.
- (b) Determine $\Delta_r G_{cell}^\circ$ at 298 K.
- (c) Using $\Delta_r S_{cell}^{\circ} = nF(dE^{\circ}/dT)$, find $\Delta_r S_{cell}^{\circ}$ and hence $\Delta_r H_{cell}^{\circ}$ (you will need to plot a graph).
- (d) Hence determine the standard enthalpy of formation of $Hg_2Cl_2(s)$ at 298 K, given that at this temperature the standard enthalpy of formation of AgCl(s) is -126.8 kJ mol⁻¹.

21.14 Consider the cell

 $Pt(m) | H_2(g) | H_2SO_4(aq) | PbSO_4(s)|Pb(m),$

whose standard potential is found to be -0.356 V at 298 K.

- (a) Write down the conventional cell reaction.
- (b) Given that the standard half-cell potential of the $Pb^{2+}(aq)/Pb(m)$ electrode is -0.126 V at 298 K, determine the solubility product of $PbSO_4(s)$ at this temperature. What will the concentration of Pb^{2+} ions be in a saturated solution of $PbSO_4$ at 298 K?
- (c) Given that the temperature variation of the standard potential of the above cell is given by $dE^{\circ}/dT = 1.1 \times 10^{-4} \text{ V K}^{-1}$, determine $\Delta_r S_{cell}^{\circ}$ and hence $\Delta_r H_{cell}^{\circ}$.
- (d) Given that at 298 K the standard enthalpy of formation of $PbSO_4(s)$ is -918.4 kJ mol⁻¹, determine the standard enthalpy of formation of $SO_4^{2-}(aq)$.
- 21.15 (a) Describe carefully what is meant by the term *standard electrode potential*. Explain how tables of standard *half-cell* potentials can be drawn up.
 - (b) An electrochemical cell is constructed from two half cells: on the right a silver wire dips into a 0.001 mol dm⁻³ AgNO₃ solution, and the half cell on left is a hydrogen electrode with hydrogen gas at 1 bar pressure and an HCl solution of variable concentration, *m*. At 298 K the cell potential was found to vary with *m* in the following way:

$m / \text{mol dm}^{-3}$	0.6	0.8	1.0	1.2	1.4
<i>E </i> V	0.6375	0.6304	0.6252	0.6214	0.6182

Determine the Nernst equation for the cell and then, by plotting a suitable straight-line graph, test how well the above data fit your equation.

(c) From your graph, estimate the standard half-cell potential of the Ag⁺/Ag couple.

22 Dimensions, units and some key mathematical ideas

Physical constants: $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$, $h = 6.626 \times 10^{-34} \text{ J s}$, $k_{\text{B}} = 1.381 \times 10^{-23} \text{ J K}^{-1}$, $N_{\text{A}} = 6.022 \times 10^{23} \text{ mol}^{-1}$, $F = 96,485 \text{ C mol}^{-1}$, $c = 2.998 \times 10^8 \text{ m s}^{-1}$.

22.1 The so-called 'SUVAT' equations apply to an object experiencing a constant acceleration a and give various relationships between the distance travelled s, the initial velocity u, the final velocity v, and the time t. Determine the dimensions of each term in these equations, and hence show that they are dimensionally consistent.

$$v = u + at$$
 $s = ut + \frac{1}{2}at^2$ $s = vt - \frac{1}{2}at^2$ $v^2 = u^2 + 2as$ $s = \frac{1}{2}(u + v)t$

22.2 A spherical particle of radius r moving with velocity v through a viscous medium (e.g. a liquid) experiences a retarding force F which can, under some circumstances, be approximated by the Stokes' Law

$$F = 6\pi\eta r v,$$

where η is the viscosity of the medium. Determine the dimensions of η , and hence its SI unit. [Hint: rearrange the expression to give $\eta = \ldots$, and then use the known dimensions of all the quantities then on the right.]

22.3 A first-order reaction has the rate law

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{1\mathrm{st}}[\mathrm{A}],$$

where [A] is the concentration of a reactant, *t* is time and k_{1st} is the rate constant. Assuming that [A] is given in amount of substance per unit volume, determine the dimensions of k_{1st} . Hence, state the SI unit of k_{1st} .

22.4 A second-order reaction has the rate law

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{2nd}}[\mathrm{A}]^2,$$

where [A] is the concentration of a reactant, *t* is time and k_{2nd} is the rate constant. Assuming that [A] is given in amount of substance per unit volume, determine the dimensions of k_{2nd} . If the concentration is expressed in mol dm⁻³, what will be the units of k_{2nd} ?

22.5 The work done when a force *F* moves a distance *x* is $F \times x$. The work done when a charge *q* moves through a potential (voltage) *V* is $q \times V$. The work done when a surface is increased in area by *A* is given by $A \times \gamma$, where γ is the surface tension (SI unit N m⁻¹). Show that each of these work terms has the dimensions of energy.

- 22.6 (a) The rotational kinetic energy of an object with *moment of inertia I* rotating at angular frequency ω is given by $\frac{1}{2}I\omega^2$. Given that *I* has dimensions ML^2 , confirm that $\frac{1}{2}I\omega^2$ has the dimensions of energy. [Hint: ω could be given in rad s⁻¹; recall that radians are dimensionless.]
 - (b) For a diatomic molecule, *I* is given by

$$I = \frac{m_1 m_2}{m_1 + m_2} R^2,$$

where m_1 and m_2 are the masses of the two atoms and R is the bond length. In quantum mechanics the energy E_J of a rotating diatomic is given by

$$E_J = BJ(J+1)$$
 where $B = \frac{\hbar^2}{2I}$;

in this expression *J* is a dimensionless quantum number which takes integer values, and \hbar is Planck's constant divided by 2π : $\hbar = h/2\pi$.

Determine the dimensions of I and B; hence show that E_J has the dimensions of energy.

22.7 In quantum mechanics, a simple model for the energy of a vibrating bond is

$$E_v = (v + \frac{1}{2})\hbar\omega$$
 where $\omega = \sqrt{\frac{k_{\rm f}}{m}}$;

in this expression v is a dimensionless quantum number which takes integer values, k_f is the force constant (SI unit N m⁻¹), m is the mass, and \hbar is Planck's constant divided by 2π : $\hbar = h/2\pi$.

Determine the dimensions of k_f and ω ; hence show that E_v has the dimensions of energy.

- 22.8 Convert the following to SI, using an prefix in your answer, where appropriate.
 - (a) The collision cross-section of O_2 , 40 Å².
 - (b) The entropy change when one mole of liquid water is vaporized at 373 K, 26.05 e.u.
 - (c) The vapour pressure of water at its triple point, 4.58τ .
 - (d) The vibrational frequency of the bond in H_2 , 4401 cm⁻¹.
 - (e) The orbital energy of a 1s electron in He, -25 eV.
 - (f) The mass of one molecule of ${}^{19}F_2$, given that the mass of ${}^{19}F$ is 18.998 u.
- 22.9 (a) What volume, in cm³, of a solution of concentration 0.15 mol dm⁻³ contains the same amount in moles as 13.5 cm³ of a solution of concentration 1.2 mol dm⁻³?
 - (b) 1.50 g of NaCl is dissolved in water and the solution made up to a total volume of 50 cm³. What is the concentration, in mol dm⁻³ and in mol m⁻³, of the resulting solution. [RFM for NaCl is 58.35 g mol⁻¹.]
 - (c) How much water needs to be added to 10 cm^3 of a solution of concentration 1.00 mol dm⁻³ to give a solution of concentration 0.15 mol dm⁻³?

22.10 In quantum mechanics, the energy of a rotating diatomic is given by

$$E_J = BJ(J+1)$$
 where $B = \frac{\hbar^2}{2I}$,

where all of the symbols are defined in question 22.7. If SI units are used for \hbar and *I*, then the energy E_J will of course be in joules.

(a) Explain why the energy expressed in cm^{-1} , \tilde{E} and the energy expressed in joules, *E*, are related by

$$E = h \times \tilde{c} \times \tilde{E},$$

where \tilde{c} is the speed on light in cm s⁻¹.

(b) Hence show that the rotational energy, expressed in cm^{-1} , is given by

$$\tilde{E}_J = \frac{B}{h\,\tilde{c}}\,J(J+1).$$

(c) By substituting in $\hbar^2/2I$ for *B*, go on to show that the rotation energy in cm⁻¹ can be written

$$\tilde{E}_J = \frac{h}{8\pi^2 \tilde{c} I} J(J+1).$$

- 22.11 Sketch $\cos(3\alpha)$ in the range $\alpha = 0$ to 2π . What is the period of this function? At what values of α (expressed in terms of π) does the function go to zero? Classify the function as even or odd about the value $\alpha = \pi$.
- 22.12 (a) Given that

$$\sin (A + B) \equiv \sin A \cos B + \cos A \sin B \qquad \cos (A + B) \equiv \cos A \cos B - \sin A \sin B.$$

show that

$$\sin(2A) \equiv 2\sin A \cos B \qquad \cos(2A) \equiv \cos^2 A - \sin^2 A$$

(b) Using $\cos^2 A + \sin^2 A = 1$, show that $\cos(2A) \equiv \cos^2 A - \sin^2 A$ can be rewritten in two different ways

$$\cos(2A) \equiv 2\cos^2 A - 1$$
 or $\cos(2A) \equiv 1 - 2\sin^2 A$.

(c) Show that these last two identities can be rearranged to give

 $\cos^2 A \equiv \frac{1}{2} [1 + \cos(2A)]$ and $\sin^2 A \equiv \frac{1}{2} [1 - \cos(2A)].$

22.13 The concentration of a reactant A in a first-order reaction varies with times as follows

$$[A](t) = [A]_0 \exp(-k_{1st}t),$$

where [A](*t*) is the concentration at time *t*, [A]₀ is the concentration at time zero, and k_{1st} is the rate constant. Show that the half life t_{half} , which is the time taken for the concentration to fall to half its initial value, is given by $t_{half} = \ln (2)/k_{1st}$.

22.14 (a) The Boltzmann distribution gives the population of energy level *i*, n_i , in terms of its energy ε_i and the population n_0 of the lowest level

$$n_i = n_0 \exp\left(\frac{-\varepsilon_i}{k_{\rm B}T}\right).$$

Rearrange this to find expressions for $\ln(n_i)$ and $\ln(n_i/n_0)$.

- (b) The standard Gibbs energy change $\Delta_r G^\circ$ and the equilibrium constant *K* are related by $\Delta_r G^\circ = -RT \ln K$. Rearrange this to find expressions for $\ln K$ and for *K*.
- 22.15 Compute the first and second derivatives of $f(t) = A \exp(-Bt^2)$ with respect to t (A and B are constants). Sketch a graph of f(t) against t and, by interpreting the first derivative as the slope, explain how your expression for df(t)/dt is consistent with the plot.
- 22.16 Differentiate the function $f(r) = r^4 \exp(-r)$ with respect to *r* and hence show that there are extrema at r = 0, r = 4 and $r = +\infty$. Explain why r = 4 must correspond to a maximum.
- 22.17 (a) Using the identity $\sin^2 \theta \equiv \frac{1}{2} [1 \cos(2\theta)]$, show that

$$\int_0^A \sin^2\left(\frac{\pi x}{A}\right) \mathrm{d}x$$

can be written

$$\frac{1}{2} \int_0^A \mathrm{d}x - \frac{1}{2} \int_0^A \cos\left(\frac{2\pi x}{A}\right) \mathrm{d}x.$$

- (b) Evaluate both integrals and show that together they come to A/2.
- 22.18 A second-order reaction has the following rate equation

$$\frac{\mathrm{d}[\mathrm{A}](t)}{\mathrm{d}t} = -k_{\mathrm{2nd}}[\mathrm{A}]^2(t),$$

where [A](t) is the concentration of reactant A at time t, and k_{2nd} is the second-order rate constant.

- (a) Separate the variables, taking the terms in [A](t) to the left, and those in t to the right.
- (b) Integrate both sides of the resulting equation.
- (c) Use the fact that at time t = 0 the concentration of A is $[A]_0$ to determine the constant of integration.