

Chemistry 4000

Introduction to Inorganic Chemistry: The Different Perspectives of Bonding

Problem Set #1

Chapter 1-

1. How many radial nodes do 3s, 4p, 3d, and 5f orbitals exhibit? How many angular nodes?
2. Write out the electronic configuration for the ions and determine the number of unpaired e^- in the ground state.

Ti^{3+} Mn^{2+} Cu^{2+} Gd^{3+}

3. Using Slater's rules, calculate Z^* for the following electrons:

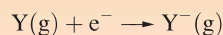
- a. a 3p e^- in P
- b. a 4s e^- in Co
- c. a 3d e^- in Mn
- d. a valence e^- in Mg

4. Book Problems: 1.1, 1.9, 1.20, 1.34, 1.40, 1.45

Chapter 2-

1. Book Problems: 2.1, 2.3, 2.8 (Answer for Ne_2 instead of He_2), 2.14, 2.18, 2.19 (Show your work), 2.25, 2.26 (Only part a)
2. Draw MO diagrams for N_2 and NO , using only the valence orbitals. Use the diagrams to rationalize which species you would expect to be more chemically inert.

The *first electron affinity*, EA_1 , of an atom is *minus* the internal energy change at 0 K associated with the gain of one electron by a gaseous atom:



For thermochemical cycles, an associated enthalpy change is used:

$$\Delta_{EA}H(298\text{ K}) \approx \Delta_{EA}U(0\text{ K}) = -EA$$

The attachment of an electron to an *atom* is usually exothermic. Two electrostatic forces oppose one another: the repulsion between the valence shell electrons and the additional electron, and the attraction between the nucleus and the incoming electron. In contrast, *repulsive* interactions are dominant when an electron is added to an *anion* and the process is endothermic (Table 1.5).

KEY TERMS

The following terms were introduced in this chapter. Do you know what they mean?

- | | | |
|-----------------------------------------------|--------------------------------------------------------------|----------------------------------------------------------------|
| <input type="checkbox"/> atom | <input type="checkbox"/> wavenumber | <input type="checkbox"/> ground state electronic configuration |
| <input type="checkbox"/> proton | <input type="checkbox"/> Avogadro number | <input type="checkbox"/> effective nuclear charge |
| <input type="checkbox"/> electron | <input type="checkbox"/> wavefunction, ψ | <input type="checkbox"/> screening effects of electrons |
| <input type="checkbox"/> neutron | <input type="checkbox"/> hydrogen-like species | <input type="checkbox"/> penetration |
| <input type="checkbox"/> nucleus | <input type="checkbox"/> principal quantum number, n | <input type="checkbox"/> shielding |
| <input type="checkbox"/> protium | <input type="checkbox"/> orbital quantum number, l | <input type="checkbox"/> Slater's rules |
| <input type="checkbox"/> nuclide | <input type="checkbox"/> magnetic quantum number, m_l | <input type="checkbox"/> periodic table |
| <input type="checkbox"/> atomic number | <input type="checkbox"/> magnetic spin quantum number, m_s | <input type="checkbox"/> <i>aufbau</i> principle |
| <input type="checkbox"/> mass number | <input type="checkbox"/> degenerate | <input type="checkbox"/> Hund's rules |
| <input type="checkbox"/> relative atomic mass | <input type="checkbox"/> radial distribution function | <input type="checkbox"/> Pauli exclusion principle |
| <input type="checkbox"/> isotope | <input type="checkbox"/> radial part of a wavefunction | <input type="checkbox"/> valence electrons |
| <input type="checkbox"/> allotrope | <input type="checkbox"/> angular part of a wavefunction | <input type="checkbox"/> core electrons |
| <input type="checkbox"/> emission spectrum | <input type="checkbox"/> atomic orbital | <input type="checkbox"/> ionization energy |
| <input type="checkbox"/> ground state | <input type="checkbox"/> nodal plane | <input type="checkbox"/> electron affinity |
| <input type="checkbox"/> excited state | <input type="checkbox"/> radial node | |
| <input type="checkbox"/> quanta | | |

FURTHER READING

First-year chemistry: basic principles

C.E. Housecroft and E.C. Constable (2010) *Chemistry*, 4th edn, Prentice Hall, Harlow – A readable text covering fundamental aspects of inorganic, organic and physical chemistry which gives detailed background of all material that is taken as assumed knowledge in this book. An accompanying multiple-choice test bank and Solutions Manual can be found through www.pearsoned.co.uk/housecroft.

P. Atkins and J. de Paula (2005) *The Elements of Physical Chemistry*, 4th edn, Oxford University Press, Oxford – An excellent introductory text which covers important areas of physical chemistry.

Basic quantum mechanics

P. Atkins and J. de Paula (2010) *Atkins' Physical Chemistry*, 9th edn, Oxford University Press, Oxford – This text

gives a solid and well-tested background in physical chemistry.

D.O. Hayward (2002) *Quantum Mechanics for Chemists*, RSC Publishing, Cambridge – An undergraduate student text that covers the basic principles of quantum mechanics.

Ionization energies and electron affinities

P.F. Lang and B.C. Smith (2003) *J. Chem. Educ.*, vol. 80, p. 938 – 'Ionization energies of atoms and atomic ions'.

D.M.P. Mingos (1998) *Essential Trends in Inorganic Chemistry*, Oxford University Press, Oxford – This text includes detailed discussions of trends in ionization energies and electron attachment enthalpies within the periodic table.

J.C. Wheeler (1997) *J. Chem. Educ.*, vol. 74, p. 123 – 'Electron affinities of the alkaline earth metals and the sign convention for electron affinity'.

PROBLEMS

1.1 Chromium has four isotopes, $^{50}_{24}\text{Cr}$, $^{52}_{24}\text{Cr}$, $^{53}_{24}\text{Cr}$ and $^{54}_{24}\text{Cr}$. How many electrons, protons and neutrons does each isotope possess?

1.2 'Arsenic is monotopic.' What does this statement mean? Using Appendix 5, write down three other elements that are monotopic.

- 1.3 Using the list of naturally occurring isotopes in Appendix 5, determine the number of electrons, protons and neutrons present in an atom of each isotope of (a) Al, (b) Br and (c) Fe, and give appropriate notation to show these data for each isotope.
- 1.4 Hydrogen possesses three isotopes, but tritium (^3H), which is radioactive, occurs as less than 1 in 10^{17} atoms in a sample of natural hydrogen. If the value of A_r for hydrogen is 1.008, estimate the percentage abundance of protium, ^1H , and deuterium, ^2H (or D) present in a sample of natural hydrogen. Point out any assumptions that you make. Explain why your answers are not the same as those quoted in Appendix 5.
- 1.5 (a) By using the data in Appendix 5, account for the isotopic distribution shown in Fig. 1.1b. (b) The mass spectrum of S_8 shows other peaks at lower values of m/z . By considering the structure of S_8 shown in Fig. 1.1c, suggest the origin of these lower-mass peaks.
- 1.6 Calculate the corresponding wavelengths of electromagnetic radiation with frequencies of (a) 3.0×10^{12} Hz, (b) 1.0×10^{18} Hz and (c) 5.0×10^{14} Hz. By referring to Appendix 4, assign each wavelength or frequency to a particular type of radiation (e.g. microwave).
- 1.7 State which of the following $n' \rightarrow n$ transitions in the emission spectrum of atomic hydrogen belong to the Balmer, Lyman or Paschen series: (a) $3 \rightarrow 1$; (b) $3 \rightarrow 2$; (c) $4 \rightarrow 3$; (d) $4 \rightarrow 2$; (e) $5 \rightarrow 1$.
- 1.8 Calculate the energy (in kJ per mole of photons) of a spectroscopic transition, the corresponding wavelength of which is 450 nm.
- 1.9 Four of the lines in the Balmer series are at 656.28, 486.13, 434.05 and 410.17 nm. Show that these wavelengths are consistent with eq. 1.4.
- 1.10 Using the Bohr model, determine the values of the radii of the second and third orbits of the hydrogen atom.
- 1.11 How is the (a) energy and (b) size of an ns atomic orbital affected by an increase in n ?
- 1.12 Write down a set of quantum numbers that uniquely defines each of the following atomic orbitals: (a) $6s$, (b) each of the five $4d$ orbitals.
- 1.13 Do the three $4p$ atomic orbitals possess the same or different values of (a) principal quantum number, (b) the orbital quantum number and (c) the magnetic quantum number? Write down a set of quantum numbers for each $4p$ atomic orbital to illustrate your answer.
- 1.14 How many radial nodes does each of the following orbitals possess: (a) $2s$; (b) $4s$; (c) $3p$; (d) $5d$; (e) $1s$; (f) $4p$?
- 1.15 Comment on differences between plots of $R(r)$ against r , and $4\pi r^2 R(r)^2$ against r for each of the following atomic orbitals of an H atom: (a) $1s$; (b) $4s$; (c) $3p$.
- 1.16 Write down the sets of quantum numbers that define the (a) $1s$, (b) $4s$, (c) $5s$ atomic orbitals.
- 1.17 Write down the three sets of quantum numbers that define the three $3p$ atomic orbitals.
- 1.18 How many atomic orbitals make up the set with $n = 4$ and $l = 3$? What label is given to this set of orbitals? Write down a set of quantum numbers that defines each orbital in the set.
- 1.19 Which of the following species are hydrogen-like: (a) H^+ ; (b) He^+ ; (c) He^- ; (d) Li^+ ; (e) Li^{2+} ?
- 1.20 (a) Will a plot of $R(r)$ for the $1s$ atomic orbital of He^+ be identical to that of the H atom (Fig. 1.5a)? [*Hint*: look at Table 1.2.] (b) On the *same axis set*, sketch approximate representations of the function $4\pi r^2 R(r)^2$ for H and He^+ .
- 1.21 Calculate the energy of the $3s$ atomic orbital of an H atom. [*Hint*: see eq. 1.16.] Is the energy of the hydrogen $3p$ atomic orbital the same as or different from that of the $3s$ orbital?
- 1.22 Using eq. 1.16, determine the energies of atomic orbitals of hydrogen with $n = 1, 2, 3, 4$ and 5 . What can you say about the relative spacings of the energy levels?
- 1.23 Write down the six sets of quantum numbers that describe the electrons in a degenerate set of $5p$ atomic orbitals. Which pairs of sets of quantum numbers refer to spin-paired electrons?
- 1.24 For a neutral atom, X, arrange the following atomic orbitals in an approximate order of their relative energies (not all orbitals are listed): $2s$, $3s$, $6s$, $4p$, $3p$, $3d$, $6p$, $1s$.
- 1.25 Using the concepts of shielding and penetration, explain why a ground state configuration of $1s^2 2s^1$ for an Li atom is energetically preferred over $1s^2 2p^1$.
- 1.26 For each of the following atoms, write down a ground state electronic configuration and indicate which electrons are core and which are valence: (a) Na, (b) F, (c) N, (d) Sc.
- 1.27 Draw energy level diagrams (see Fig. 1.15) to represent the ground state electronic configurations of the atoms in problem 1.26.

- 1.28 Write down the ground state electronic configuration of boron, and give a set of quantum numbers that uniquely defines each electron.
- 1.29 Write down (with reasoning) the ground state electronic configurations of (a) Li, (b) O, (c) S, (d) Ca, (e) Ti, (f) Al.
- 1.30 Draw energy level diagrams to show the ground state electronic configurations of only the *valence* electrons in an atom of (a) F, (b) Al and (c) Mg.
- 1.31 The ground state electronic configuration of a group 16 element is of the type $[X]ns^2np^4$ where X is a group 18 element. How are the outer four electrons arranged, and what rules are you using to work out this arrangement?
- 1.32 (a) Write down an equation that defines the process to which the value of IE_4 of Sn refers. Is this process exothermic or endothermic? (b) To what overall process does a value of $(IE_1 + IE_2 + IE_3)$ for Al refer?
- 1.33 The first four ionization energies of an atom X are 403, 2633, 3900 and 5080 kJ mol^{-1} . Suggest to what periodic group X belongs and give reasons for your choice.
- 1.34 In Fig. 1.16, identify the trends in the first ionization energies of the elements in (a) descending group 1, (b) descending group 13, (c) crossing the first row of the *d*-block, (d) crossing the row of elements from B to Ne, (e) going from Xe to Cs, and (f) going from P to S. Rationalize each of the trends you have described.
- 1.35 Figure 1.17 shows the values of IE_1 for the first 10 elements. (a) Label each point with the symbol of the appropriate element. (b) Give detailed reasons for the observed trend in values.
- 1.36 (a) Using the data in Table 1.5, determine a value for ΔH for the process:
- $$\text{O}(\text{g}) + 2\text{e}^- \rightarrow \text{O}^{2-}(\text{g})$$
- (b) Comment on the relevance of the sign and magnitude of your answer to part (a) in the light of the fact that many metal oxides with ionic lattices are thermodynamically stable.

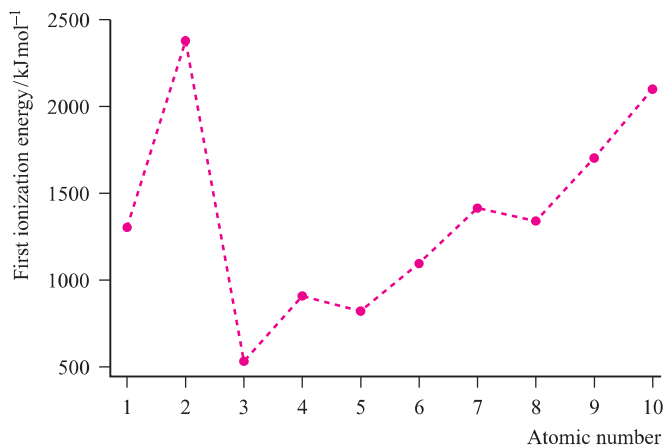


Fig. 1.17 Graph for problem 1.35.

OVERVIEW PROBLEMS

- 1.37 How do you account for the fact that, although potassium is placed after argon in the periodic table, it has a lower relative atomic mass?
- 1.38 What is the evidence that the *aufbau* principle is only approximately true?
- 1.39 The first list in the table opposite contains symbols or phrases, each of which has a 'partner' in the second list. Match the 'partners'; there is only one match for each pair of symbols or phrases.
- 1.40 Suggest explanations for the following.
- (a) High values of ionization energies are associated with the noble gases.
- (b) The enthalpy changes associated with the attachment of the first and second electrons to an O atom are exothermic and endothermic, respectively.
- (c) In an Li atom in its ground state, the outer electron occupies a $2s$ rather than a $2p$ orbital.

List 1	List 2
S_6 and S_8	electron
^{19}F and ^{31}P	proton
isotope of hydrogen	pnictogens
^{12}C and ^{13}C	<i>d</i> -block elements
hydrogen ion	protium
group 1 elements	fundamental particles
same energy	$m_s = \pm\frac{1}{2}$
negatively charged particle	allotropes
spin-paired electrons	degenerate
electron, proton and neutron	monotopic elements
group 15 elements	alkali metals
Cr, Mn, Fe	isotopes of an element

- 1.41 Using data from Appendix 8, construct a graph to show the trend in the third ionization energies of the elements from Li to Kr. Compare the graph with that shown in Fig. 1.16, and rationalize what you observe.
- 1.42 The sign convention for electron affinity can often cause confusion for students. In this textbook, why have we referred to ‘an enthalpy change for the attachment of an electron’ rather than to an ‘electron affinity’?
- 1.43 (a) How would Fig. 1.9 have to be modified to show boundary surfaces for the $2s$ and the $3p$ wavefunctions of a one-electron species?
 (b) ‘The probability of finding the electron of a ground-state hydrogen atom at a distance r from the proton is at a maximum when $r = 52.9$ pm.’ Why is this statement compatible with the maximum in the value of $R(r)$ at $r = 0$?

INORGANIC CHEMISTRY MATTERS

- 1.44 Ruthenium, osmium, rhodium, iridium, palladium and platinum (Fig. 1.14) are called the platinum group metals. Most of the world’s reserves of these metals are in mineral deposits in Russia, Canada and South Africa. The platinum group metals are important as catalysts for air pollution control (e.g. in catalytic converters) and in the manufacture of organic and inorganic chemicals, and they have applications in the electronics industry. Thus, countries such as the US depend upon importing the metals and upon their recycling. The table below gives import data for the US for 2008:

Metal	Ru	Os	Rh	Ir	Pd	Pt
Imported amount/kg	49 800	11	12 600	2550	120 000	150 000

Plot bar charts to illustrate these data, first using mass on the vertical axis, and then using a logarithmic scale. Comment on the advantages or disadvantages of the two plots.

- 1.45 Figure 1.18 shows the emission spectrum of sodium. Low-pressure sodium street lamps depend upon this bright yellow emission from sodium atoms excited by an electrical discharge. Figure 1.18 shows a

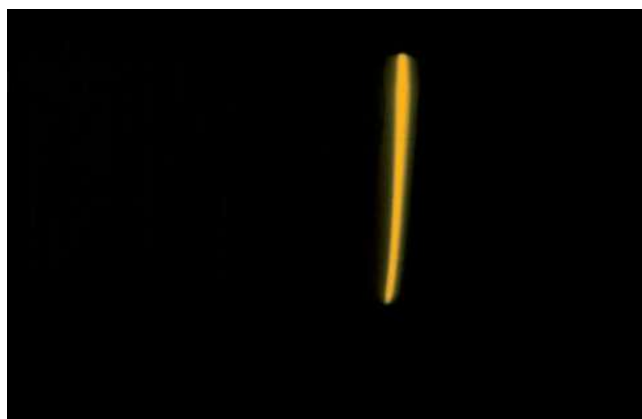


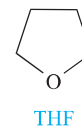
Fig. 1.18 The emission spectrum of sodium. The apparent single line consists of two very close emissions at 589.0 and 589.6 nm.

simple spectrum (see figure caption), but the National Institute of Standards and Technology (NIST) atomic spectra database lists 5888 lines in the emission spectrum of sodium. Suggest *three* reasons why no other lines are visible in Fig. 1.18. (b) The wavelengths of the yellow lines in Fig. 1.18 are close to 589 nm. To what frequency does this correspond? (c) Give a *general* explanation of how a series of spectral lines such as those in Fig. 1.18 arises.

Self-study exercises

1. Draw the structures of the two isomers of octahedral $[\text{Cr}(\text{OH}_2)_4\text{Cl}_2]^+$ and give labels that distinguish the isomers.
2. $[\text{PtCl}_2(\text{PEt}_3)_2]$ possesses two stereoisomers. Is the complex square planar or tetrahedral? Rationalize your answer.
3. Draw the structures of *mer*- and *fac*- $[\text{RhCl}_3(\text{OH}_2)_3]$. What is the coordination geometry at the metal centre?

4. Tetrahydrofuran (THF) has the following structure and coordinates to metal ions through the oxygen atom. Draw the structures of the three possible isomers of trigonal bipyramidal $[\text{MnI}_2(\text{THF})_3]$.



FURTHER READING

- P. Atkins and J. de Paula (2010) *Atkins' Physical Chemistry*, 9th edn, Oxford University Press, Oxford – This text gives a solid and well-tested background in physical chemistry.
- J. Barrett (2002) *Structure and Bonding*, RSC Publishing, Cambridge – An introductory text that includes valence bond, molecular orbital and VSEPR theories.
- R.J. Gillespie (2008) *Coord. Chem. Rev.*, vol. 252, p. 1315 – ‘Fifty years of the VSEPR model’.
- R.J. Gillespie and E.A. Robinson (2005) *Chem. Soc. Rev.*, vol. 34, p. 396 – A ‘tutorial review’ ‘Models of molecular geometry’ that considers the VSEPR model and the more recently developed ligand close-packing (LCP) model.
- D.O. Hayward (2002) *Quantum Mechanics for Chemists*, RSC Publishing, Cambridge – An undergraduate student text that covers the basic principles of quantum mechanics.
- C.E. Housecroft and E.C. Constable (2010) *Chemistry*, 4th edn, Prentice Hall, Harlow – This text provides clear discussion of the fundamental principles of bonding in molecules at an introductory level.
- R. McWeeny (1979) *Coulson's Valence*, 3rd edn, Oxford University Press, Oxford – A classic book containing a general treatment of chemical bonding with a detailed mathematical approach.
- D.W. Smith (2004) *J. Chem. Educ.*, vol. 81, p. 886 – A useful article entitled ‘Effects of exchange energy and spin-orbit coupling on bond energies’.
- M.J. Winter (1994) *Chemical Bonding*, Oxford University Press, Oxford – This ‘primer’ for first year undergraduates approaches chemical bonding non-mathematically.

PROBLEMS

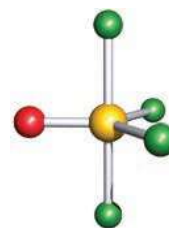
- 2.1 Draw Lewis structures to describe the bonding in the following molecules: (a) F_2 ; (b) BF_3 ; (c) NH_3 ; (d) H_2Se ; (e) H_2O_2 ; (f) BeCl_2 ; (g) SiH_4 ; (h) PF_5 .
- 2.2 Use the Lewis structure model to deduce the type of nitrogen–nitrogen bond present in (a) N_2H_4 , (b) N_2F_4 , (c) N_2F_2 and (d) $[\text{N}_2\text{H}_5]^+$.
- 2.3 Draw the resonance structures for the O_3 molecule. What can you conclude about the net bonding picture?
- 2.4 Draw Lewis structures for (a) CO_2 , (b) SO_2 , (c) OF_2 and (d) H_2CO .
- 2.5 Each of the following is a radical. For which does a Lewis structure correctly confirm this property: (a) NO , (b) O_2 , (c) NF_2 ?
- 2.6 (a) Use VB theory to describe the bonding in the diatomic molecules Li_2 , B_2 and C_2 . (b) Experimental data show that Li_2 and C_2 are diamagnetic whereas B_2 is paramagnetic. Is the VB model consistent with these facts?
- 2.7 Using VB theory and the Lewis structure model, determine the bond order in (a) H_2 , (b) Na_2 , (c) S_2 , (d) N_2 and (e) Cl_2 . Is there any ambiguity with finding the bond orders by this method?
- 2.8 Does VB theory indicate that the diatomic molecule He_2 is a viable species? Rationalize your answer.
- 2.9 (a) Use MO theory to determine the bond order in each of $[\text{He}_2]^+$ and $[\text{He}_2]^{2+}$. (b) Does the MO picture of the bonding in these ions suggest that they are viable species?
- 2.10 (a) Construct an MO diagram for the formation of O_2 ; use only the valence orbitals of the oxygen atoms. (b) Use the diagram to rationalize the following trend in O–O bond distances: O_2 , 121 pm; $[\text{O}_2]^+$, 112 pm; $[\text{O}_2]^-$, 134 pm; $[\text{O}_2]^{2-}$, 149 pm. (c) Which of these species are paramagnetic?
- 2.11 Confirm that the octet rule is obeyed by *each* of the atoms in the following molecules: (a) CF_4 , (b) O_2 , (c) AsBr_3 , (d) SF_2 .


- 2.12 Draw charge-separated resonance structures to give a representation of the bonding in PF_5 such that the octet rule is strictly obeyed.
- 2.13 One member of each of the following sets of compounds is not isoelectronic with the others. Which one in each set is the odd one out?
- (a) $[\text{NO}_2]^+$, CO_2 , $[\text{NO}_2]^-$ and $[\text{N}_3]^-$
 (b) $[\text{CN}]^-$, N_2 , CO , $[\text{NO}]^+$ and $[\text{O}_2]^{2-}$
 (c) $[\text{SiF}_6]^{2-}$, $[\text{PF}_6]^-$, $[\text{AlF}_6]^{3-}$ and $[\text{BrF}_6]^-$
- 2.14 In the following table, match a species in list 1 with an isoelectronic partner in list 2. Some species may have more than one partner. Qualify how you have interpreted the term *isoelectronic*.

List 1	List 2
F_2	$[\text{H}_3\text{O}]^+$
NH_3	$[\text{GaCl}_4]^-$
$[\text{GaBr}_4]^-$	Cl_2
$[\text{SH}]^-$	$[\text{NH}_4]^+$
$[\text{BH}_4]^-$	$[\text{OH}]^-$
$[\text{AsF}_6]^-$	$[\text{O}_2]^{2-}$
$[\text{PBr}_4]^+$	SeF_6
HF	SiBr_4

- 2.15 Using the data in Table 2.2, determine which of the following covalent single bonds is polar and (if appropriate) in which direction the dipole moment acts. (a) $\text{N}-\text{H}$; (b) $\text{F}-\text{Br}$; (c) $\text{C}-\text{H}$; (d) $\text{P}-\text{Cl}$; (e) $\text{N}-\text{Br}$.

- 2.16 Pick out *pairs* of isoelectronic species from the following list; not all species have a 'partner': HF ; CO_2 ; SO_2 ; NH_3 ; PF_3 ; SF_4 ; SiF_4 ; SiCl_4 ; $[\text{H}_3\text{O}]^+$; $[\text{NO}_2]^+$; $[\text{OH}]^-$; $[\text{AlCl}_4]^-$.
- 2.17 Use the VSEPR model to predict the structures of (a) H_2Se , (b) $[\text{BH}_4]^-$, (c) NF_3 , (d) SbF_5 , (e) $[\text{H}_3\text{O}]^+$, (f) IF_7 , (g) $[\text{I}_3]^-$, (h) $[\text{I}_3]^+$, (i) SO_3 .
- 2.18 Use the VSEPR model to rationalize the structure of SOF_4 shown in Fig. 2.19. What are the bond orders of (a) each $\text{S}-\text{F}$ bond and (b) the $\text{S}-\text{O}$ bond?
- 2.19 Determine the shapes of each of the following molecules and then, using the data in Table 2.2, state whether each is expected to be polar or not: (a) H_2S ; (b) CO_2 ; (c) SO_2 ; (d) BF_3 ; (e) PF_5 ; (f) *cis*- N_2F_2 ; (g) *trans*- N_2F_2 ; (h) HCN .
- 2.20 State whether you expect the following species to possess stereoisomers and, if so, draw their structures and give them distinguishing labels: (a) BF_2Cl ; (b) POCl_3 ; (c) MePF_4 ; (d) $[\text{PF}_2\text{Cl}_4]^-$.



 **Fig. 2.19** The structure of SOF_4 .

OVERVIEW PROBLEMS

- 2.21 (a) Draw resonance structures for CO , choosing only those that you think contribute significantly to the bonding.
 (b) Figure 2.15a shows an MO diagram for CO . Two MOs are illustrated by schematic representations. Draw similar diagrams for the remaining six MOs.
- 2.22 (a) On steric grounds, should *cis*- or *trans*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ be favoured?
 (b) Use the VSEPR model to rationalize why SNF_3 is tetrahedral but SF_4 has a see-saw geometry.
 (c) Suggest why KrF_2 is a linear rather than bent molecule.
- 2.23 Account for each of the following observations.
 (a) IF_5 is a polar molecule.
 (b) The first ionization energy of K is lower than that of Li .
 (c) BI_3 is trigonal planar while PI_3 is trigonal pyramidal in shape.
- 2.24 Suggest reasons for the following observations.
 (a) The second ionization energy of He is higher than the first despite the fact that both electrons are removed from the $1s$ atomic orbital.
 (b) Heating N_2F_2 at 373 K results in a change from a non-polar to polar molecule.
 (c) S_2 is paramagnetic.
- 2.25 Account for each of the following observations.
 (a) The mass spectrum of molecular bromine shows three lines for the parent ion $[\text{Br}_2]^+$.
 (b) In the structure of solid bromine, each Br atom has one nearest neighbour at a distance of 227 pm, and several other next nearest neighbours at 331 pm.
 (c) In the salt formed from the reaction of Br_2 and SbF_5 , the $\text{Br}-\text{Br}$ distance in the $[\text{Br}_2]^+$ ion (215 pm) is shorter than in Br_2 .

- 2.26 (a) Draw possible stereoisomers for the trigonal bipyramidal $[\text{SiF}_3\text{Me}_2]^-$ anion (Me = CH_3). An X-ray diffraction study of a salt of $[\text{SiF}_3\text{Me}_2]^-$ shows that two F atoms occupy axial sites. Suggest why this stereoisomer is preferred over the other possible structures that you have drawn. (b) Account for the fact that members of the series of complexes $[\text{PtCl}_4]^{2-}$, $[\text{PtCl}_3(\text{PMe}_3)]^-$, $[\text{PtCl}_2(\text{PMe}_3)_2]$ and $[\text{PtCl}(\text{PMe}_3)_3]^+$ do not possess the same number of stereoisomers.
- 2.27 (a) Write down the ions that are present in the compound $[\text{PtCl}_4][\text{PtCl}_3\text{F}_3]$. What shape do you expect each ion to adopt? In theory, does either ion possess stereoisomers?
- (b) Use the VSEPR model to rationalize why BCl_3 and NCl_3 do not adopt similar structures. Is either molecule expected to be polar? Rationalize your answer.
- 2.28 Assuming that the VSEPR model can be applied successfully to each of the following species, determine how many different fluorine environments are present in each molecule or ion: (a) $[\text{SiF}_6]^{2-}$, (b) XeF_4 , (c) $[\text{NF}_4]^+$, (d) $[\text{PHF}_5]^-$, (e) $[\text{SbF}_5]^{2-}$.
- 2.29 Critically compare the VB and MO treatments of the bonding in O_2 , paying particular attention to the properties of O_2 that the resulting bonding models imply.

INORGANIC CHEMISTRY MATTERS

- 2.30 The table below gives the average composition of the Earth's atmosphere (ppm = parts per million). Water vapour is also present in small and variable amounts.

Gas	Average amount/ppm	Gas	Average amount/ppm
He	5.2	CH_4	1.72
Ne	18	CO	0.12
Ar	9340	CO_2	355
Kr	1.1	N_2O	0.31
Xe	0.09	NO	<0.01
H_2	0.58	O_3	0.1–0.01
N_2	780840	SO_2	$<10^{-4}$
O_2	209460	NH_3	$<10^{-3}$

- (a) Draw a Lewis structure for N_2O , ensuring that each atom obeys the octet rule. (b) Use the VSEPR model to predict the molecular shapes of SO_2 , NH_3 , N_2O , CH_4 and CO_2 . (c) Which of the gases in the table are radicals? For each of the gases you have chosen, explain how the radical nature arises. (d) O_3 (ozone) is only present in <0.1 ppm. Nonetheless, it is a vital component of the Earth's atmosphere. Why? (e) Draw an MO diagram for the formation of N_2 from two N atoms, using only the valence orbitals. Use the diagram to rationalize why N_2 is chemically very inert. (f) What is the relationship between the monoatomic gases in the Earth's atmosphere?
- 2.31 Carbon monoxide is a toxic pollutant which arises from the partial combustion of carbon-based fuels. Complete combustion produces CO_2 . The toxicity of CO is a result of its competition for the O_2 -binding sites in blood, i.e. the iron present in haemoglobin (see Chapter 29). When CO binds to the iron, it prevents O_2 from being carried in the bloodstream. The following are resonance structures for CO:
- $$:\text{C}=\ddot{\text{O}}: \longleftrightarrow :\ddot{\text{C}}\equiv\overset{+}{\text{O}}:$$
- (a) Comment on these structures in terms of the octet rule. (b) How is the right-hand resonance structure related to a Lewis structure for N_2 ? (c) A primary interaction between CO and iron in haemoglobin involves a lone pair of electrons on the carbon atom. Using MO theory, explain how this lone pair arises. (d) Without treatment, severe CO poisoning is fatal. Explain why a hyperbaric chamber containing pure O_2 at a pressure of 1.4 bar is used to treat a patient with severe CO poisoning. Normal air contains 21% O_2 .
- 2.32 Volcanoes and deep sea hydrothermal vents are both associated with sulfur-rich environments. Mount Etna is classed as a continuously degassing volcano and emissions of SO_2 and H_2S are around 1.5 Tg y^{-1} and 100 Gg y^{-1} , respectively ($\text{Tg} = 10^{12} \text{ g}$; $\text{Gg} = 10^9 \text{ g}$). (a) Draw Lewis structures for H_2S and SO_2 , ensuring that the octet rule is obeyed by the S and O atoms. Your answer must be consistent with the fact that in SO_2 , the two sulfur–oxygen bonds are the same length. (b) Are H_2S and SO_2 polar or non-polar molecules? If polar, draw a diagram to show the direction of the molecular dipole moment. (c) In the troposphere, SO_2 reacts with HO^\bullet radicals. Construct an MO diagram for HO^\bullet from H and O atoms, and deduce what you can about the bonding in HO^\bullet .

Topics

Symmetry operators
Symmetry elements
Point groups
Character tables
Vibrational modes in molecules
Chiral molecules

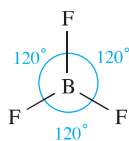
3

Introduction to molecular symmetry

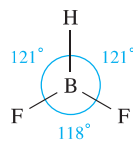
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
	1	1	1	1	z	x^2, y^2, z^2
	1	1	-1	-1	R_z	xy
	1	-1	1	-1	x, R_y	xz
	1	-1	-1	1	y, R_x	yz

3.1 Introduction

In chemistry, symmetry is important both at a molecular level and within crystalline systems. An understanding of symmetry is essential in discussions of molecular spectroscopy and calculations of molecular properties. A discussion of *crystal symmetry* is not included in this book, and we introduce only *molecular symmetry*. For qualitative purposes, it is sufficient to refer to the shape of a molecule using terms such as tetrahedral, octahedral or square planar. However, the common use of these descriptors is not always precise, e.g. consider the structures of BF_3 , **3.1**, and BF_2H , **3.2**, both of which are planar. A molecule of BF_3 is correctly described as being trigonal planar, since its symmetry properties are fully consistent with this description; all the F–B–F bond angles are 120° and the B–F bond distances are all identical (131 pm). It is correct to say that the boron centre in BF_2H , **3.2**, is in a *pseudo-trigonal planar* environment but the molecular symmetry properties are not the same as those of BF_3 . The F–B–F bond angle in BF_2H is smaller than the two H–B–F angles, and the B–H bond is shorter (119 pm) than the B–F bonds (131 pm).



(3.1)



(3.2)

The descriptor *symmetrical* implies that a species possesses a number of indistinguishable configurations. When structure **3.1** is rotated in the plane of the paper

through 120° , the resulting structure is indistinguishable from the first; another 120° rotation results in a third indistinguishable molecular orientation (Fig. 3.1). This is *not* true if we carry out the same rotational operations on BF_2H .

Group theory is the mathematical treatment of symmetry. In this chapter, we introduce the fundamental language of group theory (*symmetry operator*, *symmetry element*, *point group* and *character table*). The chapter does not set out to give a comprehensive survey of molecular symmetry, but rather to introduce some common terminology and its meaning. We include an introduction to the vibrational spectra of simple inorganic molecules and show how to use this technique to distinguish between possible structures for XY_2 , XY_3 and XY_4 molecules. Complete normal coordinate analysis of such species is beyond the remit of this book.

3.2 Symmetry operations and symmetry elements

In Fig. 3.1, we applied 120° rotations to BF_3 and saw that each rotation generated a representation of the molecule that was indistinguishable from the first. Each rotation is an example of a *symmetry operation*.

A *symmetry operation* is an operation performed on an object which leaves it in a configuration that is indistinguishable from, and superimposable on, the original configuration.

The rotations described in Fig. 3.1 are performed about an axis perpendicular to the plane of the paper and passing through the boron atom; the axis is an example of a *symmetry element*.