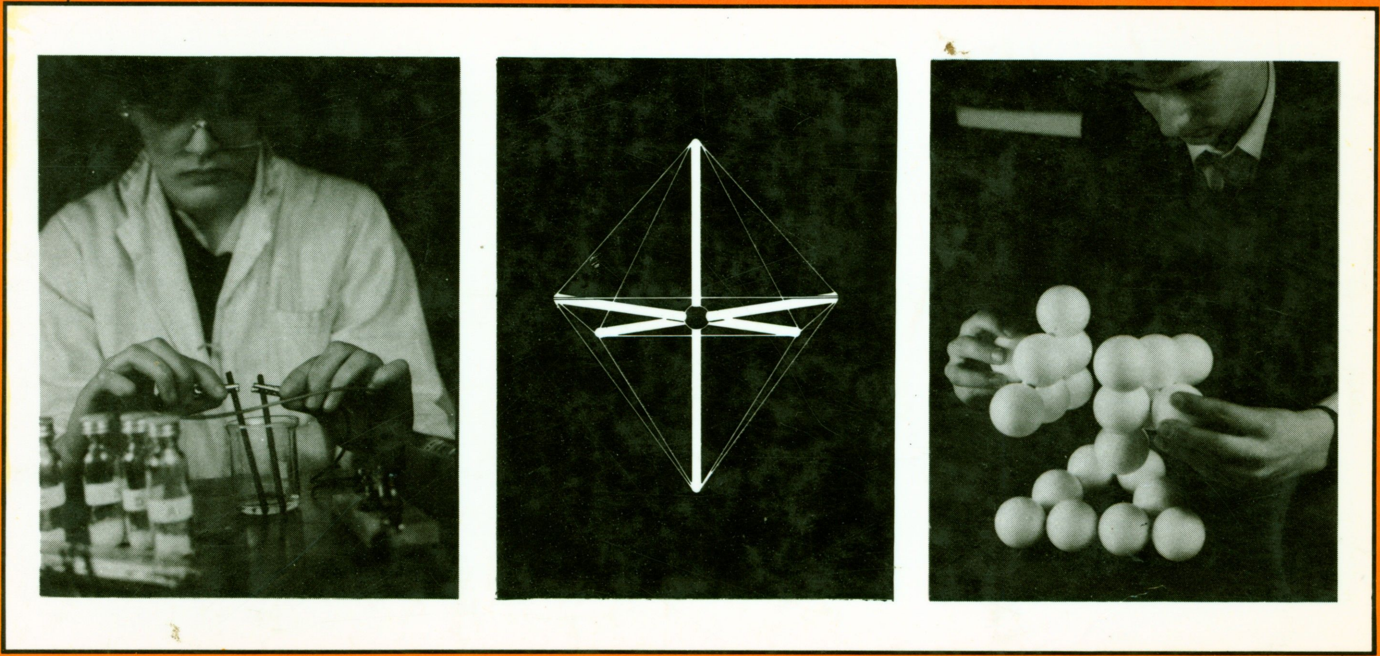
ILPAC

UNIT S4

INDEPENDENT LEARNING PROJECT FOR ADVANCED CHEMISTRY

Bonding and Structure



Periodic Table of the Elements

I	II											III	IV	V	VI	VII	O
						1 H 1.0											2 He 4.0
3 Li 6.9	4 Be 9.0											5 B 10.8	6 C 12.0	7 N 14.0	8 O 16.0	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 39.9
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.9	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc 99.0	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 181.0	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 210.0	85 At 210.0	86 Rn 222.0
87 Fr 223.0	88 Ra 226.0	89 Ac 227.0															

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.1	93 Np (237)	94 Pu 239.1	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lw (257)

A value in brackets denotes the
mass number of the most stable isotope.

UNIT

S4

Bonding and Structure

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CONTENTS

LEVEL ONE

LEVEL TWO

PREFACE

This volume is one of twenty Units produced by ILPAC, the Independent Learning Project for Advanced Chemistry, written for students preparing for the Advanced Level examinations of the G.C.E. The Project has been sponsored by the Inner London Education Authority and the materials have been extensively tested in London schools and colleges. In its present revised form, however, it is intended for a wider audience; the syllabuses of all the major Examination Boards have been taken into account and questions set by these boards have been included.

Although ILPAC was initially conceived as a way of overcoming some of the difficulties presented by uneconomically small sixth forms, it has frequently been adopted because its approach to learning has certain advantages over more traditional teaching methods. Students assume a greater responsibility for their own learning and can work, to some extent, at their own pace, while teachers can devote more time to guiding individual students and to managing resources.

By providing personal guidance, and detailed solutions to the many exercises, supported by the optional use of video-cassettes, the Project allows students to study A-level chemistry with less teacher-contact time than a conventional course demands. The extent to which this is possible must be determined locally; potentially hazardous practical work must, of course, be supervised. Nevertheless, flexibility in time-tabling makes ILPAC an attractive proposition in situations where classes are small or suitably-qualified teachers are scarce.

In addition, ILPAC can provide at least a partial solution to other problems. Students with only limited access to laboratories, for example, those studying at evening classes, can concentrate upon ILPAC practical work in the laboratory, in the confidence that related theory can be systematically studied elsewhere. Teachers of A-level chemistry who are inexperienced, or whose main discipline is another science, will find ILPAC very supportive. The materials can be used effectively where upper and lower sixth form classes are timetabled together. ILPAC can provide 'remedial' material for students in higher education. Schools operating sixth form consortia can benefit from the cohesion that ILPAC can provide in a fragmented situation. The project can be adapted for use in parts of the world where there is a severe shortage of qualified chemistry teachers. And so on.

A more detailed introduction to ILPAC, with specific advice both to students and to teachers, is included in the first volume only. Details of the Project Team and Trial Schools appear inside the back cover.

LONDON 1983

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8(L1976), 9(N1978), 10(L1979), 11(L1981), 12(L1976)
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Where answers to these questions are included, they are provided by ILPAC and not by the examination boards.

Questions from papers of other examining boards appear in other Units.

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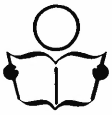
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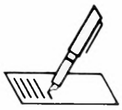
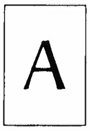

Exercise

Test



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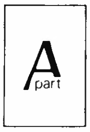

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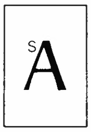
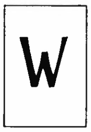


'A' Level question
Special paper



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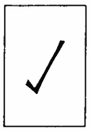
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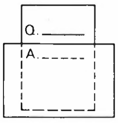
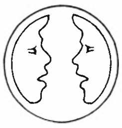
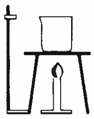


Revealing exercise


Discussion


Computer programme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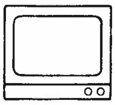
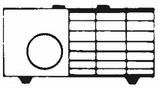

Video programme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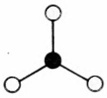

Model-making

INTERNATIONAL HAZARD SYMBOLS


Harmful


Flammable


Corrosive


Toxic


Explosive


Oxidising


Radioactive

INTRODUCTION

Whenever atoms, ions or molecules approach each other, there are electrostatic forces acting between them. When the net forces are forces of attraction, and they are strong enough to bind the particles together, we refer to them as chemical bonds. When particles are bound together by chemical bonds, the resulting arrangement is known as the structure of the substance concerned.

In this Unit, we identify five types of bond, all of which are electrostatic in nature, i.e. the result of attraction between positive and negative charges. They fall into two groups:

Strong interatomic bonds - ionic bonds
covalent bonds
metallic bonds
Weak intermolecular bonds - hydrogen bonds
van der Waals bonds

In Level One, we discuss the nature of the three strong interatomic bonds, and the different structures which result from them. We also consider the shapes of molecules and a simple explanation for them.

In Level Two, we introduce the ideas of polarization and electronegativity to show that the distinction between ionic and covalent bonds is rather blurred. In order to explain some of the observed properties of compounds with multiple covalent bonds, we introduce the concept of delocalized electrons.

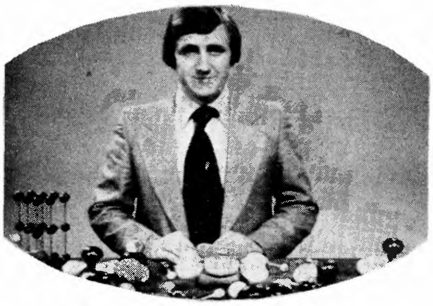
We then deal, in simple terms, with the interaction of atomic orbitals to form new molecular orbitals, including hybridization of atomic orbitals, and show how this gives an alternative description of the shapes of molecules.

We also look very briefly at weak intermolecular bonds, but a fuller treatment appears in a later Unit.

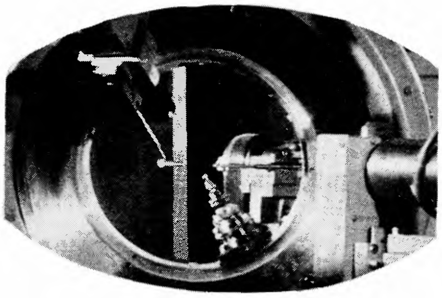
Finally, we deal with the concept of oxidation number as a method of book-keeping or accounting to keep track of the outer shell electrons in compounds.

There are two experiments in this Unit, both in Level One. The first of these is an exercise in model building.

There are two video-programmes designed to accompany this Unit. They are not essential but you should try to see them at the appropriate times if they are available.



Molecules and models



Instrumental techniques

PRE-KNOWLEDGE

Before you start work on this Unit, you should be able to:

(1) write the names and electron configurations of the first twenty elements in the Periodic Table;

(2) state and apply the 'noble gas rule' (sometimes called the 'octet rule') to describe the likely electron configurations of atoms in compounds;

(3) describe ionic bonding in simple cases (e.g. sodium chloride) in terms of electron transfer, using simple electron-shell diagrams;

(4) describe covalent bonding in simple cases (e.g. chlorine and methane) in terms of electron sharing, using simple electron-shell diagrams;

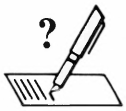
(5) draw structural formulae for simple covalent molecules, using short straight lines to represent covalent bonds;

(6) recognise that elements and compounds exist either as molecules or as giant structures, and give some examples of each;

(7) write formulae (not structural) for the following polyatomic ions - nitrate, carbonate, hydroxide, sulphate, hydrogencarbonate, ammonium;

(8) define oxidation and reduction in terms of electron transfer and give some simple examples.

PRE-TEST



To find out whether you are ready to start Level One, try the following test, which is based on the pre-knowledge items. You should not spend more than 30 minutes on this test. Hand your answers to your teacher for marking.

PRE-TEST

1. Write the electronic configurations of the following atoms, using the *s*, *p*, *d*, *f* notation.

   (a) B (b) F (c) Ca (d) P (e) Ne (5)

2. Why does calcium form a cation (positive ion), Ca^{2+}, whereas bromine forms an anion (negative ion), Br^-? (2)

3. Describe, by means of a sketch and an equation in each case, the rearrangement of electrons in the formation of:

   (a) sodium chloride from atoms of sodium and atoms of chlorine;

   (b) chlorine molecules from chlorine atoms. (6)

4. Draw electron shell diagrams for the following:

   (a) CH_4 (b) H_2O (2)

5. Draw structural formulae for the following:

   (a) C_3H_8 (b) NH_3 (c) C_2H_5OH (d) C_2H_4 (4)

6. Classify each of the following according to whether their atoms are held together in:

   A - simple molecules,

   B - giant structures held together by covalent bonds,

   C - giant structures held together by ionic bonds.

   (a) carbon (as diamond), C

   (b) magnesium oxide, MgO

   (c) methane, CH_4

   (d) potassium bromide, KBr

   (e) silicon(IV) oxide (silicon dioxide, silica), SiO_2

   (f) sulphur, S_8 (6)

7. Write formulae (not structural) for the following ions:

   (a) ammonium (d) nitrate

   (b) carbonate (e) sulphate

   (c) hydroxide (5)

(Continued overleaf.)

8. Classify the following changes as

A - oxidation

B - reduction

C - neither oxidation nor reduction

(a) $Mg \rightarrow Mg^{2+} + 2e^-$

(b) The conversion of chlorine to chloride ions.

(c) The precipitation of lead chloride by mixing solutions containing lead ions and chloride ions.

(d) The formation of copper at the cathode during the electrolysis of copper sulphate solution.

(e) The conversion of iron(II) ions to iron(III) ions. (5)

(Total 35 marks)

LEVEL ONE

We have produced a video-programme called 'Molecules and Models' which takes a broad view of much the subject matter of this Unit. If it is available we suggest that you view it now, or as soon as possible Don't expect to be able to take in everything at the first viewing - you should see it again when you have finished the Unit or, even better, look at parts of it as you work through the various topics.

Of the three types of strong interatomic bonding we deal first with ionic bonding. In the following sections, you extend your pre-A-level knowledge of the formation of ions.

IONS

Objectives. When you have finished these sections, you should be able to:

(1) describe the various electron configurations of stable simple ions;

(2) for polyatomic ions, distinguish between the covalent bonding within the ion and the ionic bonding between ions;

(3) explain the term ionic radius ;

(4) explain why the radius of an ion differs from the radius of its parent atom.

Read the whole section on ionic bonding in your text book. Bear in mind the objectives above, but also note down any sub-headings dealing with other aspects of ionic bonding. This will help you to locate material for more specific reading tasks later. Note that ionic bonding is still sometimes called electrovalent bonding and ionic giant structures are sometimes called ionic crystals or ionic lattices. You need not concern yourself at this stage with the details of different ionic giant structures.

Formation of ions

You have already learned that simple ions are formed from atoms by the gain or loss of electrons, and that the ions so formed have the electron configurations of noble gases in which the outer shell usually consists of a stable octet of electrons. In your pre-A-level course you have depicted the formation of ions by drawing electron-shell diagrams like Fig. 1.

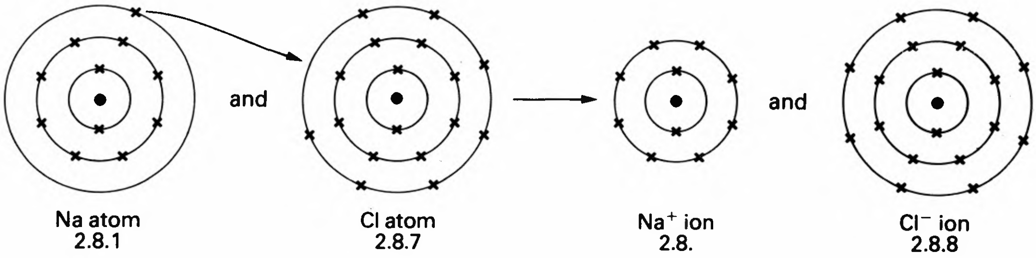
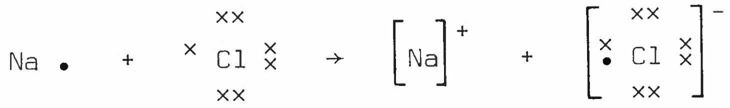


Fig. 1.

You will soon be aware of the limitations of these diagrams, but they are nevertheless quite useful even in A-level work for describing electron transfer and for checking that all electrons are accounted for. However, electron shell diagrams are rather tedious to draw, and give more information than we usually need when only the outer shell electrons are involved in reactions. We can simplify Fig. 1 to draw what we call a 'dot-and-cross' diagram showing only the outer shell electrons:



Electrons shown by dots and crosses are of course indistinguishable - we use different symbols only to show where they come from. Note also the use of brackets to separate the charge symbol from the symbols for electrons.

In the first exercise you draw some similar dot-and-cross diagrams yourself.

Exercise 1 Draw dot-and-cross diagrams for the formation of:

(a) magnesium oxide from magnesium atoms and oxygen atoms;

(b) calcium fluoride from calcium atoms and fluorine atoms.

(Answers on page 85)

Dot-and-cross diagrams are most often used to describe molecules and ions whose structures conform to the octet rule. However, not all ions have such structures, as you see in the next exercise.

Exercise 2 (a) Write down electron configurations, in *s*, *p*, *d*, *f* notation, using a noble gas core where appropriate, for the following ions:

(i) H^+

(ii) H^-

(iii) Sn^{2+}

(iv) Ca^{2+}

(v) Zn^{2+}

(vi) Mn^{2+}

(vii) Fe^{3+}

(viii) Cd^{2+}

(ix) Ga^+

Note that in the formation of Zn^{2+}, Mn^{2+}, Fe^{3+} and Cd^{2+} it is the outer *s*-electrons which are lost first - the reason for this, and the structures of other transition metal ions, are discussed in Unit I5: Transition Elements.

(b) Excluding H^+, which is unique, use the answers to (a) to identify three commonly occurring arrangements for outer shell electrons in addition to the 'stable octet'.

(c) Si^{4+}, C^{4-}, P^{5+} and B^{5-} are all isoelectronic with the noble gas neon, i.e. they have the same electron configurations. Why, therefore, do they not have a stable existence?

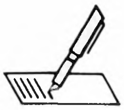
(Answers on page 85)

All the examples in Exercise 2 are simple ions, i.e. they are formed from single atoms. However, you have already met some polyatomic ions, such as NH_4^+ and CO_3^{2-}. It is important for you to distinguish between the ionic bonding which binds these ions to other ions, and the covalent bonding which binds the atoms within each ion. You will look more closely at this covalent bonding later - for the moment, treat polyatomic ions just like large simple ions. This simplification is useful when considering the shapes of ions.

Shapes of ions and ionic radii

The most useful model of an ion is to regard it as a uniformly charged sphere. You are aware that this is a simple model from your study of atomic structure and the shapes of orbitals, but it is nevertheless an adequate one for much of your A-level work, even for polyatomic ions. You can easily refine the model when it becomes necessary.

If an ion is a sphere, its radius is a convenient measure of its size. The next exercise concerns ionic radius.



Exercise 3 Do you expect the radius of (a) a sodium ion, Na^+, and (b) a chloride ion, Cl^-, to be greater or smaller than the radius of the parent atom? Explain your answer.

(Answer on page 85)

In Exercise 3, we were thinking of atoms and ions in isolation. However, there is no way of measuring the size of isolated atoms or ions. What we can measure very precisely are the distances between nuclei in crystalline solids and in molecules. Such measurements are made by X-ray diffraction (and electron diffraction) which you may study in a later Unit.

The results of X-ray diffraction experiments are often presented in the form of electron density maps. These are rather like the charge clouds you looked at in Unit S2 except that contour lines, rather than density of shading, are used to indicate the most probable position of electrons. An example is shown in Fig. 2, and you can derive ionic radius from it in the next exercise.

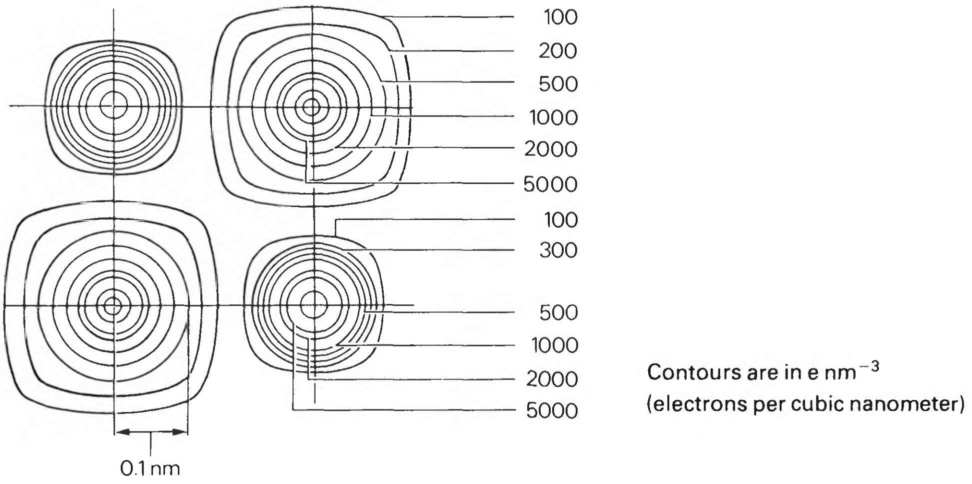


Fig. 2. Electron density map for sodium chloride

Exercise 4 (a) Fig. 2 shows two sodium ions and two chloride ions. Look at the electron densities, especially near the nuclei, to decide which are the chloride ions.

(b) Does the map show precisely the boundaries between chloride ions and sodium ions?

(c) Use a ruler and the map scale to obtain approximate values for the radii of sodium ions and chloride ions.

(Answers on page 85)

If it is available, view the section of the ILPAC video-programme 'Instrumental Techniques' which deals with X-ray diffraction. This programme does not cover any theory but shows how an X-ray diffractometer, in conjunction with a computer, is used to determine the structure of a crystalline solid.

Because ions do not have precise boundaries and because they are not precisely spherical, ionic radii obtained from different sources do not always agree very closely. Nevertheless, by thinking of ions as charged spheres of fixed radius, we can easily visualize the nature of ionic bonding.

IONIC BONDING

A charged sphere is surrounded by a uniform electric field and therefore attracts oppositely charged spheres in all directions - see Fig. 3. No particular orientation is favoured, so we often say that ionic bonding is non-directional. What we really mean by this is that the forces of attraction are non-directional.

However, when large numbers of oppositely-charged spherical ions are attracted to each other, the repulsion of the like-charges also comes into play. Mutual repulsion of similarly-charged ions limits the number which can come into contact with an oppositely-charged ion, and effectively fixes their relative positions.

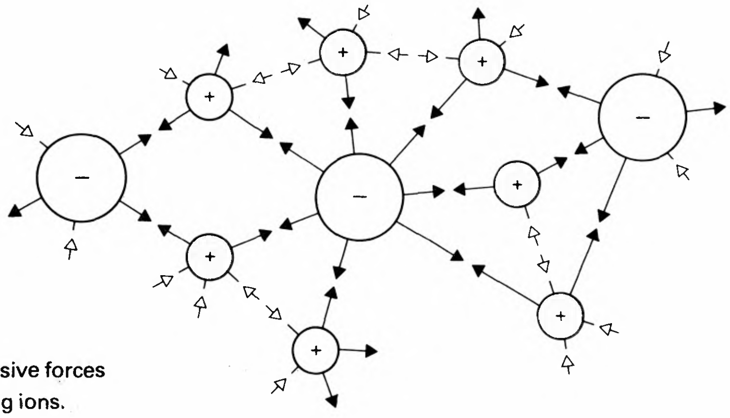


Fig. 3. Attractive and repulsive forces between approaching ions.

Ions, therefore, tend to cling together in large clusters known as ionic lattices (ionic giant structures, ionic crystals) in which attractive and repulsive forces are balanced. The particular arrangement of ions depends on their relative charges and sizes. You now study two common arrangements.

Caesium chloride and sodium chloride structures

The structures of these two compounds are typical of many ionic compounds. The differences between them are accounted for by the different relative sizes of the ions.

Objectives. When you have finished this section, you should be able to:

(5) describe and sketch the caesium chloride structure;

(6) describe and sketch the sodium chloride structure;

(7) explain why radius ratio determines the structure of an ionic lattice;

(8) explain the term co-ordination number;

(9) explain the term unit cell.

Read about the structures of caesium chloride and sodium chloride in your text-book(s). Look for an explanation of the difference between these structures in terms of ionic radii and coordination number. Look also for a description of the unit cell as the smallest unit of structure which has all the features of the whole and which could therefore be used to build up the structure by simple repetition. Note that you do not need to remember numerical values for radius ratio.

To do the following exercises ask your teacher for crystal models of sodium chloride and caesium chloride. You also need to refer to good drawings in text-books.

Exercise 5 (a) Sketch the unit cell of the caesium chloride structure, using marks of different colour or shape to represent the centres of ions. (Don't try to draw touching spheres!)

(b) Sketch the sodium chloride structure in the same way.

(c) Write down the coordination numbers for each ion in the two structures.

(Answers on page 85)

Exercise 6 (a) Explain why sodium chloride could not adopt the caesium chloride structure.

(b) Look up the relevant ionic radii and predict which of these two structures would be adopted by:

(i) potassium fluoride, KF

(ii) sodium bromide, NaBr

(iii) magnesium oxide, MgO

(Answers on page 85)

Exercise 7 (a) Why is ionic bonding referred to as 'non-directional'?

(b) Why is it misleading to refer to 'a molecule of sodium chloride'?

(Answers on page 86)

Having looked at some different types of ionic lattice, we now remind you of lattice energy, which you studied in the last Unit, and show how it gives an idea of the strength of ionic bonding.

Strength of ionic bonding - lattice energy

Objective. When you have finished this section you should be able to:

(10) use lattice energy as an indication of the strength of ionic bonding.

You have already studied lattice energies in the previous Unit. In the following exercise you recall some of what you have learned, and go on to discover a limitation in the use of lattice energy as an indication of the strength of ionic bonds.

Exercise 8 (a) Define lattice energy, using sodium chloride as an example.

(b) Is it possible to say how many ionic bonds are made in the formation of one mole of NaCl from gaseous ions?

(c) Is is possible to obtain from the lattice energy the strength of an ionic bond between Na^+ and Cl^-?

(Answers on page 86)

Despite the fact that lattice energy does not refer to the strength of individual bonds, it is nevertheless a very useful quantity for comparing the strength of ionic bonding in different substances, especially if they have the same structure.

Having looked at the nature and strength of ionic bonding, we now turn to the properties which enable us to recognise ionic compounds.

Recognition of ionic compounds

Objectives. When you have finished this section, you should be able to:

(11) list properties typical of ionic compounds;

(12) indicate, for each of the properties listed, how useful it is in testing whether or not a given substance is ionic.

Read the section in your text-book(s) on the properties of ionic compounds and then attempt the following exercise.

Exercise 9 How do the following simple properties help us to recognise ionic compounds?

(a) hardness;

(b) melting point;

(c) solubility in water;

(d) action of electricity on

  (i) the molten substance (or melt),

  (ii) an aqueous solution.

In each case suggest, with reasons, how useful the property might be in a simple test to decide whether a substance is ionic.

(Answers on page 86)

Another interesting property, though it is not very useful in identification, is that ionic crystals can be split or cleaved.

Cleavage of crystals

Crystals can be split, with varying degrees of difficulty, to reveal new flat surfaces. This is known as cleavage of crystals, and it always occurs in preferred directions, along the planes of atoms, molecules or ions which make up the structure. Such planes are often known as cleavage planes.

Cleavage of ionic crystals might be expected to be difficult because ionic bonding is usually very strong. However, some planes cleave much more readily than others because a slight displacement along the plane, caused by a sharp blow, brings ions of like charge opposite one another so that strong attraction between planes suddenly becomes strong repulsion. This is shown in Fig. 4.

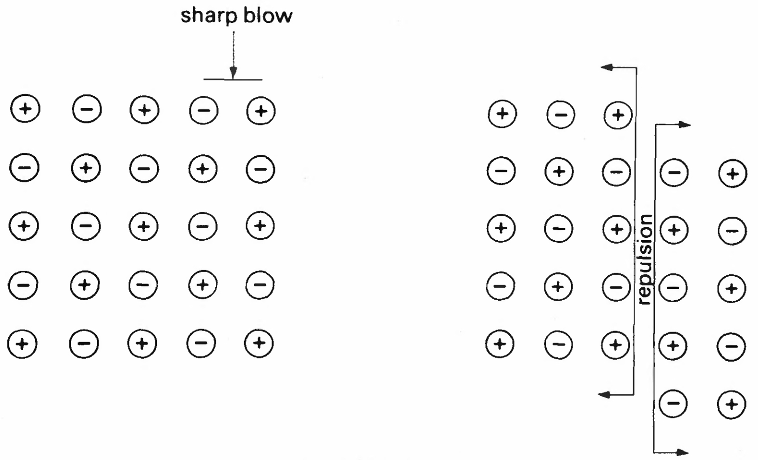


Fig. 4. Cleavage of an ionic lattice.

If you have never cleaved a calcite crystal, ask your teacher if you can do so now. Calcite is an ionic compound with a hexagonal structure. It is somewhat similar to the sodium chloride structure except that the anions, CO_3^{2-} ions in this case, are not spherical. This distorts the cubic shape of the unit cell.

The cleavage of a calcite crystal shows clearly that certain planes separate more easily than others. You investigate the preferred directions of cleavage planes in an ionic structure in the next exercise.

Exercise 10 Fig. 5 shows the orientation of three sets of planes of ions in a sodium chloride lattice. Look at these planes in a ball and spoke model of the sodium chloride structure, or drawings, and decide which of the three sets are likely to be cleavage planes. Explain your answer.

(Hint. Look at the composition of adjacent parallel planes and see whether a slight displacement would bring ions of the same charge opposite each other.)

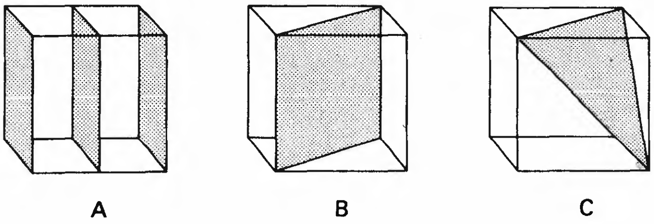


Fig. 5.

(Answer on page 86)

You have seen in your study of ionic bonding how the transfer of electrons from one atom to another gives rise to electrostatic forces of attraction which bind the ions together. Electrostatic forces of attraction can also arise from a different way of rearranging electrons. You pursue this in the following sections on covalent bonding.

COVALENT BONDING

You should already be familiar with the representation of covalent bonding such as Fig. 6 which shows the formation of a chlorine molecule.

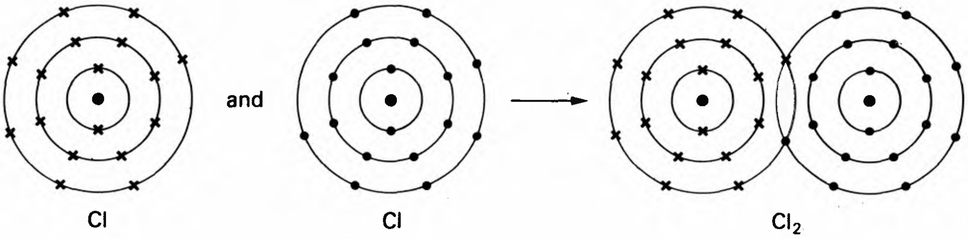


Fig. 6.

In view of what you have learned about electrons and orbitals in Unit S2, you should see that this is clearly an inadequate model because it suggests that a pair of electrons is stationary between the two nuclei. A better model uses the idea of overlapping charge clouds as in Fig. 7.

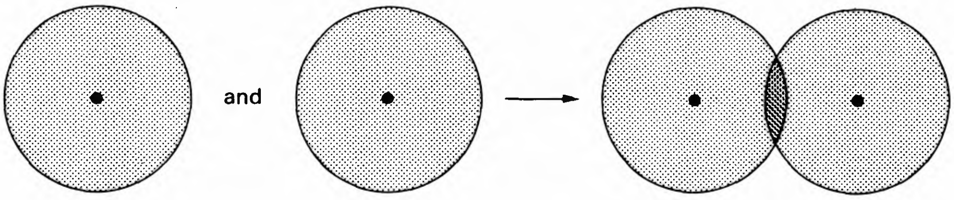


Fig. 7.

It seems that even this model exaggerates the concentration of negative charge between the nuclei. The actual charge distribution has been worked out for a hydrogen molecule ion, H_2^+, which has only one electron, and is shown in Figs. 8 and 9.

Fig. 8. Charge cloud for H_2^+

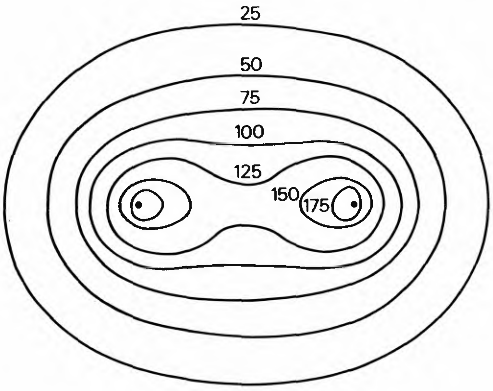


Fig. 9. Electron density map for H_2^+ (contours in e nm^{-3})

In each of these models, however, we can think of a region of negative charge interposed between two positive charges. The attractive forces between opposite charges show that covalent bonding, as well as ionic bonding, has electrostatic character.

Objectives. When you have finished this section, you should be able to:

(13) describe covalent bonding in terms of shared pairs of electrons;

(14) draw dot-and-cross diagrams for a variety of covalent molecules.

Read through the whole section or chapter dealing with covalent bonding in your text-book(s). Pay particular attention to the objectives above, but note down also any sub-headings dealing with other aspects of the topic. This will enable you to locate material for more intensive reading later and for help with exercises.

Dot-and-cross diagrams

Despite the limitations of the shared-pair model shown in Fig. 6, it is nevertheless very useful because it helps us to account for the number of covalent bonds actually formed in a great many known compounds. We can also make predictions about bonding in unknown compounds.

You can think of dot-and-cross diagrams as simplified versions of diagrams like Fig. 6, showing only outer shell electrons. Fig. 10 illustrates this for a chlorine molecule.

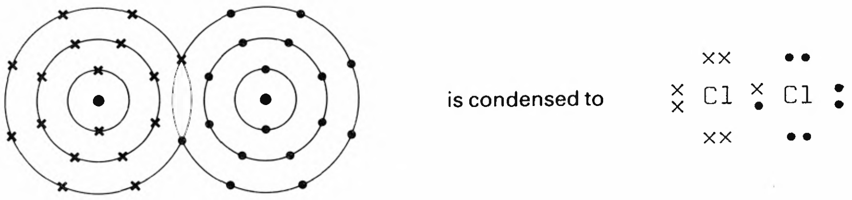
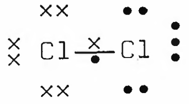


Fig. 10.

Note that the use of two (or even more) different symbols for the electrons does not mean that the electrons are different - it simply identifies the 'parent' atoms.

You may also encounter dot-and-cross diagrams with bond lines added, and also versions showing only the bonding electrons, such as



or

$\mathrm{Cl} \overset{\times}{\bullet} \mathrm{Cl}$

Use the version shown in Fig. 10 for the following exercise.

Exercise 11 Draw dot-and-cross diagrams and structural formulae for the following molecules:

(a) H_2 (d) CH_4 (g) C_2H_4

(b) HI (e) H_2O (h) $CHCl_3$

(c) NH_3 (f) CO_2 (i) F_2O

(Answers on page 86)

Exercise 12 (a) How many electrons are associated with the outer shell of each atom in the molecules in Exercise 11?

(b) You have learned in your pre-A-level course that hydrogen has a 'valency' or 'combining power' of 1, oxygen 2 and carbon 4. Explain these values in terms of your answer to part (a).

(Answer on page 86)

We now consider a special type of covalent bond known as the dative covalent bond or coordinate bond.

Dative covalent bonds

Objective. When you have finished this section, you should be able to:

(15) explain the term dative covalent bond;

(16) write dot-and-cross diagrams and structural formulae including dative bonds.

Read about dative covalent bonds in your text-book(s) - you may find them called, more simply, dative bonds or co-ordinate bonds. Look for some examples to help you do the following exercises. Note that there are two alternative ways of representing a dative bond, either $X \rightarrow Y$ or $X^{+}—Y^{-}$. We shall use the arrow in this Unit.

Exercise 13 A dative bond differs from a covalent bond in only one respect. What is this?

(Answer on page 87)

Exercise 14 Draw dot-and-cross diagrams and structural formulae for the following molecules and ions. In the structural formulae use an arrow to represent a dative bond.

(a) NH_4^+ (i.e. NH_3 linked with H^+)

(b) HNO_3 ($HONO_2$)

(c) CO

(d) N_2O (NNO)

(Answers on page 87)

So far, we have considered only those covalent compounds which observe the 'noble gas rule' or 'octet rule'. However, there are a number of cases where the rule does not apply. We now consider some of these.

Covalent compounds with fewer than eight outer-shell electrons per atom

When elements with fewer than four outer-shell electrons per atom form compounds they usually lose those electrons to form ions. However, for small atoms, the relevant ionization energies may be so high that covalent bonding occurs instead. Since there are fewer than four electrons available for sharing, there will then be fewer than eight outer shell electrons per atom in the resulting compound. Such compounds are often called 'electron-deficient', but you should not imagine there is anything wrong with them!

Objectives. When you have finished this section, you should be able to:

(17) draw dot-and-cross diagrams for at least two covalent compounds in which an atom other than hydrogen has fewer than eight outer-shell electrons.

The following exercises enable you to achieve this objective. You may need to use a text-book and a data book.

Exercise 15 Look at the ionic radii of elements with fewer than four electrons in their outer shells and select the three most likely to form covalent compounds. Explain your choice.

(Answer on page 87)

Exercise 16 Draw dot-and-cross diagrams for beryllium chloride, boron fluoride and aluminium chloride ($AlCl_3$). How many outer-shell electrons are there around the central atoms?

(Answer on page 87)

The molecules in Exercise 16 undoubtedly exist in certain conditions, as do all the other halides of Be, B and Al, but in each case there is a tendency for the 'stable octet' to be reached by means of dative bonding between neighbouring molecules. Read about this in your text-book(s) so that you can do the next exercise.

Exercise 17 Draw the structural formulae of:

(a) the long chain molecule found in solid beryllium chloride;

(b) the Be_2Cl_4 molecule found in gaseous beryllium chloride below 600 °C;

(c) the Al_2Cl_6 molecule found in the vapour at low temperatures;

(d) the molecule formed by combination between ammonia and boron trifluoride.

(Answers on page 87)

Now we consider some examples where the stable octet is exceeded.

Covalent compounds with more than eight outer-shell electrons per atom

Objective. When you have finished this section, you should be able to:

(18) draw dot-and-cross diagrams for at least two covalent compounds in which an atom has more than eight outer-shell electrons.

If the noble gas rule or octet rule always applied, no atom could have more than eight electrons in its outer shell. As a result no atom could have more than four single covalent bonds (or the equivalent) associated with it. The octet rule always applies for elements in the first two periods of the Periodic Table (H to Ar) but many other elements show a covalency greater than four in some of their compounds. The following formulae represent some examples.

PF_5 BrF_5 SF_6

SiF_6^{2-} PCl_6^- IF_7

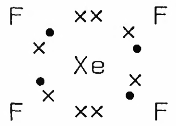
Outermost shells of twelve electrons are quite common.

Exercise 18 Draw dot and cross formulae and count the electrons round the central atoms of the following:

(a) PF_5 (b) SF_6 (c) PCl_6^-

(Answers on page 87)

A final example is xenon tetrafluoride XeF_4. (You have, no doubt, heard that the heavier noble gases do form a few compounds.) The molecule has two non-bonding electron pairs, as shown below.



You have now seen that the structural formulae of a great many compounds can be accounted for by regarding every covalent bond as a pair of shared electrons. A further application of this idea concerns the shapes of molecules.

SHAPES OF MOLECULES

Molecules cannot be seen - their existence is, of course, inferred from the larger-scale properties of matter but their shapes and dimensions can be worked out from the results of X-ray and electron diffraction photography and other physical investigations. You will consider some of these methods later, in Unit 02.

However, at this stage you can use a simple model which enables you to account for, and predict, the shapes of many molecules, and will help you to organise your factual knowledge. The model is known as the 'valence shell electron pair repulsion theory', but we will refer to it simply as the 'electron pair repulsion theory'.

Objectives. When you have finished this section, you should be able to:

(19) apply the electron pair repulsion theory to molecules involving 2,3,4,5 and 6 pairs of bonding electrons;

(20) extend the electron pair repulsion theory to include non-bonding pairs of electrons (lone pairs);

(21) use the following terms correctly to describe shapes of molecules linear, trigonal planar, tetrahedral, trigonal-pyramidal, trigonal-bipyramidal, octahedral.

Read about the valence shell electron pair repulsion theory in your text-book (it is also known as the Sidgwick-Powell theory). Note that the term valence shell is often used for what we call the outer-shell electrons. Look for descriptions and explanations of the typical shapes of simple molecules. Under the general heading shapes of molecules, you may find some extra discussion in terms of hybridization of orbitals - we consider this topic later in the Unit.

The exercises in the following sections test your understanding of the theory. Some model building, using balloons, is included as a useful analogy. Ask your teacher if balloons and some thread are available.

Linear molecules

Exercise 19 (a) How many pairs of bonding electrons are there in a molecule of beryllium hydride, BeH_2?

(b) If the electron pairs repel each other so that they occupy regions of space as far apart as possible, what shape must the molecules have? (If you cannot answer this, or if you do not understand the answer, try using the balloon model below.)

(Answers on page 87)

Blow up a long balloon, twist it in the centre, and tie a piece of thread tightly round the constriction to keep the two lobes separate, as in Fig. 11.

Fig. 11.

Think of each lobe as a region of space containing an electron pair. If you push the lobes together by bending the model, they repel each other and restore the linear shape. Can you see now why BeH_2 has a linear molecule? Other compounds of beryllium, such as the halides, have similar linear molecules.

You can apply the same principle to molecules containing multiple bonds in the next exercise.

Exercise 20 What shape would you expect for the following molecules? Explain your answer.

(a) CO_2 (b) HCN

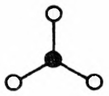
(Answers on page 87)

Trigonal (triangular) planar molecules

Exercise 21 (a) How many pairs of bonding electrons are there in a molecule of boron trifluoride, BF_3?

(b) By considering repulsion of electron pairs, what shape do you expect for BF_3? (You may need to use the balloon model below to convince you of the answer.)

(Answers on page 87)



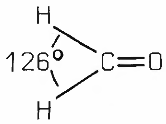
Blow up and tie a long balloon with a constriction in the middle. Also blow up and tie a shorter balloon the same size as each of the lobes in the long balloon - see Fig. 12. Use a length of thread to draw the neck of the shorter balloon as close to the constriction as possible. What shape do you have? If you move one of the lobes relative to the others, does it return to its original position?

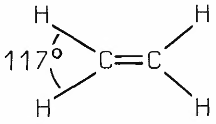
Fig. 12.

Trigonal planar molecules are found for other Group 3 elements but, as you have seen, they tend to form a dative bond to attain an octet of electrons.

Once again, you can apply the principle to molecules with multiple bonds, but now there is a slight modification to the shape, as you can see in the next exercise.

Exercise 22 The molecule of methanal (formaldehyde) is trigonal planar, and the molecule of ethene is based on a trigonal planar arrangement around each carbon atom, as shown below.





Explain why the bonds around each carbon atom are in a trigonal planar arrangement.

(Answer on page 88)

Note that equal bond angles of 120° are only found in symmetrical molecules, such as BF_3, where all the bonds are identical. Where the bonds are not identical, the repulsive forces are not identical either. In the absence of other factors, a double bond would repel the two single bonds rather more than they repel each other. Hence the H—C—H bond angle is <u>less</u> than 120° in ethene.

In methanal, however, another factor is present. Oxygen has such an affinity for electrons that the electron pairs in the double bond are drawn away from the carbon, thus reducing the repulsive forces between double and single bonds. The net result is an H—C—H bond angle <u>greater</u> than 120°.

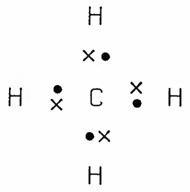
Tetrahedral molecules

Both the shapes we have considered so far are planar and are therefore easy to draw on paper. For this reason, dot-and-cross diagrams for linear and trigonal planar molecules can correspond also to their actual shapes. This is not the case for tetrahedral molecules, which are three-dimensional, as you can see in the next exercise.

Exercise 23 (a) How many pairs of bonding electrons are there in a molecule of methane, CH_4?

(b) By considering repulsion of electron pairs, what shape do you expect for the CH_4 molecule? If you cannot answer this, try the balloon modelling exercise which follows this exercise.

(c) By considering bond angles, show that electron pair repulsion would not give the square planar shape of the dot-and-cross diagram below.



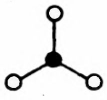
(d) State whether you expect the following molecules and ions to have an identical shape or a very similar shape to the CH_4 molecule. Give reasons.

(i) NH_4^+ (ii) $POCl_3$ (iii) $SiCl_4$

(iv) SO_4^{2-} (assume two dative bonds to O and two covalent bonds to O^-).

(Answers on page 88)

It is most important for you to be able to visualize tetrahedral bonding and to be able to draw it adequately, because it forms the basis of so many molecular shapes, especially in organic chemistry. We therefore suggest that you make the balloon model described below even if you have not needed to do so for the other shapes.



Blow up and tie two long balloons making them the same size and shape. Twist each one in the centre and tie thread round each constriction to keep the two lobes apart, as in Fig. 13.

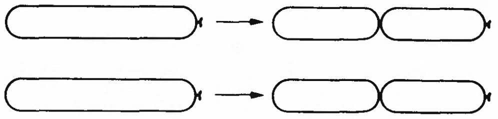


Fig. 13.

Now make a cross with the two balloons and force the two constrictions as close together as possible. You can pull them together with thread, or simply push the two balloons together.

You will find that the four lobes point to the corners of a tetrahedron, as in Fig. 14.

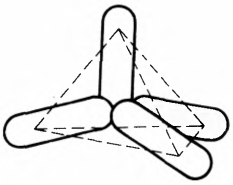


Fig. 14.

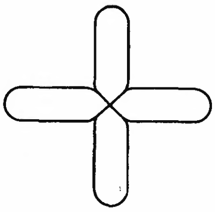


Fig. 15.

You can force the lobes into one plane, as in Fig. 15 but you will find that, when you leave go, they will return to their original positions.

Hold two lobes together with an elastic band to represent two pairs of electrons in a double bond. You will find that the balloons now have a trigonal planar arrangement, as in Fig. 16, similar to that in CH_2O and C_2H_4.

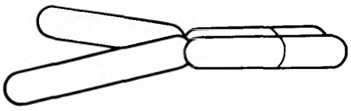


Fig. 16.

Now we consider two more molecular shapes which you may come across from time to time.

Trigonal-bipyramidal and octahedral molecules

If a molecule has five pairs of bonding electrons, e.g. phosphorus(V) fluoride, PF_5, its shape is a trigonal bipyramid - that is, two pyramids sharing the same triangular base, as in Fig. 17.

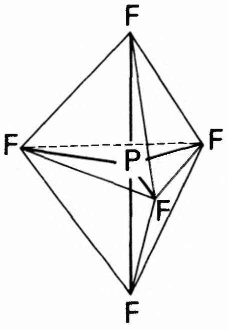


Fig. 17.

In this arrangement, the phosphorus atom is surrounded by three fluorine atoms in the same plane, and the other two fluorine atoms lie above and below this plane.

Exercise 24 What are the values of the bond angles in the molecule PF_5?

(Answer on page 88)

You can show that this shape follows from electron pair repulsion by making a balloon model. Blow up and tie five long balloons of the same size. Draw all five necks together with a length of thread. Do you have a trigonal bipyramid?

For a molecule like SF_6 or an ion like $FeCl_6{}^{3-}$, the shape is a regular octahedron, as in Fig. 18. This consists of two pyramids sharing a square base.

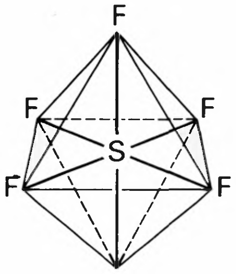


Fig. 18.

Here the central atom is at the centre of a plane containing four of the other atoms, while the other two lie above and below this plane.

Exercise 25 What are the values of the bond angles in the molecule SF_6?

(Answer on page 88)

You can show that the octahedral shape would be expected from electron pair repulsion by making a balloon model. Blow up three long balloons of the same size and make a tetrahedron with two of them as described on page 20. Make a constriction in the centre of the third balloon and then push the constriction into the centre of the tetrahedron so that you make a model with a six lobes. Is it octahedral?

So far, we have considered only molecules where all the outer shell electrons are used in bonding. However, many molecules have some electrons, called non-bonding pairs or lone pairs, which are not shared between two atoms. These electrons also affect the shape of the molecule by electron pair repulsion.

Non-bonding pairs

Ammonia provides a simple example of how a non-bonding pair affects the shape of a molecule. The next exercise concerns the ammonia molecule.

Exercise 26 (a) Draw a dot-and-cross diagram of the ammonia molecule, and count the pairs of electrons surrounding the nitrogen atom.

(b) In which directions (from the N atom) would you expect to find the electron pairs (or regions of greatest charge density)?

(c) What shape is outlined by the four atoms in the molecule?

(Answers on page 88)

Make sure that you can draw the shape of an ammonia molecule and show its relationship to a tetrahedron. However, the tetrahedron is not quite regular, because the four electron pairs are not identical - the lone pair, since it is not shared, remains closer to the N atom than the bonding pairs. You can see the effect on the shape in the next exercise.

Exercise 27 The three H N H bond angles in the ammonia molecule are found to be identical at 107° - see Fig. 19. Explain the difference between this angle and the tetrahedral angle.

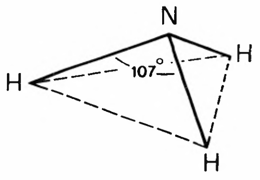


Fig. 19.

(Answer on page 88)

Trigonal pyramidal molecules are also found for other Group 5 elements. You can illustrate their shape using balloons as follows. Blow up and tie three long balloons of the same size to represent the bonding pairs and one rather shorter and fatter balloon to represent the lone pair, as in Fig. 20.

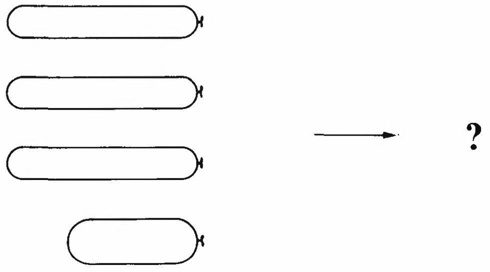


Fig. 20.

Draw the four necks tightly together with thread. Do you have a slightly distorted tetrahedron?

Now we consider molecules with two non-bonding pairs.

Two non-bonding pairs

You can apply what you have learned about the lone pair in the ammonia molecule in the following exercises.

Exercise 28 List the following electron pair repulsions in order of increasing magnitude (i.e. put the weakest repulsion at the top of the list).

(a) Bonding pair/bonding pair.

(b) Bonding pair/non-bonding pair.

(c) Non-bonding pair/non-bonding pair.

(Answers on page 88)

Exercise 29 (a) Draw a dot-and-cross diagram of a water molecule.

(b) Draw the shape of a water molecule, showing how it fits into a tetrahedron.

(c) Use your answer to the previous exercise to predict approximately the H—O—H bond angle.

(Answers on page 88)

Similar bent molecules (sometimes called 'dog-leg' molecules) are formed from other Group VI elements, e.g. H_2S, H_2Se, etc.

Exercise 30 Explain why the molecule of xenon tetrafluoride, XeF_4, is square planar in shape.

(Answer on page 88)

In our discussion of covalent bonding so far we have considered only the formation of separate molecules, which are most often found in gases and liquids. Now we look at some giant covalent structures, which are solids at ordinary temperatures.

GIANT COVALENT STRUCTURES

The sharing of pairs of electrons does not necessarily result in distinct (discrete) molecules. In a few cases, covalent bonding is extended indefinitely in three dimensions. However, the number of bonds per atom, and the directions they take up, are usually the same as in molecules. You now examine this extended covalent bonding in the two allotropes (different structural forms of the same element) of carbon - diamond and graphite.

Objectives. When you have completed this section, you should be able to:

(22) describe the structures of diamond and graphite;

(23) account for some of the difference in properties between diamond and graphite by reference to their structures.

The structure of diamond

Read about diamond and ask your teacher for a model of the diamond structure. Compare it with drawings in your text-book(s). The exercise which follows tests your understanding of the structure of diamond.

Exercise 31 (a) How many pairs of bonding electrons are there around each carbon atom in diamond?

(b) What is the co-ordination number of each atom?

(c) Draw a sketch showing how each atom in a diamond structure is related to its immediate neighbours. Include bond angles.

(Answers on page 88)

The sketch you have drawn is very useful in describing the diamond structure, but it does not, in fact, represent a unit cell. The unit cell has to contain all the features of the whole structure and is rather more complex, containing four tetrahedral units in a cube. You need not concern yourself with the precise arrangement.

Several other elements have the same structure as diamond (although the bonds are not as strong!) e.g. silicon, germanium and one form of tin. It is interesting that these are all Group 4 elements.

Many compounds have structures related to the diamond structure, in that they show a co-ordination number of 4 with tetrahedrally-directed bonds. One example is the crystobalite form of silica, SiO_2, in which the Si atoms are arranged as in diamond, but with an oxygen atom midway between each pair.

Another allotrope of carbon is graphite, which has a unique structure and, consequently, some very unusual properties.

The structure of graphite

Read about the properties and structure of graphite and ask your teacher for a model to compare with the drawings in your text-books.

Note that there are various ways of arranging the layers relative to one another in a model of graphite but the question of which one is 'correct' is not important because the layers can move so readily. For this reason, we will not consider the unit cell. The usual arrangement is to have the third layer directly above the first, with the second layer displaced diagonally by half the width of a hexagon.

The exercise which follows tests your understanding of the structure.

Exercise 32

(a) Sketch part of a single layer of the graphite structure, in plan view. (This sketch should form the basis of any description you may be asked to give of the structure.)

(b) What is the co-ordination number of each atom?

(c) Compare the inter-atomic distance within a layer with the inter-atomic distance between layers, and comment on the difference.

(d) The C—C bond length in a graphite layer is 0.143 nm, while in diamond it is 0.154 nm, and in a typical double bond compound like ethene, C_2H_4, it is 0.134 nm. What does this suggest about the distribution of electrons and the nature of this bond?

(Answers on page 89)

Having looked at the structures of diamond and graphite, you now compare their properties.

The properties of diamond and graphite

The properties of diamond and graphite are in dramatic contrast. Since both solids consist of identical carbon atoms only, the differences in properties must be entirely due to differences in structure.

In the following exercise you explore the relationship between structure and properties for diamond and graphite. Use your text-books as necessary to help you with your answers.

Exercise 33

(a) Why is diamond so much harder than graphite?

(b) Why does graphite conduct electricity while diamond does not?

(c) Why does diamond have a high melting point (3770 K)?

(d) Graphite contains weak van der Waals bonds, but nevertheless has a very high melting point - even higher than diamond. Explain.

(e) Why is graphite used in 'lead' pencils, and also as a lubricant?

(f) Look up the densities of diamond and graphite. Comment on the differences.

(g) Both graphite and diamond are almost totally insoluble in all kinds of solvent. Why is this?

(Answers on page 89)

The properties of giant covalent structures generally are similar to those of diamond - they tend to:

(i) have very high melting and boiling points, (ii) be hard and brittle, (iii) be insoluble, (iv) be non-conducting.

Compare these properties with those you have already noted for ionic compounds. Melting points and boiling points are only approximate indications of the strength of bonding. You can get a better idea in the next exercise by considering (or calculating) the energy required to break the bonds in both covalent and ionic giant structures.

<u>Exercise 34</u> (a) Use your data book to find the enthalpy changes for the following reactions. (You will probably find the first three listed, but may have to calculate the fourth.)

(i) $NaCl(s) \rightarrow Na^{+}(g) + Cl^{-}(g)$

(ii) $CaO(s) \rightarrow Ca^{2+}(g) + O^{2-}(g)$

(iii) $C(diamond) \rightarrow C(g)$

(iv) $SiO_2(s) \rightarrow Si(g) + 2O(g)$

(b) Does the range of values in your answer to part (a) suggest ionic and covalent bonds are of similar strengths?

(Answers on page 89)

You may have realised that the enthalpy changes you calculated in Exercise 34 are not strictly comparable as measures of bond strengths. This is because different numbers of bonds are involved in each case. Indeed, as we showed in Exercise 8, it is difficult to say how many ionic bonds there are in a given structure. Nevertheless, it is generally accepted that ionic and covalent bonding are similar in strength although there is quite a wide range for each type. The energies required to break the weak intermolecular forces in molecular crystals are much smaller, as we now show.

MOLECULAR CRYSTALS

You already know that weak forces of attraction exist between separate molecules and atoms. If this were not so, it would be impossible to liquefy and solidify gases. These forces are often known collectively as van der Waals forces although we shall distinguish two or three different types in Level Two of this Unit.

If the temperature of a gas is lowered, the molecules move more slowly and molecular collisions may be gentle enough to allow the forces to form van der Waals bonds between molecules in liquid and solid structures. Such solids are called molecular crystals.

Objectives. When you have finished this section, you should be able to:

(24) explain the term molecular crystal, and quote some examples;

(25) compare approximately the strength of van der Waals bonds with the strengths of ionic and covalent bonds;

(26) describe the general properties of molecular crystals.

Read about molecular crystals in your text-book(s). You should be able to quote examples, but you do not need to know the details of their structures. Look also for an account of the ways in which molecular crystals differ in their properties from other solid structures.

In the next exercise you get an idea of the strength of van der Waals bonds in a number of molecular crystals.

Exercise 35 (a) For each of the following substances, find the sum of the enthalpy changes associated with melting (fusion) and boiling (vaporization).

(i) iodine, I_2 (iii) benzene, C_6H_6

(ii) xenon, Xe (iv) tetrachloromethane, CCl_4

(Hint: look carefully at the units of any quantities you find listed.)

(b) How do the values you calculated in (a) compare with the values you obtained in Exercise 34?

(Answers on page 89)

The relatively small quantity of energy required to break van der Waals bonds is reflected in the low melting points and boiling points of molecular crystals. In the next exercise you consider how these properties, and others, help you to recognise molecular substances.

Exercise 36 How do the following properties help you to recognise molecular substances?

(a) physical state, (d) solubility in water,

(b) melting point, (e) solubility in organic solvents.

(c) conductivity,

(Answers on page 89)

Although you do not need to know the detailed structures of molecular crystals, one feature is important in relation to your use of the term 'atomic radius'.

Atomic radius, covalent radius and van der Waals radius

When we use the term 'atomic radius', we usually have in our minds an imprecise picture of a single isolated atom. Covalent radius and van der Waals radius have more precise definitions.

Objectives. When you have finished this section, you should be able to:

(27) explain why the term atomic radius cannot be used with precision;

(28) distinguish carefully between covalent radius and van der Waals radius.

Read about the different types of radius in your text-book(s). Your data book may also be helpful. (You may also find reference to metallic radius, which you will need in the next section.) Although 'atomic radius' is really rather a vague term, you may find it used to mean either covalent radius or van der Waals radius, or even both! The next exercise tests your understanding of the term.

Exercise 37 (a) Use your knowledge of electron orbitals as probability patterns to explain why it is impossible to give a value for the radius of an isolated atom.

(b) Copy Fig. 21 which represents part of an iodine crystal, and label clearly the covalent radius and van der Waals radius of iodine. Insert values from your data book.

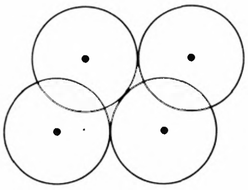


Fig. 21.

(c) Why is the van der Waals radius always greater than the covalent radius for a given element?

(d) What techniques are used to measure these radii?

(Answers on page 90)

Having dealt at some length with covalent bonding and ionic bonding, we now consider, much more briefly, the third type of strong interatomic bonding.

METALLIC BONDING

In this section, we elaborate a little on the simple model of metallic bonding you have used in your pre-A-level course. We look at some structures adopted by metals and also at their general properties.

Nature of metallic bonding

Objectives. When you have finished this section, you should be able to:

(29) describe a simple model of metallic bonding;

(30) explain why a metal is able to conduct electricity.

Read about metallic bonding in your text-book. Look for a description which will enable you to do the next exercise.

Exercise 38 Fig. 22 represents a simple model of part of a metallic structure.

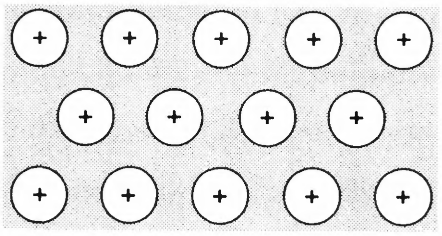


Fig. 22.

(a) Which electrons make up the 'sea' or 'cement' of electrons?

(b) Why are these electrons referred to as 'mobile' or 'delocalized'?

(c) How does a metal conduct electricity?

(d) In what two ways is metallic bonding similar to both ionic and covalent bonding?

(Answers on page 90)

The strong electrostatic attraction between positive ions and a diffuse cloud of mobile or delocalized electrons generally results in an ordered arrangement in which the ions approach as close to each other as possible, minimizing the space occupied by the electrons between them. Such an arrangement is known as close-packing, and you will study it more fully in the next section.

Close-packed metal structures

In this section you look carefully at two ways in which spheres can be close-packed.

Objectives. When you have finished this section, you should be able to:

(31) explain the term close-packing with reference to spheres;

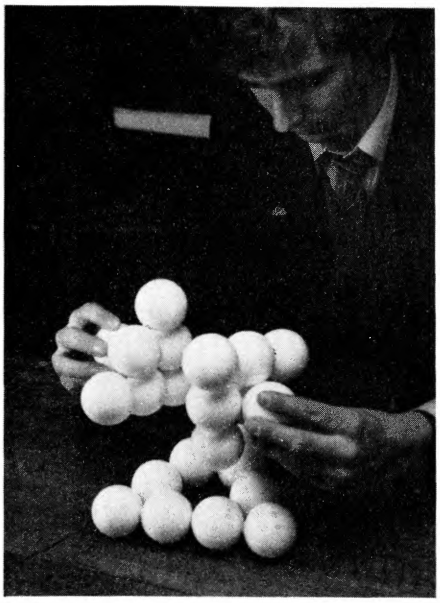
(32) describe the face-centred-cubic and hexagonal close-packed structures and sketch their unit cells;

(33) describe the difference between face-centred-cubic and hexagonal structures in terms of the relative positions of close-packed layers.

Read about the face-centred-cubic and hexagonal close-packed structures for metals in your text-book(s). The face-centred-cubic close-packed structure is sometimes more simply called 'cubic close-packing'. Look also for the meanings of the terms 'close-packing' and 'co-ordination number'. We suggest you do not make detailed notes until after you have done the model-building experiment, which now follows.

EXPERIMENT 1

Making models of two metallic structures



Aim

The aim of the experiment is to make and compare models of two structures commonly found in metals - cubic close-packing and hexagonal close-packing. In the course of the construction, the concepts of close-packing, co-ordination number, and unit cell are illustrated and clarified.

Introduction

The model-building experiment is in the form of a revealing exercise. You should cover with a sheet of paper that part of the page below the next ruled line until you have followed the instruction and answered the question above the line.

You will use expanded polystyrene spheres to represent atoms of metals and stick them together with small blobs of Blu-tak or a similar demountable adhesive. To get maximum rigidity, you should use adhesive on every contact (except where you are told not to do so!) and press the spheres firmly together so that they are as close as possible.

Do not dismantle any structure until the end except where you are told.

Requirements

31 expanded polystyrene spheres
Blu-tak or similar adhesive

Procedure

1. Put one sphere on a flat surface and surround it with as many others as you can fit in the same plane, i.e. all must touch both the flat surface and the central sphere. Stick the surrounding spheres together but not to the central sphere (you will need to remove it later).

Q1. How many spheres touch the central sphere, and what shape would be outlined by joining their centres?

A1. Six spheres touch the central sphere, outlining a regular hexagon.

2. You have just constructed part of a close-packed layer or plane. Satisfy yourself that this arrangement can be continued to infinity in any direction by adding more spheres (without sticking) around any of the outer ones.

Q2. What is the co-ordination number of any sphere in an infinite close-packed layer?

A2. Six. Note that this only refers to a 2-dimensional structure. You will work out the co-ordination number for a 3-dimensional structure later.

3. Stick three more spheres to your hexagon to make a triangular layer. Now you will extend close-packing to three dimensions. Try a single sphere, without adhesive, in different positions as part of a second layer to help you answer Q3 and Q4.

Q3. What is the maximum number of spheres in the first layer that can be touched by a single sphere in the second layer?

A3. Three.

Q4. How many sites are there where you can add a single sphere in the second layer so that it touches three others in the first layer?

A4. Nine. These are shown by crosses in Fig. 23.

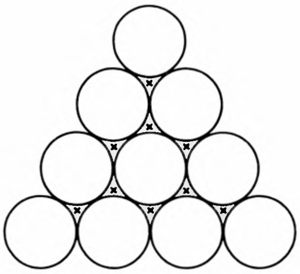


Fig. 23.

5. Add more spheres to make a close-packed second layer - do not stick them together yet.

Q5. How many of the nine sites can you actually use to make a close-packed layer?

A5. Either six or three. In an infinite layer, half the sites can be used, corresponding to alternate crosses in Fig. 23.

6. Consider both ways of adding the second layer - adding three spheres or six spheres - and answer the questions for each of the ways.

Q6. (a) Is the second layer close-packed?

(b) Is it close-packed with respect to the first layer?

(c) If the layers were extended in all directions, could you distinguish between the two ways of adding the second layer?

A6. (a) Yes, for both ways. (b) Yes, for both ways.

(c) No, the two ways of adding the second layer are indistinguishable. It is only the fact that you are looking at a small part of the structure that makes them seem different.

7. Arrange your second layer to have six close-packed spheres and stick them together as a triangle. This is best done on a flat surface - then lift the complete layer back into position. Do not stick the layers together.

Now consider the different ways of adding a third layer.

Q7. How many close-packing sites are there? Can you use them all?

A7. There are four sites. You can use three or one. In an extended layer, half the sites can be used.

8. Look carefully at the four sites from a position vertically above each one, so that you look through to the first layer.

Q8. Is there any difference between the sites? If so, what difference can you see?

A8. The central site is directly above a sphere in the first layer. The other three sites are directly above holes in the first layer.

9. Use the three outer sites to make a third layer. Stick the spheres together but not to the second layer.

Now stick another sphere in position to make a fourth layer. You have now constructed a model of part of the structure adopted by many metals, e.g. copper, silver and gold. This structure is known by two names - *abc* close-packing or cubic close-packing. It is sometimes called a face-centred cubic structure, which is correct but not precise because there are other face-centred cubic structures.

Q9. Why do you think the structure is known as *abc* close-packing? (You have answered this in a different way in Q8.)

A9. The third layer is not directly above the first, but the fourth layer is. The first three layers are referred to as *a*, *b* and *c*, while the fourth is regarded as another *a* layer. The sequence continues *abcabcabcabc*....

10. It is not so easy to see why the structure is called cubic, although you may perhaps know that the shape of your pyramid is a regular tetrahedron which fits into a cube with its points at four of the eight corners, as shown in Fig. 24.

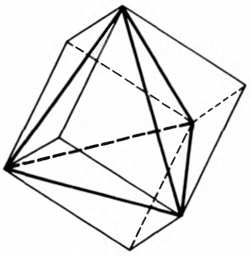


Fig. 24.

To show the cubic nature of the structure more clearly, take the second layer of your tetrahedron, six spheres still firmly stuck together, and place it on a flat surface. Stick one more sphere in the central site so that you have a two-layer structure of 7 spheres.

Make another identical 7-sphere structure by adding three spheres to the third and fourth layers removed from the tetrahedron.

Hold one structure in each hand by means of the single sphere and bring the two six-sphere triangles together. Then rotate one triangle till it fits into the other, using three close-packing sites in each triangle.

Q10. Describe the structure you now have in a few words - what is its overall shape and how do the spheres fit into it?

A10. It is a cube, each face of which has a sphere at each corner and one at the centre touching the other four - hence the name 'face-centred cubic'

Q11. Do the faces of your cube represent close-packed layers?

A11. No. The co-ordination number is 4 and not 6.

Q12. Where are the close-packed layers in the cube?

A12. Along planes joining any diagonal of a face with one other corner. The shaded spheres in Fig. 25 make one such layer.

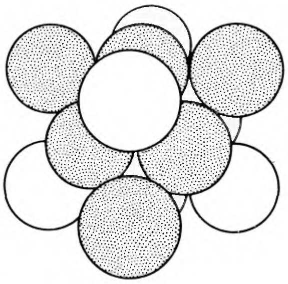


Fig. 25.

Q13. What is the co-ordination number of any sphere in the extended structure?

A13. Twelve. Six touch it in one close-packed layer, three in the layer above, and three in the layer below.

14. Turn the cube and stand it on one corner so that the close-packed planes are horizontal. There are four such planes, containing 1, 6, 6 and 1 sphere. Check that the sequence is *abca* as in A9.

Another way of seeing that the face-centred cube you have made has the same structure as the pyramid you built at first is to remove the central sphere from the original first layer and stand the cube with a corner sphere in the hole in such a way that the original pyramid shape can be seen, but with an extra sphere projecting from three of its faces.

Draw an outline cube and draw small blobs (ideally they should be just points) in positions corresponding to the centres of the spheres in your model structure. Compare your drawing with drawings in your text-book. The drawing represents the unit cell of the cubic close-packed structure since the whole structure can be built up by repeating it.

Q14. However, the face-centred cube you have made from spheres is not, strictly speaking, a unit cell. Can you see why not?

A14. The stacking of identical cubes side-by-side would not repeat the structure, unless the spheres are regarded as being shared between neighbouring cubes, as in Fig. 26. You will do an exercise later which will make clearer the sharing of spheres between neighbouring unit cells.

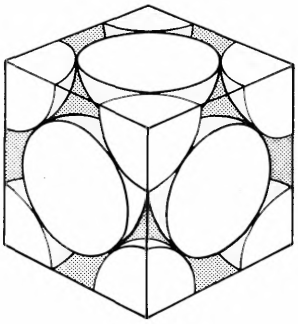


Fig. 26.

15. Now you will investigate the structure made by using the second way of arranging the third layer.

Return half of your face-centred cube to the hole in the first layer so that you have two triangular layers just as you did at the beginning. You recall that to make the cubic close-packed structure, the third layer spheres used the outer three close-packing sites. This time, place a sphere in the central site and stick six more spheres to it to make a third layer.

Q15. How do the positions of the third layer spheres relate to those in the first layer?

A15. Each sphere is vertically above a sphere in the first layer.

16. You have now made a model of part of the structure adopted by a number of other metals, e.g. magnesium and calcium. This structure is also known by two names - *aba* close-packing or hexagonal close-packing.

Q16. Why is it called *aba* close-packing?

A16. The third layer is directly above the first. Compare this with cubic close-packing where the fourth layer is directly above the first.

17. The hexagonal nature of the structure is best seen by removing the three corner spheres from the first layer and making these three the second layer (first filling the hole in the first layer). Finally, replace the third layer directly above the first, so that the overall hexagonal shape is apparent.

Compare your model with drawings in your text-books and with a permanent model if one is available. You should be able to draw an outline of the hexagonal close-packed unit cell using only dots and lines as you did for cubic close-packing. Remember that your model is not strictly a unit cell unless spheres are shared with neighbouring cells.

18. Before you dismantle your models, look at them again, side by side, and make sure that you can:

(a) pick out the close-packed layers;

(b) see that the overall co-ordination number is 12 in both cases;

(c) draw unit cells, representing the centres of spheres by dots.

Now we consider two simple structures which are not close-packed.

Body-centred cubic structure and simple cubic structure

A body-centred cubic structure is found in a number of metals, e.g. the alkali metals, and while examples of the simple cubic structure are rare in elements, knowledge of it is useful in describing some compound structures.

Objectives. When you have finished this section, you should be able to:

(34) describe the body-centred-cubic metal structure and its unit cell;

(35) describe the simple cubic structure and sketch its unit cell.

Read about these two structures in your text-books (without considering compounds at this stage) and then do the following two exercises.

If you wish to construct models to help you think in three dimensions, ask for 17 spheres and some Blu-tak; this will be enough for both structures.

Exercise 39 (a) Sketch the unit cell for the body-centred-cubic structure (using points to represent the centres of atoms).

(b) What is the co-ordination number?

(c) Are there any close-packed layers?

(d) What physical property of the alkali metals, not shared by many other metals, is explained by their adoption of the body-centred-cubic structure?

(Answers on page 90)

Exercise 40

(a) Sketch the unit cell for the simple cubic structure. (Use points to represent the centres of atoms.)

(b) What is the coordination number?

(c) Are there any close-packed layers?

(d) Why do few, if any, metals adopt this structure?

(Answers on page 90)

We mentioned in the last revealing exercise that some atoms in unit cells are shared with neighbouring unit cells - see Fig. 26. You can explore this idea further in the next section.

Sharing of atoms between neighbouring unit cells

Objective. When you have finished this section, you should be able to:

(36) calculate the number of atoms in a unit cell by considering the extent to which they are shared.

Exercise 41 Look at Fig. 27, which is a drawing of a space-filling unit cell, and answer the questions which follow. You can see that every sphere is shared with neighbouring unit cells.

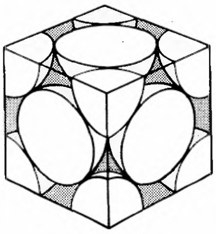


Fig. 27.

(a) What structure does Fig. 27 represent?

(b) How many neighbouring unit cells share (i) a corner atom, (ii) a centre-face atom?

(c) Calculate the total number of spheres in the unit cell by adding the fractions of spheres indicated in the diagram.

(d) (OPTIONAL - for the mathematically inclined. However, if you do not do the calculation, you should look up the answer.) Calculate the percentage of the total volume of the structure which consists of spaces between spheres.

Hint: calculate the length of the side of the unit cell in terms of the radius of a sphere, and then compare the volume of the cell with the volume of the spheres.

(e) What percentage of the total volume of a hexagonal close-packed structure would you expect to consist of spaces between spheres? (You need not do a calculation this time.)

(Answers on page 90)

Now that you have looked at some metallic structures, you should be able to see what is meant by the term 'metallic radius'.

Metallic radius

'Metallic radius' is another specific term, like covalent radius and van der Waals radius, covered by the vague general term 'atomic radius'.

Objectives. When you have finished this section, you should be able to:

(37) explain the term metallic radius ;

(38) explain why metallic radius is greater than ionic radius for any given element.

See what your text-book(s) and your data book say about metallic radius. Then try the following exercise.

Exercise 42 (a) Calculate the total number of spheres in unit cells of the body-centred-cubic and the simple cubic structures. You will find it difficult to draw space-filling unit cells similar to Fig. 27, but you should now be able to work from unit cell drawings using points only.

(b) (OPTIONAL - see Exercise 41(d).) Calculate the percentage of the total volumes of these structures which consists of spaces between spheres. Hint: as in Exercise 41(d).

(c) What is the link between coordination number and the answers to Exercises 41(d) and 42(b)?

(Answers on page 91)

Exercise 43 (a) Fig. 28 shows an electron density map for aluminium. Use the scale to find the metallic radius for aluminium.

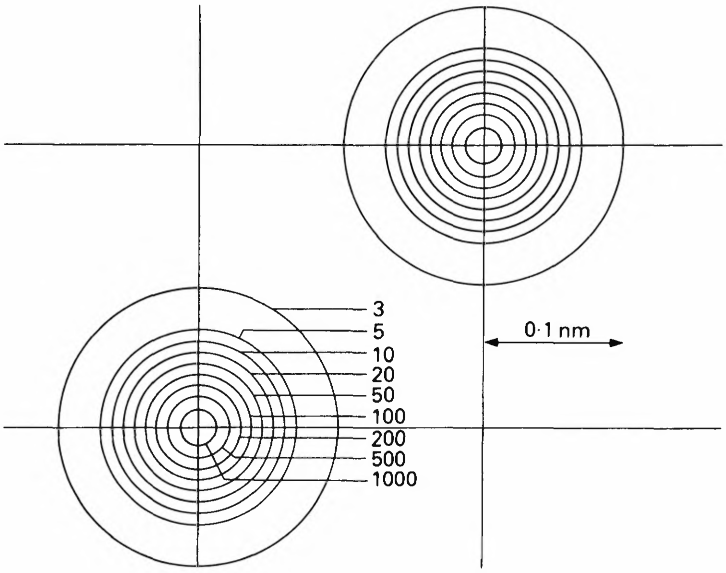


Fig. 28.

Contours are in e $nm^{-3}/10^4$

(b) The ionic radius for Al^{3+} is 0.045 nm. Why is this so much smaller than the metallic radius?

(Answers on page 91)

Recognition of metallic structures

Just as ionic compounds have typical properties determined by the nature of ionic bonding, so do metals have properties determined by the nature of metallic bonding.

Objectives. When you have finished this section, you should be able to:

(39) list properties typical of metallic structures;

(40) describe how useful these properties are in the recognition of metals.

Read about the physical properties of metals in your text-book, so that you can do the next exercise.

Exercise 44 How do the following physical properties help us to recognise metals?

(a) appearance,

(b) malleability and ductility,

(c) melting point,

(d) conductivity.

In each case, state whether or not the property is exclusive to metals and, where appropriate, mention a metal which does not have the typical property.

(Answers on page 91)

A metal is usually defined in terms of its chemical properties because there are so many exceptions to the general rules about physical properties. A metal is an element which tends to form positive ions by losing electrons in chemical reactions - a familiar example is the reaction with a dilute acid forming metal ions and hydrogen. Even with this definition there is an exception, namely hydrogen, which is not regarded as a metal even though it forms positive ions.

In order to consolidate what you have learned so far about bonding and molecular shapes, do the following exercise and hand it to your teacher for marking.

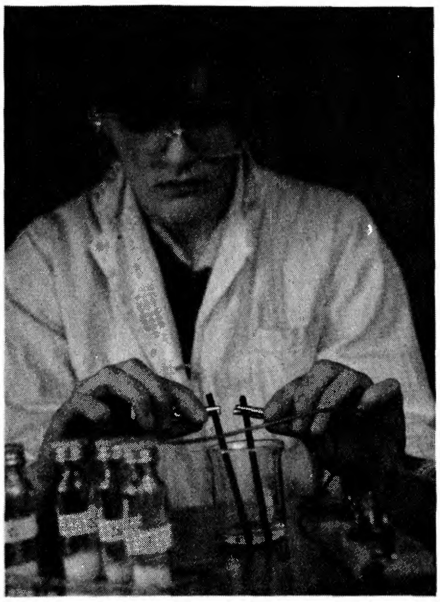
Teacher-marked Exercise Explain the terms (a) covalent bonding, (b) electrovalent bonding, (c) metallic bonding. Illustrate your answer by reference to chlorine, magnesium and magnesium chloride.

Use the concept of electron pair repulsion to predict the shapes of (i) CH_3^+, (ii) CH_3^-, (iii) covalent $BeCl_2$.

Now that you have summarised the typical properties of metals, as well as those of ionic and covalent compounds (Exercises 9, 33 and 36), you should do the next Experiment in which you have to allocate a structure to each of a number of unknown substances.

EXPERIMENT 2

Recognising ionic, covalent and metallic structures



Aim

The aim of this experiment is to examine some unknown substances and to determine their structures (as far as possible) using the minimum number of tests.

Introduction

A number of tests are suggested, as shown in Results Table 1. You should devise your own simple procedures, using only the apparatus provided.

Do not necessarily perform every test on each substance, but aim at getting the maximum information from the minimum number of tests. The result of one test may suggest which test to do next. In some cases, it may not be possible to come to a definite conclusion. In estimating melting points to the nearest 100 °C, you should note that the maximum temperature of an ordinary Bunsen burner flame is about 800 °C.

Requirements

safety spectacles
6 test-tubes in rack
6 ignition tubes
test-tube holder
Bunsen burner and protective mat
beaker, 100 cm^3
battery and lamp in holder
2 carbon electrodes
3 connecting leads with crocodile clips
unknown substances, in bottles labelled A-G

Results Table 1

	A	B	C	D	E	F	G
Appearance							
Estimate of melting point							
Solubility in water							
Conductivity of solution							
Conductivity of solid							
Action of dilute HCl							
Structure							

(Specimen results on page 92)

Questions

1. What further tests would probably help to identify the structures which you could not identify in the experiment?
2. Why is it more difficult to recognise a powdered metal than a solid lump?

(Answers on page 92)

In the final section of Level One, you apply what you have learned about the sharing of atoms in unit cells to calculate a value for the Avogadro constant.

THE AVOGADRO CONSTANT FROM UNIT CELL DIMENSIONS

This method can be applied to any substance for which the structure and dimensions of the unit cell have been determined by X-ray diffraction or other means. You are most likely to apply it to an ionic structure.

Objective. When you have finished this section, you should be able to:

(41) calculate the Avogadro constant from the dimensions of a unit cell.

You can achieve this objective by doing the following exercise. You may find it helpful to refer also to Exercise 41.

Exercise 45 Fig. 29 shows a unit cell for sodium chloride.

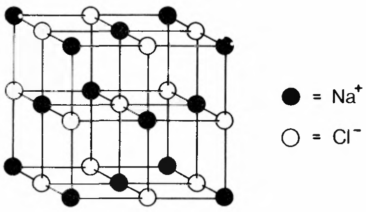


Fig. 29.

(a) By considering the sharing of ions with neighbouring unit cells, calculate the number of ions of each sort in each unit cell. Does your answer correspond to the formula for sodium chloride?

(b) The ionic radius for Na$^+$ is 0.098 nm and for Cl$^-$ is 0.181 nm. Calculate the dimensions of the unit cell, remembering that its corners lie at the centres of ions.

(c) Use your answers to (a) and (b) to calculate the volume taken up by one ion pair, Na$^+$Cl$^-$. This volume includes the 'space' between ions.

(d) The density of sodium chloride is 2.17 g cm^{-3} and its molar mass is 58.4 g mol^{-1}. Calculate the volume of one mole of ion pairs.

(e) From your answers to (c) and (d) calculate the number of ion pairs in one mole, i.e. the Avogadro constant.

(Answers on page 92)

LEVEL ONE CHECKLIST

You have now reached the end of Level One of this Unit. The following is a summary of the objectives in Level One. Read carefully through it and check that you have adequate notes.

At this stage you should be able to:

(1) describe the various electron configurations of stable simple ions;

(2) for polytatomic ions, distinguish between the covalent bonding within the ion and the ionic bonding between ions;

(3) & (4) explain the term ionic radius and why it differs from atomic radius;

(5) & (6) describe and sketch the caesium chloride and sodium chloride structures;

(7) explain why radius ratio determines the structure of an ionic lattice;

(8) & (9) explain the terms coordination number and unit cell;

(10) use lattice energy as an indication of the strength of ionic bonding;

(11) & (12) list properties typical of ionic compounds and indicate how useful each one is in deciding whether a substance is ionic;

(13) describe covalent bonding in terms of shared pairs of electrons;

(14) draw dot-and-cross diagrams for a variety of covalent molecules;

(15) explain the term dative covalent bond;

(16) draw dot-and-cross diagrams and structural formulae including dative bonds;

(17) draw dot-and-cross diagrams for at least two covalent compounds in which an atom other than hydrogen has fewer than eight outer-shell electrons;

(18) draw dot-and-cross diagrams for at least two covalent compounds in which an atom has more than eight outer-shell electrons;

(19) apply the electron-pair-repulsion theory to molecules involving two, three, four, five and six pairs of bonding electrons;

(20) extend the electron-pair-repulsion theory to include non-bonding pairs (lone pairs) of electrons;

(21) use the following terms correctly to describe the shapes of molecules - linear, trigonal planar, tetrahedral, trigonal pyramidal, trigonal bipyramidal, octahedral;

(22) & (23) describe the structures of diamond and graphite and account for some of their differences in properties by reference to their structures;

(24) & (26) explain the term molecular crystal, quote some examples and describe their general properties;

(25) compare approximately the strength of van der Waals bonds with the strengths of ionic and covalent bonds;

(27) explain why the term atomic radius cannot be used with precision;

(28) distinguish carefully between covalent radius and van der Waals radius;

(29) describe a simple model of metallic bonding;

(30) explain simply why a metal is able to conduct electricity;

(31) explain the term close-packing with reference to spheres;

(32) describe the face-centred cubic and hexagonal close-packed structures and sketch their unit cells;

(33) describe the difference between face-centred cubic and hexagonal structures in terms of the relative positions of close-packed layers;

(34) & (35) describe the body-centred-cubic and simple cubic structures and sketch their unit cells;

(36) calculate the number of atoms in a unit cell by considering the extent to which they are shared;

(37) & (38) explain the term metallic radius and explain why it is greater than ionic radius for any given element;

(39) & (40) list properties typical of metallic structures and describe how useful they are in the recognition of metals;

(41) calculate the Avogadro constant from the dimensions of a unit cell.

LEVEL ONE TEST

To find out how well you have learned the material in Level One, try the test which follows. Read the notes below before starting:

1. You should spend about 1 hour on this test.
2. Hand your answers to your teacher for marking.

LEVEL ONE TEST

A

Questions 1-6 concern the following types of structure:

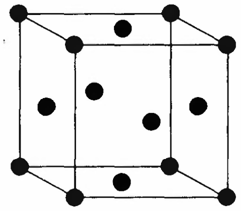
A Giant structure of ions
B Giant structure of atoms
C Widely-spaced molecules
D Widely-spaced atoms
E Molecular crystals

Select from A to E, the structure possessed by each substance below, at room temperature and atmospheric pressure.

1. Naphthalene (1)
2. Carbon monoxide (1)
3. Graphite (1)
4. Silicon(IV) oxide (1)
5. Helium (1)
6. Caesium chloride (1)

A

7. In the face-centred cubic lattice of a metal shown below, the equivalent of how many atoms are contained in each unit cell?



A 4
B 5
C 7
D 10
E 14 (1)

In questions 8-11, one, more than one, or none, of the suggested responses may be correct. Answer as follows:

A if only 1, 2 and 3 are correct
B if only 1 and 3 are correct
C if only 2 and 4 are correct
D if only 4 is correct
E is some other response, or combination, is correct.

A

8. Particles having the electronic configuration 2.8.8 include

1. Ar 3. Sc^{3+}
2. Ca^{2+} 4. Br^-

(1)

9. Which of the following will apply to the structure of sodium chloride?

A

1. It is an example of hexagonal close-packing.
2. The distance between the nuclei of adjacent ions of opposite charge equals the sum of the ionic radii.
3. It is the same as the structure of caesium chloride.
4. Each Na^+ ion is surrounded by six Cl^- ions. (1)

10. Which statement(s) about the shapes of the molecules below is/are correct?

A

1. Silane (SiH_4) is tetrahedral.
2. Beryllium fluoride (BeF_2) is linear.
3. Boron trifluoride (BF_3) is trigonal planar.
4. Sulphur hexafluoride (SF_6) is cubic. (1)

11. A tetrahedral structure is possessed by

A

1. NH_4^+
2. Carbon (graphite)
3. CCl_4
4. H_2O

(1)

In questions 12-15, choose an answer from A to E as follows:

A Both statements true: second explains first

B Both statements true: second does not explain first

C First true: second false

D First false: second true

E Both false.

	FIRST STATEMENT	SECOND STATEMENT	
12.	Most covalent compounds are more volatile than most ionic compounds.	Covalent bonds are much weaker than ionic bonds.	A (1)
13.	Molecules of PCl_3 have planar triangular structures with bond angles of 120°.	Each pair of electrons in a covalent molecule tends to separate from other pairs as much as possible.	A (1)
14.	The H—N—H bond angle in ammonia (NH_3) is less than the H—C—H bond angle in methane (CH_4).	There is greater repulsion between an electron pair bond and a lone pair of electrons than between two electron-pair bonds.	A (1)
15.	A beryllium bromide ($BeBr_2$) molecule is non-linear.	The beryllium atom in beryllium bromide has both shared and unshared pairs of electrons around it.	A (1)

16. (a) Describe, with illustrations, the types of crystal lattice present in graphite, diamond and sodium chloride.

A part

By reference to the type of bonding present, explain the relative hardness and electrical conductivity shown by these substances. (14)

(b) Sodium chloride exhibits 6:6 co-ordination whilst caesium chloride shows 8:8 co-ordination. Explain what these underlined terms mean. (3)

17. (a) An atom X can form a cation X^+ and an anion X^-. Which of the three species has:

A part

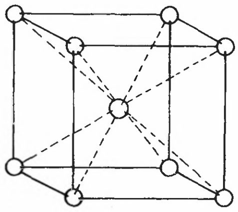
(i) the smallest radius;

(ii) the largest radius? (2)

(b) In descending group I from lithium to caesium, how do ionic radii change and how do you explain the trend? (3)

18. The diagram represents one way in which atoms or ions can be arranged in a crystal.

A



(a) What name is given to the arrangement if all the particles in the diagram are atoms of a metal? (1)

(b) What is the co-ordination number of each atom? (1)

(c) If the central particle is an ion X^+ and the corner particles are ions Y^-, deduce the empirical formula of the substance, showing your method clearly. (2)

(d) (i) Name an alkali metal halide that adopts the arrangement shown in the diagram.

(ii) From the data provided, suggest the ONE other compound most likely to adopt the arrangement shown in the diagram.

Cation	Radius/nm	Anion	Radius/nm
Na^+	0.10	F^-	0.13
K^+	0.13	Cl^-	0.18
Rb^+	0.15	Br^-	0.20
Cs^+	0.17	I^-	0.22

Give your reason. (4)

(Total 45 marks)

LEVEL TWO

In Level One, we considered ionic bonding and covalent bonding as being quite separate and distinct. We begin Level Two by showing that there is a continuous range of bonding types between the two extremes we have described, with no clear-cut division.

INTERMEDIATE BONDING TYPES

In many compounds, the bonding is intermediate in character between 'pure' ionic and 'pure' covalent. We can discuss intermediate bonding in two ways - by seeing how covalent bonds can have ionic character, and by seeing how ionic bonds can have covalent character.

Covalent character of ionic bonds

The model of ionic bonding you have used so far assumes the complete transfer of electrons from one atom to another giving separate spherical ions. However, the spherical charge cloud in an anion is fairly easily distorted, or polarized, by neighbouring cations, because the nuclear charge is insufficient to hold it firmly. This distortion leads to a degree of overlap of charge clouds, and therefore a degree of covalent character.

Objectives. When you have finished this section, you should be able to:

(42) explain the terms polarization and polarizability with reference to negatively-charged ions (anions);

(43) explain the term polarizing power with reference to positively-charged ions (cations);

(44) explain how both polarizability and polarizing power depend on ionic radius and ionic charge;

(45) explain how polarization of an ion leads to a degree of covalent character in ionic bonding.

Read about covalent character in ionic bonding in your text-book(s), so that you can attempt the following exercises. If there is a reference to Fajans' rules, this should be helpful. You will find it useful to refer to the ionic radii in Table 1.

Table 1 Ionic radii (in nm)

Li^+ 0.068	Be^{2+} 0.030			N^{3-} 0.171	O^{2-} 0.146	F^- 0.133
Na^+ 0.098	Mg^{2+} 0.065	Al^{3+} 0.045		P^{3-} 0.212	S^{2-} 0.190	Cl^- 0.181
K^+ 0.133	Ca^{2+} 0.094	Sc^{3+} 0.081				Br^- 0.196
Rb^+ 0.148	Sr^{2+} 0.110	Y^{3+}				I^- 0.219
Cs^+ 0.167	Ba^{2+} 0.134	La^{3+}				

Exercise 46 Explain why:

(a) I^- is more readily polarized (has greater polarizability) than F^-;

(b) O^{2-} is more readily polarized than F^-;

(c) Li^+ has greater polarizing power than K^+;

(d) Al^{3+} has greater polarizing power than Li^+.

(Answers on page 92)

Exercise 47 Complete the following:

The polarization of an anion is favoured by { ......size / ......charge

The polarizing power of a cation is favoured by { ......size / ......charge

(Answer on page 92)

Exercise 48 What would be the result of combining very small, highly charged cations, with large highly charged anions?

(Answer on page 93)

The rules you wrote down in Exercise 47 are known as Fajans' rules. You should remember them although you may not need to know the name of the originator. They are very useful in predicting the nature of bonding in compounds of metals, as we now show.

You have probably learned the simple rule, very useful in a pre-A-level course, that compounds of metals are ionic. In the next exercise, you suggest some exceptions to the rule.

Exercise 49 Study Table 1 and write down the formula of

(a) the compound which has the 'purest' ionic bonding, i.e. polarization of the anion is a minimum,

(b) three compounds of different stoichiometry which are likely to be covalent, i.e. polarization of the anion is very great.

(Answers on page 93)

Having seen that all ionic bonds have some degree of covalent character, we now go on to consider the possibility of ionic character in covalent bonds.

Ionic character of covalent bonds

The model of covalent bonding you have used so far assumes the equal sharing of a pair of electrons between two atoms. Very often the electrons are not shared equally, and this makes the bond polar.

Objectives. When you have finished this section, you should be able to:

(46) explain how a covalent bond can have ionic character;

(47) explain the term bond polarity;

(48) explain the term dipole moment;

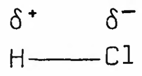
(49) explain why some molecules with polar bonds have no dipole moment.

Read about the polarity of covalent bonds and polar molecules in your text-book(s). You will probably find reference to electronegativity, which you will need in the next section, and also an account of a simple experiment to demonstrate the existence of polar molecules. You will use this experiment in Unit P4 as a very approximate measure of dipole moment - but you do not need to worry about more precise measurement.

Bond polarity in diagrams

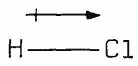
You may find in text-books four ways of representing bond polarity in diagrams:

(1)



(2)

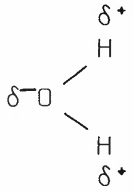
(3)

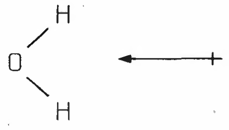


(4)

In (1) the electron pair is shown shifted from its central position. In (2) a partial charge separation is shown by the symbols δ^+ and δ^-. In (3) an arrow head is added in the centre of the bond line (not at the end as for a dative bond) to indicate unequal sharing of the electron pair. In (4) a dipole moment is shown by a separate arrow with a short line across it at the positive end.

We shall use (2) most often in this Unit, but (3) is useful in organic chemistry and (4) is useful for indicating the combined effect of two or more polar bonds, as shown below.





Now you should be able to do the following exercises.

Exercise 50 In what type of molecule do we find non-polar covalent bonding (sometimes called 'pure' covalent bonding)?

(Answer on page 93)

Exercise 51 (a) Draw a dot-and-cross diagram for a sulphur dichloride molecule, SCl_2.

(b) Look up first ionization energies for sulphur and chlorine atoms. Which is more likely to lose electrons?

(c) Look up electron affinities for sulphur and chlorine atoms. Which is more likely to gain electrons?

(d) Do your answers to (b) and (c) suggest that the electron pair in the S—Cl bond is unequally shared?

(e) Sketch the shape of the SCl_2 molecule. Insert symbols to indicate the polarity of the bonds and the direction of the overall dipole moment (if any).

(Answers on page 93)

Similar considerations suggest that almost all covalent bonds are polar to some extent, and this can usually be confirmed by measuring dipole moments of molecules. However, not all molecules with polar bonds have dipole moments, as you see in the next exercise.

Exercise 52 Tetrachloromethane, CCl_4, is a non-polar liquid, but it has polar bonds. Explain this statement, including a diagram in your answer.

Has tetrachloromethane any 'ionic character'?

(Answer on page 93)

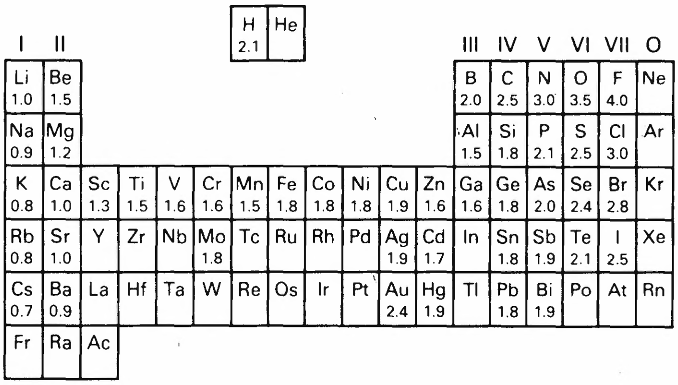
We have used two different approaches to describe the range of bonding types between pure ionic and pure covalent. We now unite these two approaches by introducing the concept of electronegativity.

ELECTRONEGATIVITY

You have probably already met the idea of electronegativity in a descriptive sense. Elements which tend to form negative ions are said to be electronegative, while those that form positive ions are said to be electropositive.

In this section we introduce a numerical scale of electronegativity which helps us to describe a continuous range of behaviour between the highly electronegative elements, such as chlorine, and the very weakly electronegative (or strongly electropositive) elements such as potassium.

Values of electronegativity are shown in Fig. 30.



I	II											III	IV	V	VI	VII	O
						H 2.1	He										
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr
Rb 0.8	Sr 1.0	Y	Zr	Nb	Mo 1.8	Tc	Ru	Rh	Pd	Ag 1.9	Cd 1.7	In	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	La	Hf	Ta	W	Re	Os	Ir	Pt	Au 2.4	Hg 1.9	Tl	Pb 1.8	Bi 1.9	Po	At	Rn
Fr	Ra	Ac															

Fig. 30.

Objectives. When you have finished this section, you should be able to:

(50) define the term electronegativity (non-mathematically);

(51) distinguish clearly between electron affinity and electronegativity;

(52) explain why electronegativity is related to atomic radius;

(53) describe the trends in electronegativity across a period and down a group in the Periodic Table.

Read about electronegativity in your text-book(s). You need not worry about a mathematical definition of electronegativity, but you should look for a general account of its relationship with electron affinity, ionization energy and atomic radius. The following exercises test your understanding of electronegativity.

Exercise 53 Both electronegativity and electron affinity refer to the attraction by an atom for electrons. What is the essential difference between the two terms?

(Answer on page 93)

Exercise 54 (a) What are the trends in electronegativity:

(i) across a period in the Periodic Table,

(ii) down a group.

(b) Explain why the trends you have described in (a) are very similar to trends in atomic radius.

(Answers on page 93)

In the next exercise, you relate electronegativity to polarizing power and polarizability (see page 50).

Exercise 55 (a) Element A forms anions which are more readily polarized than those of element B. Which element has the greater electronegativity? Explain your answer.

(b) Element C forms cations which have greater polarizing power than those of element D. Which element has the greater electronegativity? Explain your answer.

(Answers on page 93)

You have seen how the polarizing power of cations and the polarizability of anions enables us to predict whether ionic bonding has some covalent character. Electronegativity can be used for the same purpose, but is also applicable to covalent bonding, as we now show.

Using electronegativity values

By looking at the difference in electronegativity between two elements, you can predict the nature of the bonding between them.

Objectives. When you have finished this section, you should be able to:

(54) use values of electronegativity to predict the nature of the bonding between two elements;

(55) use values of electronegativity to explain differences between experimental and calculated lattice energies.

In the following exercises, you should use the values given in Fig. 30. Some data books give a slightly different set of values. For this reason, you should regard electronegativities, and conclusions you draw from them, as approximate.

Exercise 56 Nitrogen and chlorine form a compound called nitrogen trichloride, NCl_3.

(a) What is the difference between the electronegativities of the two elements?

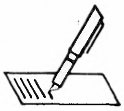
(b) Would you expect the electrons involved in bonding between nitrogen and chlorine to be drawn more powerfully towards one atom than the other?

(c) Describe the bonding between nitrogen and chlorine in terms of ionic and covalent character.

(d) Would you expect nitrogen trichloride to have a dipole moment?

(Answers on page 93)

Exercise 57 Rubidium and oxygen form a compound, rubidium oxide, Rb_2O.



(a) What is the difference between the electronegativities of the two elements?

(b) Would you expect the electrons involved in bonding between rubidium and oxygen to be drawn more powerfully to one atom than to the other?

(c) Only a few pairs of elements have a greater difference in electronegativity. Which are these?

(d) Describe the bonding between rubidium and oxygen in terms of ionic and covalent character.

(Answers on page 93)

You have seen that very small differences in electronegativity are associated with predominantly covalent bonding while differences close to the maximum of 3.3 are associated with predominantly ionic bonding.

Between the two extremes there are varying degrees of ionic and covalent character. Some text-books calculate a 'percentage ionic character' based on a difference of 3.3 equivalent to 100% ionic and zero difference equivalent to 0% ionic (i.e. 100% covalent). However, you will not need to do these calculations. In the following exercise you should comment (in words only) on the nature of the bonding between elements.

Note also that electronegativity differences can only tell you the nature of the bonding if it exists. You cannot predict whether or not a compound exists by using electronegativities.

Exercise 58 Describe the bonding in each of the following compounds:

(a) KF (b) CuO (c) CS_2 (d) NaCl (e) PBr_3

using one of the following phrases:

(i) pure covalent,

(ii) predominantly covalent,

(iii) partly covalent and partly ionic,

(iv) predominantly ionic,

(v) pure ionic.

For your own interest, you may choose to calculate the % ionic character for each.

(Answers on page 94)

Electronegativity can also be used to help explain the differences between experimental and calculated lattice energies, as we now show.

Theoretical lattice energies

It is a simple problem in electrostatics to calculate the energy required to move two charged spheres from contact to infinite separation. If you study physics, you have probably done such a calculation. If we assume that ions are charged spheres, we can extend the calculation to work out lattice energies for ionic crystals.

We do not deal with the method of calculation here but in Table 2 we show these theoretical lattice energies for a number of compounds. We also list lattice energies obtained from experimental results using the Born-Haber cycle.

Table 2

Compound	Theoretical lattice energy /kJ mol^{-1}	Experimental lattice energy /kJ mol^{-1}
NaCl	769	786
NaBr	732	747
NaI	682	704
CsCl	657	659
CsBr	632	631
CsI	600	604
AgCl	864	915
AgBr	830	904
AgI	808	889

In the next exercise you compare the two sets of values for lattice energy and try to account for the differences.

Exercise 59 (a) For each compound in Table 2, calculate the difference between the two values for lattice energy.

(b) For any halogen, which metal halide shows:

(i) the best agreement between the two values,

(ii) the poorest agreement between the two values?

(c) For any metal, which halide shows the poorest agreement between the two values?

(d) Explain your answers to (b) and (c) in terms of electronegativity difference. (Hint: what has electronegativity difference to do with the shapes of ions?)

(Answers on page 94)

The calculation of lattice energies has been incorporated into a computer programme which we describe in the next section.

Lattice energies - a computer program

The Schools Council 'Computers in the curriculum project' has produced a computer program called 'Lattice energy', which you may like to use. Ask your teacher if it is available. You do not need to know anything about computing, but if you have not used a program before, you will need a few minutes of instruction to get started and use the keyboard.

Using the program, you can investigate the various factors which affect lattice energy - ion size, ion charge and coordination number - and also use a mathematical model to calculate lattice energies for comparison with experimental values.

You should read the students' notes accompanying the program before you sit down at the computer.

So far, we have limited our discussion of covalent compounds to structures which can be described adequately by allocating (or localizing) a pair of electrons to each single bond, two pairs to a double bond, and so on. We have accounted for the known shapes of these structures by considering the mutual repulsion of the electron pairs.

Although there are large numbers of compounds for which this model of covalent bonding is a good one, there are many structures where the model is inadequate. We now consider a refinement of the electron-pair model, which introduces the idea of delocalization of electrons.

DELOCALIZATION OF ELECTRONS

When we refer to delocalization of electrons, we mean that some of the outer-shell electrons in a structure are not allocated in pairs to particular bonds but are shared out between two or more bonds. A good example is provided by the molecule of benzene, C_6H_6.

Objectives. When you have finished this section, you should be able to:

(56) explain the term delocalization of electrons;

(57) describe the structure of benzene as an intermediate between two electron-pair structures.

Read about delocalization of electrons in your text-book with special reference to the structure of benzene. Avoid, or skim over, any discussion in terms of orbitals - we deal with this more advanced model of covalent bonding later. Look for alternative electron-pair structures for benzene - you may find these called Kekulé structures, classical structures, Lewis structures, or canonical structures. Look also for reasons why the Kekulé structures cannot be regarded as good descriptions. In some books, the terms resonance hybrid and mesomer may be used for the structure intermediate between the electron-pair structures.

Use what you have read to help you with the next section.

The structure of benzene - a first look

Benzene, C_6H_6, is known to have a structure in which the six carbon atoms are arranged in a hexagonal 'ring', with equal C-C bond lengths of 0.139 nm.

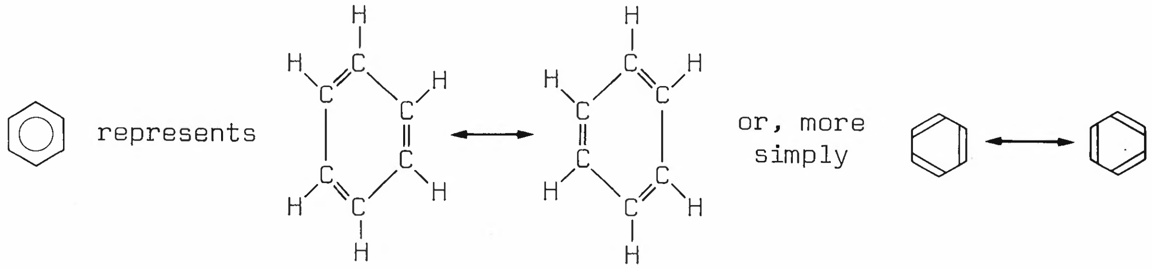
Exercise 60 (a) Draw two electron-pair structures for benzene. (If you find more than two, draw the two you think most likely.)

(b) Why can neither of these structures represent the actual structure of benzene? (Hint: look up bond lengths.)

(c) How is the structure of benzene usually represented on paper by a single drawing?

(Answer on page 94)

The actual structure of benzene is intermediate between the two electron-pair structures (Kekulé structures). Although we have invented a way of representing this structure on paper by a single drawing, it is often described by referring to the two electron-pair structures, as shown below.



Note that the double-ended arrow does not mean that there is an equilibrium in which both forms exist. You can clarify this by describing a mule as a hybrid between a horse and a donkey.

HORSE ←——→ DONKEY

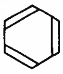
Obviously, a mule does not spend some of its time as a horse and some as a donkey! But it does have some of the character of a horse (e.g. strength) and some of the character of a donkey (e.g. stubbornness) as well as its own unique character. In the same way, the C—C bonds in benzene have some of the character of single bonds and some of the character of double bonds, as you will see when you study organic chemistry in Unit 01. That is why these bonds are sometimes said to have a 'bond order' of 1½ and are sometimes represented by C=C.

In the next exercise you look at some further evidence which shows that the Kekulé structures are wrong.

Exercise 61 (a) Construct a suitable Hess's law cycle to calculate $\Delta H^{\ominus}$ for the reaction:

$6C(g) + 6H(g) \rightarrow$  (g)

(b) Look up mean bond energy terms for C-H, C-C and C=C bonds. Use them to calculate $\Delta H^{\ominus}$ for the reaction

$6C(g) + 6H(g) \rightarrow$  (g)

(c) Which of the structures for benzene would be the more stable? What is the stabilization energy?

(d) Assuming that the C-H bond energy is 412 kJ mol^{-1}, calculate the mean bond energy for the six bonds between carbon atoms in benzene. How does this compare with the mean bond energies for C-C and C=C?

(Answers on page 94)

Electrons are delocalized in some other structures too as you discover in the next section.

Delocalization of electrons in some ions

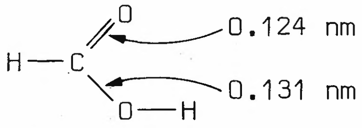
Although the structures of many acids are conveniently described by the electron-pair model, the same may not be true for their ions.

Objectives. When you have finished this section, you should be able to:

(58) describe, in terms of intermediates between electron-pair structures, the actual structures of the following ions - methanoate (formate), ethanoate (acetate), carbonate, nitrate.

You should be able to achieve this objective by doing the following exercises, but you may also need to refer to your text-book(s).

Exercise 62 The measured bond lengths and angles in a molecule of methanoic acid, HCO_2H, correspond well to the electron-pair structure:



Write two electron-pair structures for the methanoate ion, HCO_2^-, to explain why its C-O bond lengths are equal at 0.127 nm. (The hydrogen atom attached to the oxygen is lost when the ion is formed.)

(Answer on page 95)

Exercise 63 Describe the structure of the ethanoate ion, $CH_3CO_2^-$, as a hybrid of two electron-pair structures. What would you expect the C—O bond lengths to be in this ion?

(Answer on page 95)

Exercise 64 Draw three possible electron pair structures for the carbonate ion, CO_3^{2-}, to explain why the ion is symmetrical in shape with equal bond lengths.

(Answer on page 95)

Exercise 65 (a) Draw two possible electron-pair structures for nitric acid, HNO_3($HONO_2$). (Hint: a dative bond is involved - you may find it helpful to draw a dot-and-cross diagram first.)

(b) Draw three possible electron-pair structures for the nitrate ion, NO_3^-.

(c) What N—O bond lengths would you expect to find in HNO_3 and NO_3^-?

(Answers on page 95)

The idea of hybrids of two (or more) electron-pair structures allows us to extend the electron-pair model of covalent bonding to virtually all known structures. A summary is as follows:

1. If more than one electron-pair structure can be drawn for a molecule or ion, then the actual structure is an intermediate form with some of the character of each of the electron-pair forms.
2. Some of the bonding electrons in the intermediate form are delocalized - i.e. they contribute to more than one bond.
3. The intermediate form is always energetically more stable than the average of the electron-pair forms by an amount known as the stabilization energy (delocalization energy, resonance energy).

The weakness of this description of delocalized electrons is that it gives us a very imprecise idea of where the electrons are most likely to be found. We now consider a rather more sophisticated model of covalent bonding which not only gives us a picture of electron distribution in molecules and ions but provides an alternative description of the shapes of molecules. Before you start on the next two sections, you should discuss with your teacher whether you need to cover the whole of it for your syllabus.

THE ORBITAL APPROACH

You have already studied atomic orbitals in Unit S2, and we briefly mentioned the overlap of these orbitals earlier in this Unit on page 13. A further consideration of the overlap of atomic orbitals to give new molecular orbitals gives you a model of covalent bonding which can be applied to all structures. In practice, you will only have to apply it to a few structures.

Molecular orbitals

The same branch of mathematics, known as wave mechanics, which gives us the shapes of atomic orbitals can also be applied to the distribution of electrons in molecules.

Objectives. When you have finished this section, you should be able to:

(59) explain simply the term molecular orbital;

(60) describe the formation of σ-orbitals and σ-bonds.

The treatment of molecular orbitals in many text-books tends to be either very sketchy or too advanced for A-level study. We suggest, therefore, that you postpone further reading on this topic until after you have looked at our simple treatment. Then you can consult a suitable text-book for clarification, or to take your study further if you wish. Note that while you may find it interesting to read about anti-bonding orbitals, you do not need to consider them for A-level.

You can regard the overlap of atomic orbitals as the interaction of two wave patterns to produce a new wave pattern. Just as waves interact in a ripple tank, or when two pebbles are thrown into a pond, so do the electron waves around atoms interact when two atoms approach each other.

The mathematics is rather difficult, but what it boils down to, in effect, is as follows:

1. When two atomic orbitals, each containing a single unpaired electron, approach each other, the two electrons can occupy a new molecular orbital which is at a lower energy.
2. The shape of the new molecular orbital can be obtained approximately by looking at the shapes of the two atomic orbitals.

The simplest molecular orbitals are known as σ (Greek letter 'sigma')-orbitals.

σ-orbitals and σ-bonds

When two *s*-orbitals, each with a single electron, approach and overlap, a new molecular orbital called a σ-orbital is formed, as in Fig. 31.

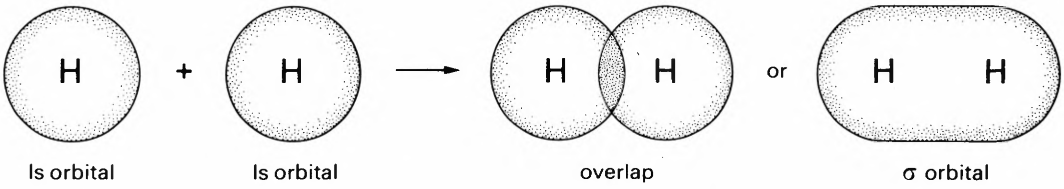


Fig. 31.

A σ-orbital is also formed from the overlap of singly-occupied *s*- and *p*-orbitals, as in Fig. 32.

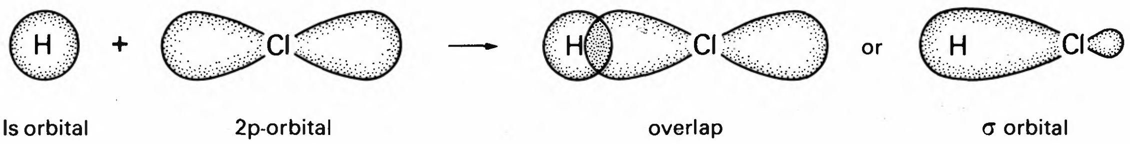


Fig. 32.

In Fig. 32, the filled 1*s*- and 2*s*-orbitals and the two filled 2*p*-orbitals in the chlorine atom are not shown because the electrons in these orbitals do not contribute to bonding. Strictly, all electrons in molecules occupy molecular orbitals, but it is only for the bonding electrons that molecular orbitals are very different from atomic orbitals.

In the same way, two *p*-orbitals can overlap to form a σ-orbital, as in Fig. 33.

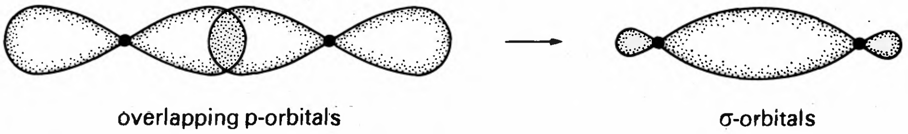


Fig. 33.

In this case, the single molecular orbital consists of three separated volumes of space, and the two electrons may be found anywhere in the total volume. However, the two smaller volumes are often omitted from simple diagrams just as we have omitted the filled 1*s*-and 2*p*-orbitals and the similar molecular orbitals formed from them.

Note that a molecular orbital, just as an atomic orbital, can only hold two electrons, and a doubly-filled σ-orbital constitutes what is known as a σ-bond.

So far, you have probably noticed there is very little difference between the orbital theory and the shared-pair theory. All the single bonds shown in classical structural formulae can be regarded as σ-bonds. The two theories diverge when we look at multiple bonds, and it is here that orbital theory gives us a much better picture, as we now show.

π-orbitals and π-bonds

The overlap of two *p*-orbitals, instead of forming a σ-orbital as described above, can form a π-orbital if the geometry is different (π = Greek letter 'pi').

Objective. When you have finished this section, you should be able to:

(61) describe the formation of a π-bond by overlap of p-orbitals.

Two singly-occupied p-orbitals, at 90° to each other, are shown in Fig. 34 for two atoms approaching each other.

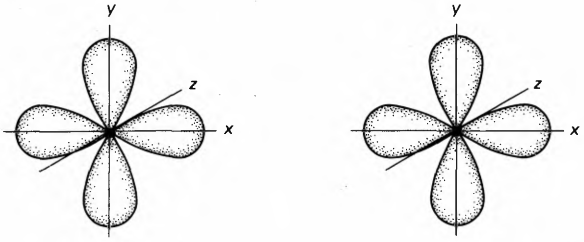


Fig. 34.

Two of these p-orbitals overlap end-on to form a σ-bond, as in the H_2 and Cl_2 molecules. The other two p-orbitals overlap side-on, and merge to form a new molecular orbital called a π-orbital, which consists of two bone-shaped volumes above and below the σ-orbital, as in Fig. 35.

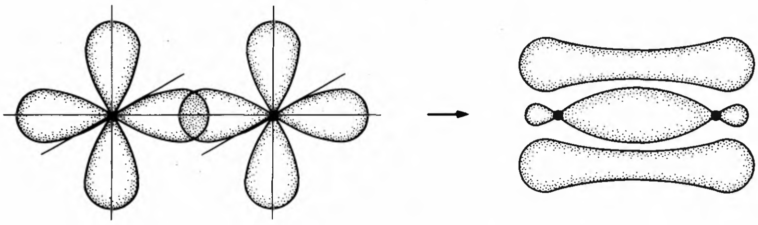


Fig. 35.

The merging of the p-orbitals draws the two atoms closer together so that the double bond is shorter than a single bond. Note that the third pair of p-orbitals at 90° to the other two pairs (not shown in Fig. 35) also approach side-on but do not merge because they already have two electrons each.

Another very important point to remember is that although the π-orbital has two lobes it is a single orbital containing a pair of electrons. The electrons may be found anywhere in the two lobes, not necessarily one electron in each.

All double bonds can be thought of as a σ-bond and a π-bond formed very much as described above. The multiple bonds which interest chemists most are those between carbon atoms, as shown by C=C and C≡C in electron-pair structures. Before we can look at these bonds by the molecular orbital approach, we must first consider a further type of atomic orbital which we have not discussed before.

HYBRIDIZED ATOMIC ORBITALS

These orbitals are formed by mixing (hybridization) of simpler s-, p- and d-orbitals in various combinations.

sp^3-hybrid orbitals and tetrahedral bonding

sp^3 hybrid orbitals are so called because they are formed by the mixing (hybridization) of one s-orbital and three p-orbitals.

Objectives. When you have finished this section, you should be able to:

(62) describe the formation of sp^3-hybrid orbitals in carbon atoms;

(63) show how sp^3-hybridization can account for the shape of a methane molecule, CH_4.

Read about sp^3-hybridization in carbon atoms in your text-book(s). Look for an account of the tetrahedral arrangement of bonds around a carbon atom in compounds such as methane, CH_4, so that you can do the next exercise.

Exercise 66 (a) Make copies of Fig. 36, label the boxes appropriately, and draw arrows in them to represent the electron arrangements in a carbon atom as it begins to form four covalent bonds.

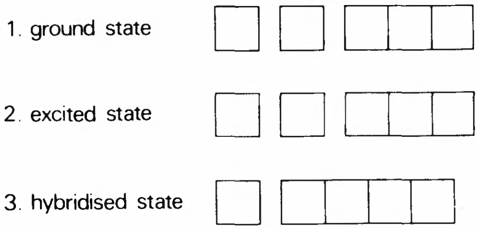


Fig. 36.

(b) Fig. 37 shows two representations of a methane molecule. (Each hybrid orbital and each molecular orbital has a small lobe opposite the large one, similar to those shown in Figs. 32, 33 and 35, but these have been omitted for simplicity.) Make rough copies and label them to show:

(i) the positions of carbon and hydrogen nuclei,

(ii) the 1s-orbitals for hydrogen,

(iii) the sp^3-orbitals for carbon,

(iv) the σ-molecular orbitals for methane.

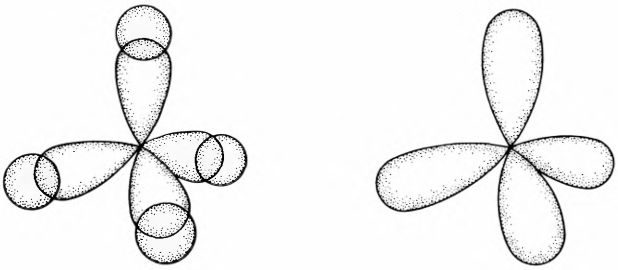


Fig. 37.

(Answers on page 95)

The shapes of other molecules can also be described by means of *sp*^{3}-hybridization giving four tetrahedrally-directed molecule orbitals in a similar way. However, some of these molecular orbitals may be occupied by lone pairs of electrons which are not available to form bonds. Some examples of molecular orbitals in simple molecules are shown in Fig. 38 with the non-bonding orbitals shaded. Note the increase in the number of non-bonding orbitals from left to right along the second period of the Periodic Table.

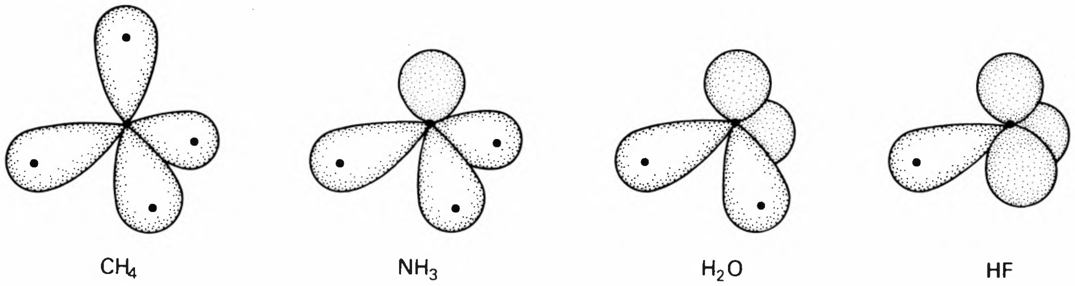

CH_4 NH_3 H_2O HF

Fig. 38.

There is no great advantage, however, in using the orbital theory to describe such molecules. Since the electron pair repulsion theory is much simpler, we advise you to use it wherever it gives a satisfactory explanation.

The superiority of the orbital theory is especially important in the description of multiple bonds between carbon atoms, and these involve some different hybrid orbitals.

sp^2-hybrid orbitals and double bonds

sp^2-hybrid orbitals are formed from the hybridization of one *s*-orbital and two *p*-orbitals.

Objectives. When you have finished this section, you should be able to:

(64) describe the formation of *sp*^{2}-hybrid orbitals in carbon atoms;

(65) show how *sp*^{2}-hybridization explains the shape of the ethene molecule, C_2H_4.

Read about *sp*^{2}-hybridization in your text-book(s). Look for an explanation of the trigonal arrangement of bonds around a carbon atom in compounds such as ethene (ethylene), C_2H_4. Don't worry about *sp*^{2}-hybridization in benzene until after you have dealt with ethene in the next exercise.

Exercise 67 (a) Make a copy of Fig. 39, label the boxes appropriately, and draw arrows in them to represent the electron arrangements in a carbon atom as it begins to form a double bond and two single bonds.

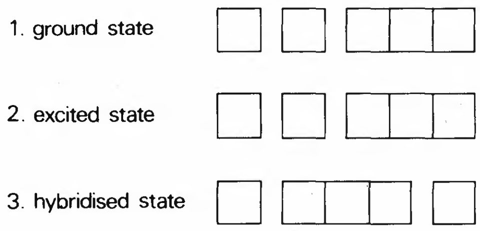


Fig. 39.

(b) Fig. 40 shows two representations of an ethene molecule. (The small lobes of the hybrid and molecular orbitals have again been omitted.) Make rough copies and label them to show:

(i) the positions of carbon and hydrogen nuclei,

(ii) the sp^2-hybrid orbitals and p-orbitals for carbon,

(iii) the σ- and π-molecular orbitals for ethene.

(c) What is the significance of the dashed lines in Fig. 40a?

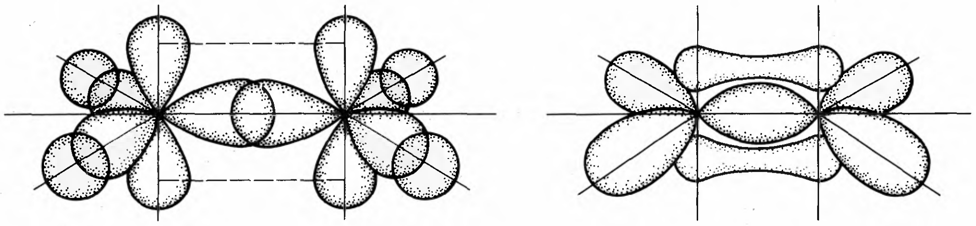


Fig. 40.

(Answers on page **95**)

Note that atoms attached by a σ-bond can rotate because the bond is symmetrical about its axis, but there is no rotation about a π-bond.

The side-on overlap of the p-orbitals effectively fixes the four hydrogen atoms in one plane and prevents rotation about the σ-bond. This is a much more satisfactory explanation of the shape than is provided by the simpler 'bent bond' model shown in Fig. 41, in which repulsion of electron pairs has to account for the planar shape. Note, however, that we still use the 'bent bond' idea when constructing simple 'ball-and-spring' molecular models.

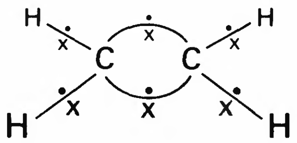


Fig. 41.

Another advantage of the orbital approach is that the σ- and π-bonds in a double bond are shown to be different. You can confirm that σ- and π-bonds have different strengths in the next exercise.

Exercise 68 (a) Compare the strengths of σ- and π-bonds in ethene, using the following information.

$$CH_3 \quad CH_3 \rightarrow CH_3\bullet + \bullet CH_3; \quad \Delta H^{\ominus} = +348 \text{ kJ mol}^{-1}$$

$$CH_2 \quad CH_2 \rightarrow CH_2\!: + :\!CH_2; \quad \Delta H^{\ominus} = +612 \text{ kJ mol}^{-1}$$

(b) What assumption about σ-bonds have you made?

(Answers on page **95**)

The last exercise suggests that a π-bond in ethene might be relatively easy to break. This accounts for the characteristic reactivity of ethene, which you study more fully in Unit 01.

sp^2-hybridization also provides a better description of the delocalization of electrons in benzene than the one we gave earlier (p. 58).

The structure of benzene - a second look

You can apply your knowledge of molecular orbitals and hybridization to the structure of benzene in this section.

Objective. When you have finished this section, you should be able to:

(66) describe the structure of benzene in terms of σ- and π-bonds.

Read about the structure of benzene in your text-book(s). Use what you find, together with the preceding section of this Unit, to attempt the following exercise.

Exercise 69 (a) Sketch the three *sp*^{2}-hybrid orbitals for a single carbon atom.

(b) What feature of the spatial arrangement of *sp*^{2}-hybrid orbitals makes it likely that a regular hexagon will be formed by repeated overlapping?

(c) Copy Fig. 42 and draw in the molecular orbitals resulting from end-on overlap of atomic orbitals.

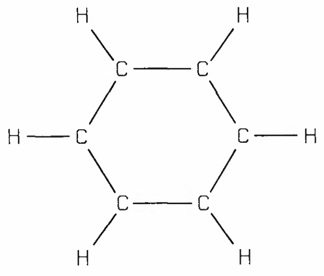


Fig. 42.

(d) Which atomic orbitals are not involved in the bonding you have described in (c), and where are they situated?

(Continued overleaf)

Exercise 69 (continued)

(e) Copy Fig. 43, which represents a regular hexagon at right angles to the plane of the paper, and sketch in the six singly-occupied *p*-orbitals. Show how they overlap to form a large orbital* consisting of two ring-shaped charge clouds.

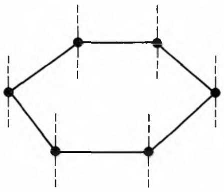


Fig. 43.

(f) Why are the six electrons occupying the ring-shaped orbitals called 'delocalized electrons'?

(g) Another structure you have studied earlier in this Unit can be described similarly in terms of sp^2-hybridization, hexagonal rings and delocalized electrons. Which structure is this?

*Strictly speaking, there are three orbitals, each occupying the same volumes of space, and each containing a pair of electrons.

(Answers on page 96)

Your extended versions of Figs. 42 and 43 can be combined to give an overall three-dimensional picture of the molecular orbitals in benzene. We show this in Fig. 44.

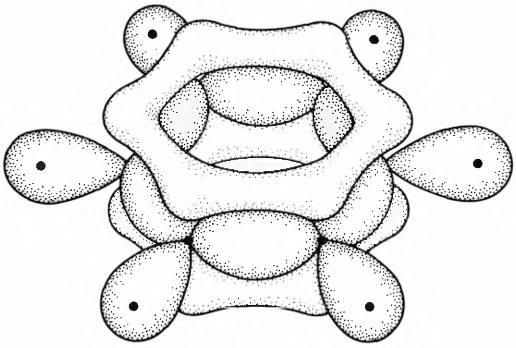
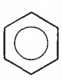


Fig. 44.

Don't worry about having to draw a diagram like Fig. 44. If you need to describe the structure of benzene in terms of orbitals, the sketches you drew for Exercise 69 will be adequate, but for many purposes the structural formula,  , is sufficient.

The most important thing for you to remember is that there are two ring-shaped charge clouds, sometimes called π-rings, in a benzene molecule, above and below the plane of the molecule. This will help you to understand the chemical reactions of benzene and similar compounds which you study in later Units.

You can also apply the idea of sp^2-hybridization to the structure of butadiene, C_4H_6, and similar compounds, in the next section.

Butadiene and other conjugated systems

Butadiene (more precisely, buta-1,3-diene) has an electron-pair structure $CH_2{=}CH{-}CH{=}CH_2$. This structure, however, does not account for its measured bond lengths or its chemical reactions.

Objectives. When you have finished this section, you should be able to:

(67) explain the term conjugated system;

(68) describe the structure of butadiene in terms of σ- and π-orbitals.

Read about the structure of butadiene in your text-book(s), so that you can do the following exercise.

Exercise 70 (a) Why is the structure of butadiene described as a conjugated system?

(b) The molecular orbitals in butadiene are shown in Fig. 45.

What do the labelled areas (A, B and C) represent and how many electrons are there in each?

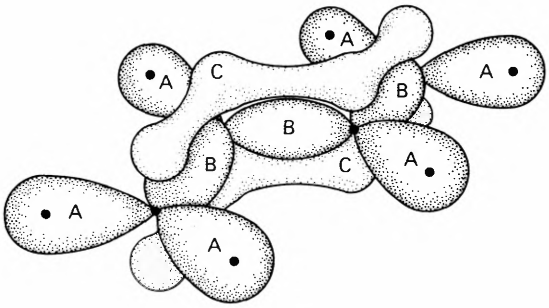


Fig. 45.

(Answers on page 96)

It is interesting to note that the delocalization of electrons in butadiene can also be described in terms of a hybrid of three electron-pair structures:

$$H_2\overset{+}{C}{-}CH{=}CH{-}\underset{\bullet\bullet}{\overset{-}{C}}H_2 \qquad H_2C{=}CH{-}CH{=}CH_2 \qquad H_2\underset{\bullet\bullet}{\overset{-}{C}}{-}CH{=}CH{-}\overset{+}{C}H_2$$

However, the electron-pair structures involving a separation of charge look rather unlikely and make this description rather 'forced'. The orbital model is far superior in this case.

Now we look briefly at the hybridization of orbitals involved in the formation of triple bonds between carbon atoms.

sp- -hybrid orbitals and triple bonds

sp-hybrid orbitals are formed from the hybridization of one *s*-orbital and one *p*-orbital.

Objectives. When you have finished this section, you should be able to:

(69) describe the formation of *sp*-hybrid orbitals in carbon atoms;

(70) show how *sp*-hybridization accounts for the shape of the ethyne molecule, C_2H_2.

Read about *sp*-hybridization in your text-book(s). Look for an explanation of the linear shape of an ethyne molecule, C_2H_2. This will help you do the following exercise. Note that ethyne is still sometimes called acetylene.

Exercise 71 (a) Make a copy of Fig. 46, label the boxes appropriately, and draw arrows in them to represent the electron arrangements in a carbon atom as it begins to form a single bond and a triple bond.

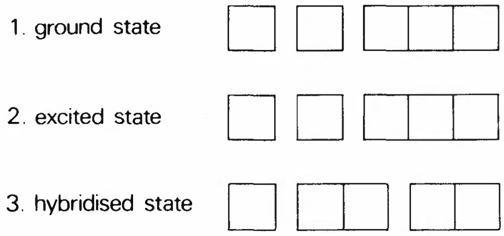


Fig. 46.

(b) Fig. 47 shows two representations of an ethyne molecule, C_2H_2. (The small lobes of the hybrid and molecular orbitals have again been omitted.) Make rough copies and label them to show:

(i) the positions of the carbon and hydrogen nuclei,

(ii) the *sp*-orbital and *p*-orbitals for carbon,

(iii) the σ- and π-molecular orbitals for ethyne.

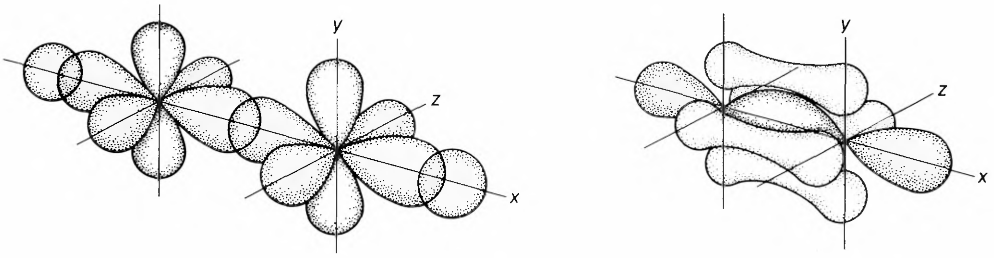


Fig. 47.

(c) The two π-orbitals also interact to delocalize the π-electrons still further. What shape describes the overall distribution of these electrons?

(Answers on page 96)

Just as for ethene, the molecular orbital description of ethyne is very helpful in understanding chemical reactions, as you will see when you study them in a later Unit.

You have now completed a study of the three types of strong interatomic bonding - ionic, covalent and metallic. For the sake of unity, we go on to consider very briefly the different types of weak bonding that can exist between molecules, but a fuller account will appear in Unit P4.

WEAK INTERMOLECULAR BONDING

In Level One, you learned that covalent bonding often leads to the formation of separate (discrete) molecules. Very weak electrostatic forces of attraction exist between these molecules due to the non-uniform or irregular distribution of charge in the molecules. At relatively low temperatures, molecules move more slowly and the disruptive effect of molecular collisions is smaller. It may be small enough to allow the weak intermolecular forces to form bonds between molecules in liquid, or even solid, structures. These bonds are often called van der Waals bonds.

Objectives. When you have finished this section, you should be able to:

(71) explain the term *van der Waals bond*;

(72) explain the existence of weak attractive forces between *polar molecules*;

(73) explain the existence of weak attractive forces between *non-polar molecules*;

(74) explain why heavier molecules generally experience larger intermolecular forces.

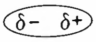
van der Waals bonding

The attractive forces between molecules may arise in several different ways. Different types of attractive force operate together to produce van der Waals bonds.

We consider first the bonding forces between polar molecules. These are the simplest to describe and understand.

Bonding forces between polar molecules

You have learned that many molecules are polar, and possess a dipole moment. If a polar molecule is represented simply as



or

then it is clear that the positive 'end' of one molecule could attract the negative 'end' of another, giving a structure which could be represented as in Fig. 48.

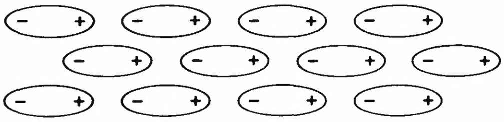
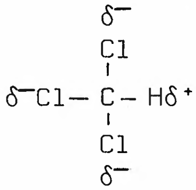


Fig. 48.

The attractive forces are sometimes called 'dipole-dipole attractions'. Substances with polar molecules, such as trichloromethane,



$$\begin{array}{c} \delta^- \\ \mathrm{Cl} \\ | \\ \delta^-\mathrm{Cl}-\mathrm{C}-\mathrm{H}\delta^+ \\ | \\ \mathrm{Cl} \\ \delta^- \end{array}$$

are frequently liquids at room temperature because the attractive forces are not strong enough to maintain the structure against the dispersing effect of molecular motion.

You will study the bonds between polar molecules more fully in Unit P4, particularly the bonds between molecules of different substances.

The dipoles we have been considering are permanent dipoles. Another type of bonding force concerns temporary dipoles.

Bonding forces between non-polar molecules

The descriptions of electron clouds, or charge-density clouds, which you have already used are probability patterns. For instance, when we draw a spherically symmetrical charge cloud for a helium atom, as in Fig. 49, we are saying that over a period of time, there is an equal probability of finding an electron in every radial direction. The atom, therefore, has no permanent dipole moment.

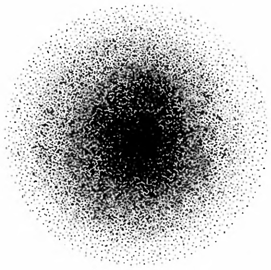


Fig. 49.

However, at any given instant, the electrons might be in positions which do give rise to a temporary dipole, only to be replaced an instant later by another in a different direction, as in Fig. 50.

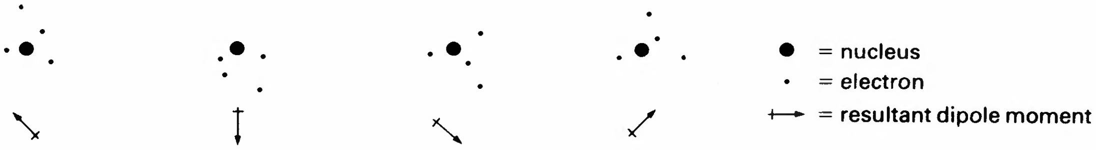


Fig. 50.

There are attractive forces between neighbouring temporary dipoles rather similar to the permanent dipole attractions discussed in the last section. Perhaps you are wondering why the attractive forces are not balanced by repulsive forces between dipoles aligned the other way round. All we can say at this level is that it can be proved mathematically that although such repulsive forces do exist they are weaker than the attractive forces.

The more electrons there are in a molecule, the greater the possibility that temporary dipoles will be large and, therefore, the stronger the attractive forces. This is why substances with high molecular mass generally have higher melting and boiling points than those with low molecular mass.

Another important point to remember is that these temporary flickering dipoles can arise in polar molecules as well as non-polar molecules. For heavy polar molecules, the attractive forces due to temporary dipoles may even be greater than those due to the permanent dipoles.

We have described van der Waals bonding in terms of attractive forces due to permanent and temporary dipoles. Now we consider another type of weak intermolecular bonding.

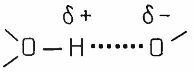
Hydrogen bonding

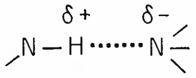
The nature of hydrogen bonds is still something of a mystery - all we will do here is describe the circumstances in which they exist.

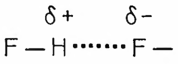
Objectives. When you have finished this section, you should be able to:

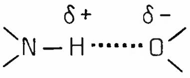
(75) describe the hydrogen bond and state the circumstances in which it may be formed.

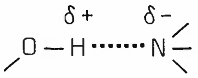
Hydrogen bonds may be formed between hydrogen atoms in one molecule and oxygen, nitrogen or fluorine atoms in another. However, only certain hydrogen atoms can form hydrogen bonds - only those which are already attached by strongly polar bonds to other atoms. The partial charge on these hydrogen atoms is attracted to partial charges in neighbouring molecules. Consequently, oxygen, nitrogen and fluorine atoms are often involved in two ways in hydrogen bonding. Typical hydrogen bonds are shown by dotted lines in the formulae below.











It is clear that dipole-dipole attractions exist in such cases, but the bonding is actually much stronger than could be accounted for in this way.

You will learn more about the strength of hydrogen bonds, and the special properties of compounds containing them, in Unit P4. You will also take a little further your study of all forms of weak intermolecular bonding but the following exercise tests your present understanding of the topic.

Exercise 72 Which of the following pairs of substances would you expect to have the higher boiling point? Explain your choice briefly.

(a) Argon and neon

(b) HF and HCl

(c) Propane, C_3H_8, and butane, C_4H_{10}

(Answers on page 96)

To consolidate your study of chemical bonding, we suggest you have another look at the ILPAC videotape 'Molecules and Models', if it is available. View it now if you can, or at any time before you complete the final section of this Unit.

Before you start the final section of this Unit, do the following exercise and hand your answer to your teacher for marking. The exercise consists of parts of two different A-level examination questions. We suggest that you answer part (b) in terms of orbital theory if you have studied it sufficiently. If you are in doubt, consult your teacher.

Teacher-marked Exercise (a) Account for the structure of the tetrachloromethane molecule in terms of orbitals.

(b) X-ray evidence leads to the following distances between adjacent carbon atoms in different compounds:

	ethane	ethene	ethyne	benzene
C—C bond length (nm)	0.159	0.132	0.120	0.139

What explanation for these variations can you offer in terms of either electron-pair repulsion or orbital theory?

You have seen, as you have progressed through this Unit, how difficult it can be to 'pin down' electrons, and to say where they are and to which atoms they 'belong'. You have also learned, in your pre-A-level course, that oxidation and reduction involve transfer of electrons*. But if we are not sure where the electrons are, how can we say anything useful about transfer? The concept of oxidation number has been developed using ideas of electronegativity, to overcome this difficulty and enable us to identify redox reactions more readily.

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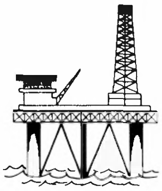
*If you experience difficulty in remembering the difference between oxidation and reduction in terms of electron transfer, this mnemonic may help you.

O xidation
I s
L oss
R eduction
I s
G ain



OXIDATION NUMBER

By assigning every bonding electron in a compound to a particular atom according to certain rules, we give each atom a number called an oxidation number. A transfer of electrons then involves a change in oxidation number.

Objectives. When you have finished this section, you should be able to:

(76) explain the term oxidation number;

(77) state the oxidation numbers of elements in a variety of compounds and ions, given their formulae;

(78) identify redox reactions by means of changes in oxidation numbers.

Read about oxidation number in you text-book(s), looking particularly for the simple rules which help us to work out oxidation numbers of elements in compounds. The following exercises, with worked examples for the more complicated cases, show how the rules are applied.

Exercise 73 What are the oxidation numbers of the following elements?

(a) Na in Na^+
(b) O in O^{2-}
(c) Al in Al^{3+}
(d) H in H^+
(e) H in H^-

(Answers on page 96)

You have learned that the *s*-block metals, with the exception of beryllium, always form ionic compounds, and the charge on the positive ion is always the same as the group number. This fact enables you to do the next exercise.

Exercise 74 What are the oxidation numbers of the elements in the following compounds?

(a) KCl
(b) Na_2O
(c) BaF_2
(d) Na_3P
(e) Mg_3N_2
(f) CsH

(Answers on page 97)

In the last exercise you made use of the fact that the sum of the ion charges in an ionic compound is zero. Since ion charge is, by definition, the same as oxidation number, it follows that the sum of the oxidation numbers for each atom in a compound is zero. This rule also applies to covalent compounds, as we now show in a worked example.

Worked example. What are the oxidation numbers of the elements in these compounds?

(a) HCl (b) H_2S

Solution to (a)

1. Consider the relative electronegativities of hydrogen and chlorine.

Electronegativity of H = 2.1
Electronegativity of Cl = 3.0

(You should know that chlorine is more electronegative than hydrogen, without having to look up values)

2. Imagine that the more electronegative atom gains both the bonding electrons so that ions are formed.

$$\overset{\delta^+}{H}-\overset{\delta^-}{Cl} \quad \text{imagined as} \quad H^+ \ Cl^-$$

3. Write down oxidation numbers from the ion charges

$$Ox(H) = +1; \quad Ox(Cl) = -1$$

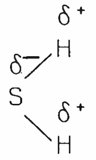
Solution to (b)

1. Consider the relative electronegativities of hydrogen and sulphur.

Electronegativity of H = 2.1

Electronegativity of S = 2.5

2. Imagine the partial separation of charge to be completed so that ions are formed.



imagined as S^{2-} H^+ H^+

3. Write down oxidation numbers from the ion charges.

$$Ox(H) = +1; \quad Ox(S) = -2$$

Note that the sum of the oxidation numbers for each atom is zero, because there are two hydrogen atoms:

$$2 \times (+1) + (-2) = 0$$

Now do the following exercise in the same way.

Exercise 75 What are the oxidation numbers of the elements in these compounds?

(a) NH_3 (b) Cl_2O

(Answers on page 97)

Repeated application of the method used above has shown that certain elements in compounds always (or nearly always) have the same oxidation number.

Group I metals - always +1

Group II metals - always +2

Fluorine - always -1

Hydrogen - always +1, except in ionic hydrides where it is -1

Oxygen - always -2, except in peroxides (which contain an O-O linkage), and when combined with fluorine.

In the next exercise, you consider some cases where oxygen does not have an oxidation number of -2.

Exercise 76 What is the oxidation number of oxygen in the following molecules?

(a) H_2O_2 (H—O—O—H) (b) F_2O

(Answers on page 97)

The knowledge that some elements have fixed oxidation numbers enables us to take a short cut in finding the oxidation numbers of other elements. We show this in a worked example:

Worked example: What is the oxidation number of As in H_3AsO_3?

Solution

$$\text{Write } \quad Ox(\text{As}) + Ox(\text{all other atoms}) = 0$$

$$\therefore \quad Ox(\text{As}) = -\,Ox(\text{all other atoms})$$

$$= -\,[3\,Ox(\text{H}) + 3\,Ox(\text{O})]$$

$$= -\,[3(+1) + 3(-2)] = -3 + 6 = +3$$

Use the same method in the following exercise.

Exercise 77 What are the oxidation numbers of the following atoms?

(a) As in H_3AsO_4 (b) Cr in $HCr_2O_7^-$

(Answers on page 97)

You have now covered all the simple rules which help you to assign oxidation numbers. Apply them, as appropriate, in the next exercise.

Exercise 78 Calculate the oxidation numbers of the underlined elements in the following compounds:

(a) $K_2\underline{Cr}_2O_7$ (d) $Na_2\underline{S}_2O_3$ (g) $\underline{N}H_4\underline{N}O_3$

(b) $Pb\underline{S}O_4$ (e) $Ca\underline{C}O_3$ (h) $Na_2\underline{S}_4O_6$

(c) $H\underline{N}O_3$ (f) $Na_8\underline{Ta}_6O_{19}$ (i) $\underline{Fe}_3O_4$

(Answers on page 97)

One of the uses of oxidation numbers is in the systematic naming of inorganic compounds by the Stock notation, which we now mention briefly.

Oxidation number and the Stock notation

We suggest that you do not at this stage try to learn all the details of the Stock notation for naming inorganic compounds. It is best learnt in stages by the experience of meeting and using systematic names. All we do here is give some illustrations.

Compounds such as the two chlorides of iron, $FeCl_2$ and $FeCl_3$, are distinguished in names by the use of oxidation numbers.

$FeCl_2$ - iron(II) chloride	(preferred to the older name ferrous chloride)
$FeCl_3$ - iron(III) chloride	(preferred to the older name ferric chloride)

The oxychlorides of sodium are distinguished as follows:

NaClO - sodium chlorate(I)	(preferred to hypochlorite)
$NaClO_3$ - sodium chlorate(V)	(preferred to chlorate)
$NaClO_4$ - sodium chlorate(VII)	(preferred to perchlorate)

Note that Roman numerals are used for oxidation numbers in names. Roman numerals are also used in conjunction with symbols. Thus P^{III} and P(III) both mean 'a compound or ion in which phosphorus has an oxidation number of 3'.

In your reading you may also find reference to oxidation state. The following example makes the meaning clear.

'Iron in oxidation state III' means exactly the same thing as 'a combined form of iron in which it has oxidation number 3'.

We mentioned earlier that oxidation numbers are useful in identifying redox reactions. Although your main study of redox reactions at A-level is in a later Unit, it is worth considering the point briefly here.

Oxidation number and redox reactions

We bring together two statements which should by now be familiar to you:

Oxidation is a loss of electrons

Oxidation number is the number of electrons 'lost' by an atom in going from its uncombined state to a particular combined state.

The combination of these two statements gives an alternative definition of oxidation:

Oxidation involves an increase in oxidation number

Similarly,

Reduction involves a decrease in oxidation number

You can apply these alternative definitions in the next exercise.

Exercise 79 By assigning oxidation numbers to the elements in both reactants and products, decide whether or not the following are redox reactions.

(a) $Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s)$

(b) $2KBr(aq) + Cl_2(aq) \rightarrow 2KCl(aq) + Br_2(aq)$

(c) $CuSO_4(aq) + Pb(NO_3)_2(aq) \rightarrow Cu(NO_3)_2(aq) + PbSO_4(s)$

(d) $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

(e) $MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow$
$Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$

(Answers on page 97)

LEVEL TWO CHECKLIST

You have now reached the end of this Unit. Look again at the checklist at the end of Level One. In addition, you should now be able to:

(42) & (43) explain the terms polarization, polarizability and polarizing power with reference to ions;

(44) explain how both polarizability and polarizing power depend on ionic radius and ionic charge;

(45) & (46) explain how ionic bonding can have covalent character and how a covalent bond can have ionic character;

(47) & (48) explain the terms bond polarity and dipole moment;

(49) explain why some molecules with polar bonds have no dipole moment;

(50) & (51) explain the term electronegativity and distinguish it clearly from electron affinity;

(52) explain why electronegativity is related to atomic radius;

(53) describe the trends in electronegativity in the Periodic Table;

(54) use values of electronegativity to predict the nature of the bonding between two elements;

(55) use values of electronegativity to explain differences between experimental and calculated lattice energies;

(56) explain the term delocalization of electrons;

(57) & (58) describe, in terms of intermediates between electron-pair structures, the actual structures of benzene and of the following ions - methanoate (formate), ethanoate (acetate), carbonate and nitrate;

(59) explain simply the term molecular orbital;

(60) describe the formation of σ-orbitals and σ-bonds;

(61) describe the formation of a π-bond by overlap of *p*-orbitals;

(62) & (63) show how sp^3-hybridization accounts for the shape of a methane molecule;

(64) & (65) show how sp^2 – hybridization accounts for the shape of the ethene molecule;

(66) describe the structure of benzene in terms of σ-bonds and π-bonds;

(67) explain the term conjugated system;

(68) describe the structure of butadiene in terms of σ- and π-orbitals;

(69) & (70) show how *sp*-hybridization accounts for the shape of the ethyne molecule;

(71) explain the term van der Waals bond;

(72) & (73) explain the existence of weak attractive forces between polar molecules and between non-polar molecules;

(74) explain why heavier molecules generally experience larger intermolecular forces;

(75) describe the hydrogen bond and state the circumstances in which it may be formed;

(76) explain the term oxidation number;

(77) state the oxidation numbers of elements in a variety of compounds and ions, given their formulae;

(78) identify redox reactions by means of changes in oxidation number.

END-OF-UNIT TEST

To find out how well you have learned the material in this Unit, try the test which follows. Read the notes below before starting:

1. You should spend about 1½ hours on this test.
2. Hand your answers to your teacher for marking.

END-OF-UNIT TEST

Questions 1-3

A

Two compounds may be similar in that they each have

A dative covalent bonds in their molecules

B delocalised electrons in their molecules

C at least one bond angle of exactly 120° in each of their molecules

D non-polar molecules

E linear molecules

Select, from A to E, the similarity between each pair of compounds below:

1. Benzene (C_6H_6) and cyclohexane (C_6H_{12}). (1)

2. Hydrogen cyanide (HCN) and carbon dioxide (CO_2). (1)

3. Boron trifluoride (BF_3) and tetrachloromethane (CCl_4). (1)

4. In which one of the following molecules would you expect to find the smallest bond angle between two adjacent covalent bonds?

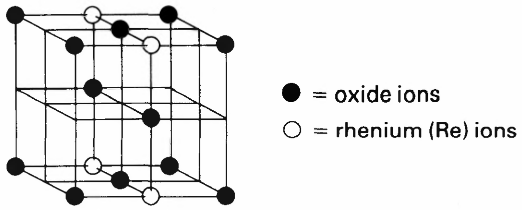
A

A BeH_2 C CCl_4 E OH_2

B BF_3 D NH_3 (1)

5. The diagram shows a unit cell of the structure of rhenium oxide.

A



From this it can be deduced that

A the coordination number of rhenium is 6

B the oxygen ions are arranged in a face-centred cubic arrangement

C the formula of this oxide is ReO_2

D the coordination number of oxygen is 4

E the number of ions in the unit cell is 16 (1)

6. Which of the following has the smallest ionic radius?

A

A Mg^{2+} C Cl^- E O^{2-}

B F^- D Na^+ (1)

7. Which of the following compounds would you expect to have the largest dipole moment in the vapour phase?

A

A CH_4 C H_2O E HF

B NH_3 D NO

(1)

8. What are the oxidation states of the element X in the following compounds?

	Na_2XO_4	$CaX(CN)_6$	$X(H_2O)_6Cl_2$	$(NH_4)_3XCl_6$
A	+2	+3	+4	+5
B	+2	+3	+4	+6
C	+2	+4	+6	+8
D	+3	+4	+5	+6
E	+4	+5	+6	+8

A

(1)

In questions 9-11, more than one (or none) of the suggested responses may be correct. Answer as follows:

A if only 1,2 and 3 are correct

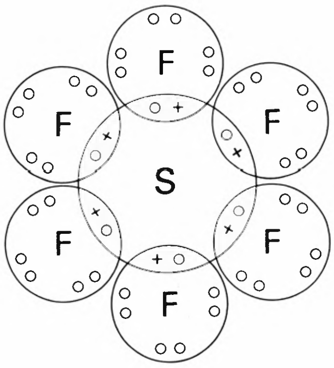
B if only 1 and 3 are correct

C if only 2 and 4 are correct

D if only 4 is correct

E if some other response, or combination, is correct.

9. The diagram represents the electronic structure of the sulphur hexafluoride molecule.



A

Correct statements about sulphur hexafluoride include that

1 all S—F bonds are equivalent

2 SF_6 is a planar molecule

3 the oxidation number of sulphur is the same as the number of electrons it uses in bonding

4 sulphur has acquired the electronic structure of the inert gas argon

(1)

10. Which of the following statements(s) is/are true?

1 The electronegativity of the alkali metals decreases with increase in atomic number of the metal.

2 Elements of high electronegativity usually react by gain of electrons.

3 Beryllium and aluminium have similar electronegativities.

4 In a given short period of the Periodic Table, the electronegativity of the elements decreases from left to right. (1)

A

11. In which case(s) do the two molecules or ions represented have similar shapes?

A

1 BCl_3 PCl_3 3 CO_2 SO_2

2 NH_4^+ ClO_4^- 4 CO_3^{2-} NO_3^{2-}

(1)

In questions 12-14 choose an answer from A to E as follows:

A Both statements true: second explains first

B Both statements true: second does not explain first

C First true: second false

D First false: second true

E Both false.

	FIRST STATEMENT	SECOND STATEMENT	
12.	In the chlorine molecule, the oxidation number of the element is zero.	The concept of oxidation number can only be applied to ionic compounds.	A (1)
13.	The molecule BF_3 has the same shape as NH_3.	The BF_3 and NH_3 molecules have the same number of bond pairs.	A (1)
14.	Lithium is less electronegative than potassium.	The outer electron in a lithium atom is more tightly bound than the outer electron in a potassium atom.	A (1)

15. (a) The six letters A,B,C,D,E,F, provide examples of five different types of bonding (or interaction) (i), (ii), (iii), (iv), (v). For each letter, append one Roman numeral so that the example best matches each type of interaction. (You need only write a letter and its appropriate Roman numeral.)

A

A Adjacent chains in polypropylene

B Adjacent chains in nylon $\left(-(CH_2)_6\text{-NH-CO-}(CH_2)_6\text{-CO-NH-}\right)$

C HF molecules in hydrofluoric acid

D Sodium and carbonate in Na_2CO_3 solid

E Silicon and chlorine in $SiCl_4$ liquid

F Aluminium and fluorine in the ion AlF_6^{3-}

(i) normal covalent bonding

(ii) ionic bonding

(iii) hydrogen bonding

(iv) co-ionic (dative covalent) bonding

(v) van der Waals interaction

(6)

(b) Contrast the differences in physical characteristics of carbon and and silicon dioxides and explain how these differences can be explained in terms of their structure and bonding. (4)

(c) Explain why carbon(IV) chloride (tetrachloromethane, carbon tetrachloride) is covalent but sodium chloride is ionic. (4)

16. (a) Explain what is meant by

(i) ion polarization, and

(ii) bond polarization. (6)

(b) Classify the following molecules as either polar or non-polar:

CO, CO_2, F_2, BF_3, CF_4, NH_3, SO_2, SO_3

Give one example of a polar bond and one example of a non-polar bond chosen from the bonds in these molecules. (6)

17. This question concerns the following elements whose electronegativities are listed.

Al	1.5	C	2.5	H	2.1	N	3.0	P	2.1
B	2.0	Cl	3.0	Li	1.0	Na	0.9	S	2.5
Be	1.5	F	4.0	Mg	1.2	O	3.5	Si	1.8

(a) What is meant by the term electronegativity? What factors determine the electronegativity of an element? (3)

(b) Arrange the elements according to their positions in the Periodic Table. (2)

(c) What is the relationship between electronegativity and the position of elements (i) in a period, (ii) in a group? In each case, give a brief explanation. (4)

(d) In what major respect do electronegativity and electron affinity differ? (1)

(e) Arrange the following substances in order of increasing ionic character (i.e. putting the least ionic first).

CO_2, $LiCl$, MgF_2, $NaCl$, NH_3, S_2Cl_2 (2)

18. Comment on, or explain, the following statements:

(a) The standard enthalpy of formation of benzene, when found from its enthalpy of combustion, is lower than when calculated by using bond energies for three C—C, three C=C and six C—H bonds. (6)

(b) Different values may be obtained for the relative molecular mass of aluminium chloride at different temperatures. (4)

19. By assuming that cadmium ions and iodide ions are charged spheres, a theoretical value for the standard molar lattice energy is calculated to be 2050 kJ mol^{-1}. Give an explanation for the difference between this value and the value determined using a Born-Haber cycle, i.e. 2346 kJ mol^{-1}. (4)

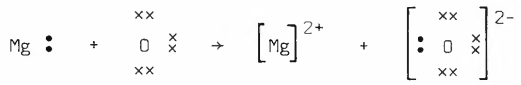
(Total 66 marks)

ANSWERS

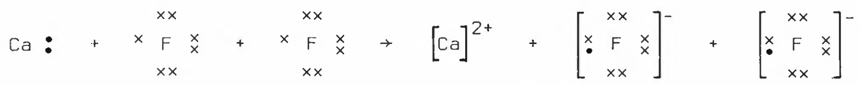
(Answers to questions from examination papers are provided by ILPAC and not by the Examination Boards.)

Exercise 1

(a)



(b)



Exercise 2

(a) (i) No electrons! (iv) (Ar) (vii) (Ar)$3d^5$

(ii) (He) (or $1s^2$) (v) (Ar)$3d^{10}$ (viii) (Kr)$4d^{10}$

(iii) (Kr)$4d^{10}5s^2$ (vi) (Ar)$3d^5$ (ix) (Ar)$3d^{10}4s^2$

(b) (i) filled *d*-subshell (d^{10}) (iii) filled *s*-subshell (s^2)

(ii) ½ filled *d*-subshell (d^5)

(c) The formation of a positive ion requires more and more energy as the number of electrons removed increases. The leaving electron is attracted by the overall positive charge of the ion, and may have to be raised from a lower energy level. (See Unit S2 on ionization energies.) The high energy required to form Si^{4+} or P^{5+} is not recovered in the formation of an ionic lattice. Alternatively, we can say that although Si^{4+} and P^{5+} have the same electron arrangment as Ne, the nuclear charge is much greater so that extra electrons would be readily added.

The formation of a negative ion becomes more and more difficult as the number of electrons added increases. The added electron is repelled by the overall negative charge of the ion, and may have to enter a higher energy level. The high energy required to form C^{4-} or B^{5-} is not recovered in the formation of an ionic lattice. Alternatively, we can say that although C^{4-} and B^{5-} are isoelectronic with Ne, the nuclear charge is much smaller, insufficient to hold all the electrons, some of which would be readily lost.

Exercise 3

(a) Na^+ would be smaller than Na because a complete electron shell (3*s*) has been removed.

(b) Cl^- would be larger than Cl because the extra electron is repelled by other electrons.

Exercise 4

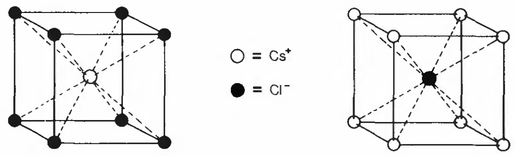
(a) The larger ions have greater electron densities near the nuclei. This implies a greater number of electrons in the ion. The larger ions are therefore chloride ions.

(b) No precise boundaries are shown.

(c) Choosing an arbitrary boundary as *half* way between the two *100 e* nm^{-3} contours, $r(Na^+)$ = 0.12 nm and $r(Cl^-)$ = 0.16 nm.

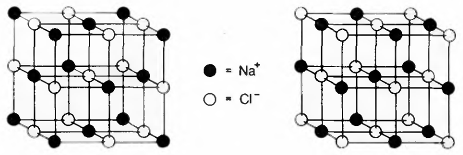
Exercise 5

(a)



Either of these structures can be taken as the unit cell.

(b)



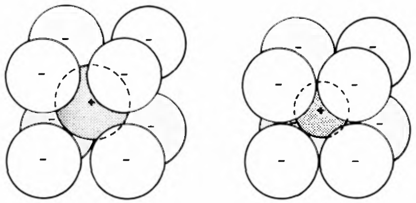
Either of these structures can be taken as the unit cell.

(c) Both ions in CsCl have a coordination number of 8.

Both ions in NaCl have a coordination number of 6.

Exercise 6

(a) Na^+ ions are much smaller than Cl^- ions. Eight Cl^- ions cannot therefore get close to a Na^+ ion before they repel each other too strongly for a stable arrangement.



8:8 co-ordination when A^+ and B^- are equal or nearly equal in size

8:8 co-ordination not possible when A^+ and B^- are quite different in size. Here the eight B^- ions repel each other

(b) (i) $r(K^+)$ = 0.133 nm, $r(F^-)$ = 0.133 nm. Ions of similar size. CsCl structure.

(ii) $r(Na^+)$ = 0.098 nm, $r(Br^-)$ = 0.196 nm. Cation smaller than anion. NaCl structure.

(iii) $r(Mg^{2+})$ = 0.065 nm, $r(O^{2-})$ = 0.146 nm. Cation smaller than anion. NaCl structure.

Exercise 7

(a) The forces of attraction between ions of opposite charge can operate in any direction.

(b) Sodium ions do not normally bond to chloride ions in pairs to form diatomic molecules as suggested by the formula. Instead they form giant lattices in which 6 Na^+ ions are held close to each Cl^- ion and vice versa.

Exercise 8

(a) The lattice energy for sodium chloride is the standard enthalpy change when one mole of NaCl is formed from gaseous ions.

(b) No. You might argue that as the coordination number is 6 for each ion, there are 6 moles of ionic bonds in one mole of sodium chloride. However, the attractive forces operate beyond the nearest neighbours, so one cannot really say how many ionic bonds there are.

(c) Since we cannot say how many bonds there are, we cannot say how strong each one is.

Exercise 9

(a) Most ionic crystals are fairly hard. This is not a conclusive test because some non-ionic solids are hard too, e.g. diamond.

(b) All ionic compounds have fairly high melting points. This is not a conclusive test because some non-ionic substances also have high melting points, e.g. diamond.

(c) Many ionic compounds are soluble in water. This is not a conclusive test because some ionic compounds are insoluble, e.g. silver chloride, magnesium oxide. Also, some non-ionic compounds are water soluble, e.g. sugar.

(d) (i) All ionic compounds conduct electricity when molten and are decomposed in the process, which is called electrolysis. This is a conclusive test because no other molten substances undergo electrolysis. (Liquid metals conduct but remain unchanged.)

(ii) All ionic compounds conduct electricity when dissolved in water. This is not a conclusive test because a few ionic substances are almost totally insoluble, and a few non-ionic substances react with water to form ions, e.g. PCl_3.

$$PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(g)$$

and $HCl(g) + aq \rightarrow H^+(aq) + Cl^-(aq)$

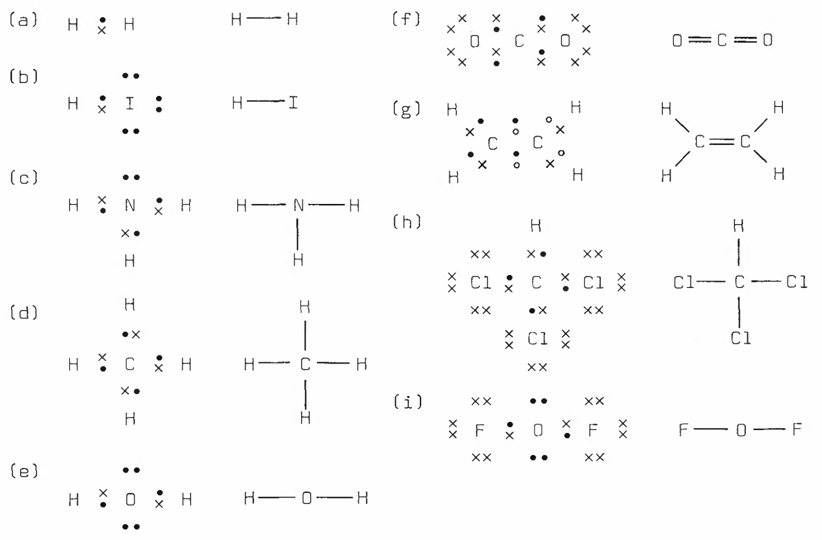
Exercise 10

Each plane parallel to those shown in A consists of alternate Na^+ and Cl^- ions. A very small movement of one plane relative to the next would bring ions of the same charge opposite each other, and the resulting repulsion would cause cleavage to occur.

Each plane parallel to the one shown in B consists of alternate rows of Na^+ and Cl^- ions. Again, a small movement could cause repulsion and cleavage. However, the movement would have to be across the rows and not along the rows.

Each plane parallel to the one shown in C consists entirely of one sort of ion. Each plane of Na^+ ions is next to a plane of Cl^- ions and vice versa. Thus, no movement along these planes could cause repulsion, and cleavage would not occur.

Exercise 11



Exercise 12

(a) Each hydrogen atom in the molecules has two electrons in its outer shell. All the other atoms have eight electrons in their outer shells.

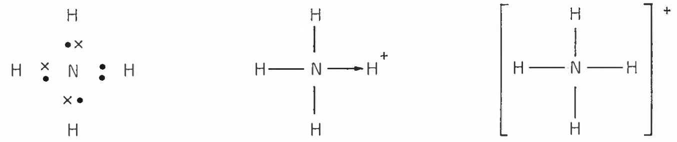
(b) An unbonded hydrogen atom has one electron in its outer shell. In order to reach the stable number of two in its outer shell it can form one covalent bond with another atom. Thus, its combining power (valency) is one. Similarly, an oxygen atom, with six electrons in its outer shell, can reach the stable number of eight by forming two covalent bonds so that its combining power (valency) is two. A carbon atom, with four electrons in its outer shell, needs to make four covalent bonds to reach the stable octet, and its combining power (valency) is therefore four.

Exercise 13

In a dative bond, both electrons originate from the same atom.

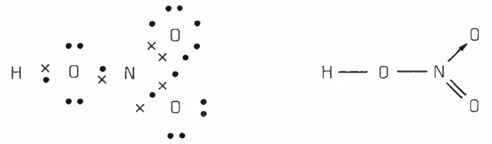
Exercise 14

(a)



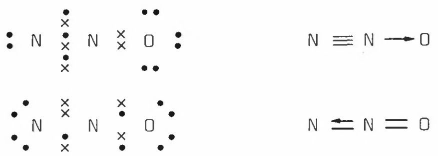
Note that in this example the dative bond is often not shown, as in the structure on the right, because the four bonds (and the four hydrogen atoms) are indistinguishable.

(b)



(c)

(d)

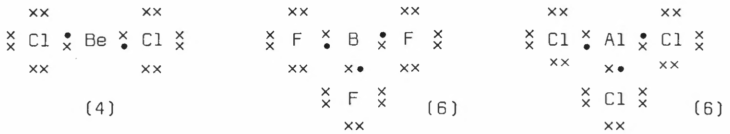


Which of these two structures is correct? We will pursue this problem later in the Unit.

Exercise 15

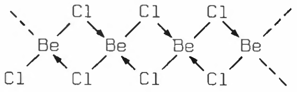
Beryllium, boron and aluminium. The 'octet-rule ions' Be^{2+}, B^{3+} and Al^{3+} have the smallest radii of all positive ions. This implies that ionization energies are high and that these ions are least likely to be formed.

Exercise 16



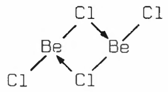
Exercise 17

(a)



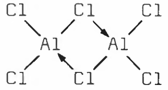
-------- etc.

(b)

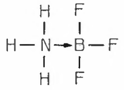


Note that there are 6 outer shell electrons around each Be atom in (b).

(c)

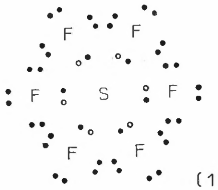


(d)



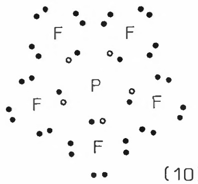
Exercise 18

(a)



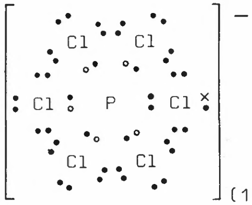
(12)

(b)



(10)

(c)

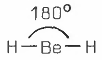


(12)

Exercise 19

(a) Two pairs.

(b) The molecule will be linear because this shape places the two pairs of electrons as far apart as possible.



Exercise 20

(a) CO_2 is linear. The structural formula is O=C=O.

The two double bonds can be thought of as two regions of high charge density which repel each other and take up positions as far away from each other as possible.

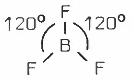
(b) HCN is linear. The structural formula is H—C≡N.

The triple bond and the single bond can be though of as two regions of high charge density which repel each other in the same way as in the previous examples.

Exercise 21

(a) Three pairs of bonding electrons.

(b) The three pairs of electrons are as far away from each other as possible in a trigonal (triangular) planar arrangement, in which the bond angles are all 120°.



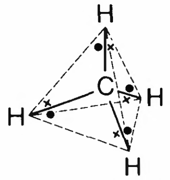
Exercise 22

The double bond, containing four electrons, can be thought of as a single region of high charge density. There are two other regions of high charge density corresponding to the single bonds. The three regions of high charge density repel each other and make the molecule adopt a trigonal planar shape.

Exercise 23

(a) Four pairs of bonding electrons.

(b) The four pairs of electrons occupy regions centred on four lines joining the centre of a regular tetrahedron to its four corners. Each bond angle is 109½°.



(c) The bond angles in a square planar shape would all be 90°. By increasing the angle to 109½°, the electron pairs get further away from each other.

(d) (i) Identical shape. There are four pairs of electrons in four identical bonds and the molecule is symmetrical.

(ii) Similar shape. There is a pair of electrons in each of the P—Cl bonds and a quartet in the P═O double bond. The four regions of high charge density repel each other to give a tetrahedral arrangement. However, the molecule is not symmetrical.

(iii) Identical shape. There are four pairs of electrons in four identical bonds.

(iv) Identical shape. There are four pairs of electrons in four identical bonds, giving a symmetrical molecule. (Remember that dative bonds are indistinguishable from covalent bonds.)

Exercise 24

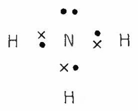
Six at 90° and three at 120°.

Exercise 25

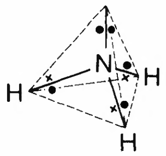
All bond angles are 90°.

Exercise 26

(a)



Four pairs of electrons



(b) The electron pairs would lie in tetrahedral directions from the nitrogen atom.

(c) The four atoms lie at the corners of a trigonal pyramid which is enclosed by a tetrahedron.

Exercise 27

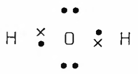
The non-bonding pair is not shared and therefore lies closer to the nitrogen atom than the bonding pairs. The repulsion between between non-bonding pairs and bonding pairs is therefore greater, which pushes the hydrogen atoms closer together. This gives a slightly smaller H—N—H bond angle than the tetrahedral angle of 109½°.

Exercise 28

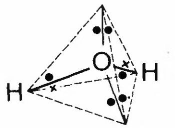
The repulsion increases in the order (a), (b), (c).

Exercise 29

(a)



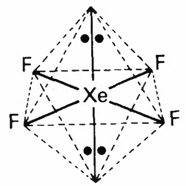
(b)



(c) The two non-bonding pairs repel each other and the bonding pairs strongly so that the H—O—H bond angle is less than 109½° and even less than the 107° in ammonia. Any answer between 100° and 106° would be a reasonable guess, but the actual angle is 104½°.

Exercise 30

There are six pairs of electrons, four bonding pairs and two non-bonding pairs. The shape is therefore based on an octahedral arrangement. However, the non-bonding pairs repel each other most strongly and therefore lie on opposite sides of a square planar molecule.

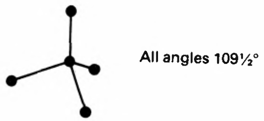


Exercise 31

(a) Four bonding pairs.

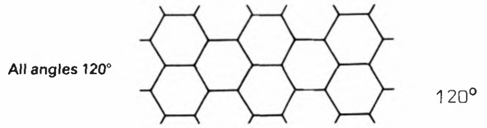
(b) Co-ordination number 4.

(c)



Exercise 32

(a)



(b) 3. Remember that coordination number refers only to nearest neighbours.

(c) The interatomic distance within a layer (0.143 nm) is less than half the interatomic distance between layers (0.335 nm). This is because there is very strong covalent bonding within each layer, and very weak bonding between layers - rather like the van der Waals bonding between separate molecules.

(d) The bond length is intermediate between the lengths of single and double bonds. This suggests that between each pair of carbon atoms there is a charge density greater than that which we associate with a pair of bonding electrons but less than that which we associate with two pairs. It seems that we cannot, in this case, allocate electrons in pairs to localized covalent bonds.

(This is an example of delocalization of electrons which we consider in more detail later.)

Exercise 33

(a) Diamond is very hard because all the bonds are strong, so that any deformation of the structure would require the breaking of strong bonds. Deformation of graphite is easy by breaking weak van der Waals bonds.

(b) Diamond cannot conduct electricity because all the electrons are strongly localized in covalent bonds. Each graphite layer has a network of delocalized electrons extending over the whole layer which can therefore move under the influence of a potential difference applied at opposite edges of a layer. Note, however, that graphite does not conduct at all well in directions across the layers.

(c) Diamond has a high melting point because all the bonds are strong.

(d) Although graphite contains some weak bonds, the breaking of these bonds does not produce small molecules capable of moving freely in the liquid state. Each layer is a giant covalent structure in its own right and, since the bonds within the layer are even stronger than in diamond, the melting point is even higher.

(e) The weak bonds between layers allow them to slip easily past one another. When a 'lead' pencil writes, layers of graphite slip off the point on to the paper. The slipping of layers is also useful in lubricants, but absorption of other molecules between the layers must also play a part because graphite is a poor lubricant at low pressure.

(f) The density of diamond is 3.53 g cm^{-3} and that of graphite is 2.25 g cm^{-3}. Graphite is less dense than diamond because the long van der Waals bonds give it a more open structure.

(g) All the bonds in diamond are very strong and no solvent is able to break up the structure. In graphite, although there are weak bonds between layers, each layer is a giant structure with strong bonds which cannot be split up by a solvent.

Exercise 34

(a) (i) +771 kJ mol^{-1} (-Lattice energy)

(ii) +3513 kJ mol^{-1} (-Lattice energy)

(iii) +715 kJ mol^{-1} (Enthalpy of atomization)

(iv) $\Delta H_r^\ominus = \Sigma\Delta H_f^\ominus[\text{products}] - \Sigma\Delta H_f^\ominus[\text{reactants}]$

$= \Delta H_f^\ominus[Si(g)] + 2\Delta H_f^\ominus[O(g)] - \Delta H_f^\ominus[SiO_2(s)]$

$= \{439 + (2 \times 248) - (-858)\}\text{kJ mol}^{-1} = \boxed{+1793 \text{ kJ mol}^{-1}}$

(Note that a much-used data book gives a false value for $\Delta H_f^\ominus[Si(g)]$)

(b) The disruption of ionic lattices {as in (a) (i) and (ii)} and covalent lattices {as in (a) (iii) and (iv)} involve similar ranges of energy.

Exercise 35

(a) (i) (7.9 + 22)kJ mol^{-1} = $\boxed{30 \text{ kJ mol}^{-1}}$

(ii) (2.3 + 12.6)kJ mol^{-1} = $\boxed{14.9 \text{ kJ mol}^{-1}}$

(iii) (9.83 + 30.8)kJ mol^{-1} = $\boxed{40.6 \text{ kJ mol}^{-1}}$

(iv) (2.5 + 30.5)kJ mol^{-1} = $\boxed{33.0 \text{ kJ mol}^{-1}}$

Note that some data books list $\Delta H^\ominus$(fusion) and $\Delta H^\ominus$(vaporization) in units kJ kg^{-1}. These values must be multiplied by the appropriate molar masses to give molar enthalpy changes.

(b) These values are very much smaller than the values obtained in the last exercise. This confirms that intermolecular bonds (van der Waals bonds) are very much weaker than ionic and covalent bonds.

Exercise 36

(a) Many molecular substances are gases or liquids at room temperature.

(b) Molecular substances have low melting points, i.e. even those which are solid at room temperature melt very easily.

(c) Molecular substances do not conduct electricity in the solid or liquid state. Their aqueous solutions do not conduct electricity either, unless there is a reaction with water which produces ions.

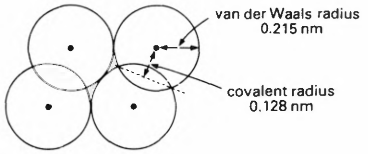
(d) Most molecular substances do not dissolve in water. However, there are some common exceptions, e.g. sugars.

(e) Most molecular substances dissolve in organic solvents such as tetrachloromethane, CCl_4, and hexane, C_6H_{14}.

Exercise 37

(a) The probability of finding an electron decreases with distance from the nucleus, but never reaches zero. There is no definite boundary to the electron charge cloud.

(b)



(c) Covalent bonds are strong and the nuclei are drawn closer together than they are in weak van der Waals bonds.

(d) Internuclear distances can be measured in solids by X-ray diffraction, neutron diffraction and electron diffraction. Halving the appropriate internuclear distances gives the covalent radius and van der Waals radius.

Exercise 38

(a) The outer-shell electrons.

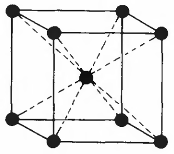
(b) The outer-shell electrons are described as mobile or delocalized because they are not confined to a single atom but can move throughout the lattice.

(c) Since the electrons are mobile, the application of a potential difference makes them move.

(d) Metallic bonding is electrostatic in nature and is of similar strength to ionic and covalent bonding.

Exercise 39

(a)



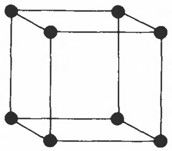
(b) The coordination number is 8.

(c) There are no close-packed layers.

(d) The relatively low density of the alkali metals is accounted for by the more 'open' nature of the body-centred-cubic structure.

Exercise 40

(a)



(b) The coordination number is 6.

(c) There are no close-packed layers.

(d) The simple cubic structure would not be expected for any metals because it is a very open structure and our model of metallic bonding naturally leads to close-packing.

Note, however, that the existence of body-centred-cubic metals implies some modification of this model of metallic bonding. Either the ions are not quite spherical, or the 'sea' of electrons is not quite uniformly distributed, or perhaps both!

Exercise 41

(a) Figure 27 represents the cubic close-packed structure.

(b) (i) 8 cells share each corner atom.

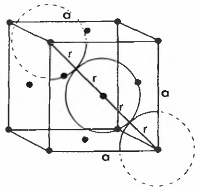
(ii) 2 cells share each centre-face atom.

(c) The 8 corners contain $\frac{1}{8}$ sphere each.

The 6 faces contain $\frac{1}{2}$ sphere each.

The total number of spheres $= (8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = \boxed{4}$

(d) Let r = radius of sphere



Then diagonal of cube face $= 4r$

$\therefore$ cube side, $a = 2\sqrt{2}r$

$\therefore$ volume of cube, $V_c = (2\sqrt{2}r)^3$

$= 22.63\ r^3$

Volume of spheres, $V_s = 4 \times 4\ \pi r^3/3$

$= 16.76\ r^3$

Volume of space between spheres $= V_c - V_s$

$\therefore$ percentage of total volume which consists of spaces between spheres

$$= \frac{V_c - V_s}{V_c} \times 100 \quad \frac{22.63 - 16.76}{22.63} \times 100 = \boxed{25.9\%}$$

(e) The hexagonal close-packed structure has the same coordination number and would have the same percentage of space between spheres as the cubic close-packed structure, i.e. 25.9%

Exercise 42

(a) Body-centred cubic. The 8 corners contain $\frac{1}{8}$ sphere each but the central sphere is not shared.

$\therefore$ total number of spheres = $(8 \times \frac{1}{8}) + 1 = \boxed{2}$

Simple cubic. The 8 corners contain $\frac{1}{8}$ sphere each.

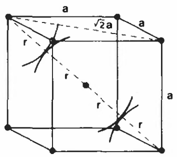
$\therefore$ total number of spheres = $(8 \times \frac{1}{8}) = \boxed{1}$

(b) Body-centred cubic

Let r = radius of sphere

Then diagonal of cube = $4r$

Let cube side = a



Then diagonal of cube face = $\sqrt{2}a$

$\therefore a^2 + 2a^2 = (4r)^2$

Hence $a = 4r/\sqrt{3}$

$\therefore$ volume of cube, $V_c = (4r/\sqrt{3})^3 = 64r^3/3\sqrt{3} = 12.32r^3$

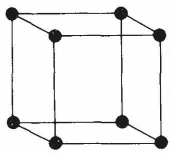
Volume of spheres, $V_s = 2 \times 4\ \pi r^3/3 = 8.38\ r^3$

Volume of space between spheres = $V_c - V_s$

$\therefore$ percentage of total volume which consists of spaces between spheres

$$= \frac{V_c - V_s}{V_c} \times 100 = \frac{12.32 - 8.36}{12.32} \times 100 = \boxed{32.0\%}$$

Simple cubic



Let r = radius of sphere

Then cube side = $2r$

$\therefore$ volume of cube, $V_c = 8r^3$

Volume of spheres, $V_s = 1 \times 4\pi r^3/3$

$= 4.19\ r^3$

Volume of space between spheres = $V_c - V_s$

$\therefore$ percentage of total volume which consists of spaces between spheres

$$= \frac{V_c - V_s}{V_c} \times 100 = \frac{8.00 - 4.19}{8.00} = \boxed{47.6\%}$$

(c) The greater the coordination number, the smaller the volume of space between the spheres. Thus, coordination number gives an indication of the extent of close-packing in a structure.

Exercise 43

(a) Internuclear distance in Fig. 28 = 5.3 cm

Scale shows 1.9 cm ≡ 0.1 nm

$\therefore$ internuclear distance = $0.1\ \text{nm} \times \frac{5.3\ \text{cm}}{1.9\ \text{cm}} = 0.28\ \text{nm}$

$\therefore$ metallic radius $= \frac{0.28\ \text{nm}}{2} = \boxed{0.14\ \text{nm}}$

(b) In the measurement of ionic radius it is assumed that the outer shell electrons have been transferred completely to another ion. The measurement of metallic radius includes the outer shell electrons, even though they are delocalized.

Exercise 44

(a) Most metals are solid with a shiny surface. These properties are not exclusive to metals - note particularly iodine and pure graphite. Mercury is liquid at room temperature. The shiny surface on the alkali metals tarnishes very rapidly.

(b) Most solid metals are malleable and ductile. These properties, if combined with reasonable strength, are exclusive to metals. However, some metals are brittle (e.g. manganese) especially in the presence of impurities (e.g. cast iron) or in some alloys.

(c) Most metals have high melting points. This is not exclusive to metals. Mercury melts below room temperature and the alkali metals melt very easily.

(d) All metals conduct electricity, whether solid or molten, and are not changed in the process. This property is almost exclusive to metals, but graphite is also a good conductor.

Experiment 2 - Specimen results

Results Table 1

	A	B	C	D	E	F	G
Appearance	white powder	black powder	black powder	white powder	white powder	grey powder	white powder
Melting point (approx.)/°C	> 800	> 800	> 800	100	700	> 800	> 800
Solubility in water	insoluble	insoluble	insoluble	soluble	soluble	insoluble	insoluble
Conductivity of solution	-	-	-	none	good	-	-
Conductivity of solid	none	none	good	none	none	good	none
Action of dilute HCl	none	dissolves, green solution. No H_2	none	dissolves, no evident reaction	dissolves, no evident reaction	dissolves hydrogen evolved	none
Structure	ionic or covalent giant	ionic or covalent giant	metal or covalent giant	molecular crystal	ionic	metal	ionic or covalent giant

Notes

1. The heavy horizontal line in each column implies that you need not have done the tests below the line.
2. You were not asked to identify the actual substances. However, for your interest we list them:

   A = barium sulphate, $BaSO_4$; B = copper(II) oxide, CuO; C = graphite, C;
   D = glucose, $C_6H_{12}O_6$; E = potassium bromide, KBr; F = zinc, Zn;
   G = silica, SiO_2.
3. Your general chemical knowledge probably enabled you to guess the identity of B and C, and hence to infer the structures. The tests alone, however, are not entirely conclusive.

Experiment 2 - Questions

1. The use of higher temperatures and/or more sophisticated conductivity apparatus might enable the solids with high melting points to be classified as ionic or giant covalent structures.
2. It may not be easy to get a powdered metal to conduct electricity because the particles may not make good contact with each other, especially if there is an oxide film on the surfaces.

Exercise 45

(a) The 8 corner Na^+ ions are shared by 8 unit cells and the 6 centre-face Na^+ ions are shared by 2 unit cells.

$\therefore$ Total Na^+ ions = $(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = \boxed{4}$

The 12 centre-edge Cl^- ions are shared by 4 unit cells, but the central Cl^- ion is not shared.

$\therefore$ Total Cl^- ions = $(12 \times \frac{1}{4}) + 1 = \boxed{4}$

Thus, there are <u>4 ions of each sort</u> in the unit cell, which corresponds with the formula <u>NaCl</u>.

(b) Each side of unit cell = $r(Na^+) + 2r(Cl^-) + r(Na^+)$

$= (0.098 + 0.362 + 0.098)\text{nm} = \boxed{0.558 \text{ nm}}$

(c) Volume of cell = $(0.558 \text{ nm})^3 = 0.1737 \text{ nm}^3$

$\therefore$ volume taken up by one ion pair = $0.1737 \text{ nm}^3/4 = \boxed{0.0434 \text{ nm}^3}$

(d) Volume of one mole of NaCl = $\dfrac{58.4 \text{ g mol}^{-1}}{2.17 \text{ g cm}^{-3}} = \boxed{26.9 \text{ cm}^3 \text{ mol}^{-1}}$

(e) Avogadro constant = $\dfrac{\text{Volume of 1 mol of ion pairs}}{\text{Volume of 1 ion pair}}$

$$= \frac{26.9 \text{ cm}^3 \text{ mol}^{-1}}{0.0434 \text{ nm}^3} = \frac{26.9 \times (10^7 \text{ nm})^3 \text{ mol}^{-1}}{0.0434 \text{ nm}^3} = \boxed{6.20 \times 10^{23} \text{ mol}^{-1}}$$

Exercise 46

(a) I^- and F^- have the same overall charge, but the charge cloud in I^- is much larger and is, therefore, more readily polarized.

(b) O^{2-} has twice the overall charge of F^- and its charge cloud is, therefore, more strongly attracted by cations. O^{2-} is also larger than F^-. Both these factors make O^{2-} more readily polarized than F^-.

(c) Li^+ and K^+ have the same overall charge, but Li^+ is much smaller. The smaller size of Li^+ gives it a greater 'surface charge density' and enables it to approach closer to anions. Li^+ can therefore distort the anion charge clouds more, i.e. it has the greater polarizing power.

(d) Al^{3+} has three times the overall charge of Li^+ which makes it attract the charge clouds of anions more strongly. Al^{3+} is also much smaller than Li^+ which further increases the 'surface charge density' and enables it to approach anions more closely. These factors together give Al^{3+} a much greater polarizing power than Li^+.

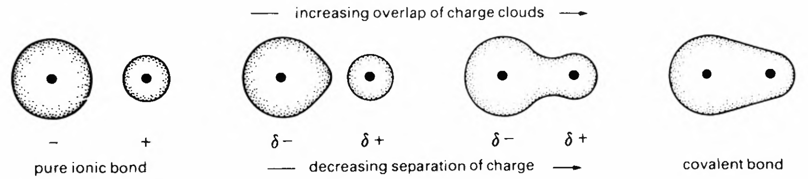
Exercise 47

$$\left.\begin{array}{l}\text{The polarization}\\ \text{of an anion}\end{array}\right\}\text{ is favoured by }\left\{\begin{array}{l}\text{large size}\\ \text{high charge}\end{array}\right.$$

$$\left.\begin{array}{l}\text{The polarizing power}\\ \text{of a cation}\end{array}\right\}\text{ is favoured by }\left\{\begin{array}{l}\text{small size}\\ \text{high charge}\end{array}\right.$$

Exercise 48

If very small, highly charged, cations approach very large, highly charged, anions, the polarization of the anions is so great that the distortion leads to some overlap of charge clouds, and covalent bonds result.



Exercise 49

(a) CsF. Cs^+ is the largest singly-charged cation. F^- is the smallest singly-charged anion.

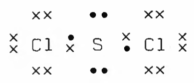
(b) AlP, Al_2S_3, AlI_3, Be_3P_2, BeS, BeI_2, Li_3P, Li_2S, etc. For each ion charge, select the smallest cation and the largest anion.

Exercise 50

Completely non-polar covalent bonding is only found between identical atoms, e.g. in molecules like Cl_2, H_2, etc.

Exercise 51

(a)



(b) $\Delta H_1^\ominus(S) = 1000\ \text{kJ mol}^{-1}$; $\Delta H_1^\ominus(Cl) = 1260\ \text{kJ mol}^{-1}$

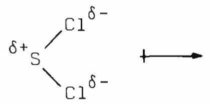
Sulphur atoms are more likely to lose electrons.

(c) Electron affinity(S) = $-200\ \text{kJ mol}^{-1}$
Electron affinity(Cl) = $-364\ \text{kJ mol}^{-1}$

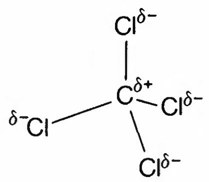
Chlorine atoms are more likely to gain electrons.

(d) The differences in both ionization energy and electron affinity suggest that a chlorine atom would take the greater share of an electron pair in a Cl–S bond.

(e)



Exercise 52



Each C—Cl bond is polar because a chlorine atom takes the greater share of a bonding pair of electrons. However, since the molecule is symmetrical, with each bond directed towards the corner of a tetrahedron, these four dipole moments cancel out so that there is no overall dipole moment. The bonds have ionic character, but the molecules do not.

Exercise 53

Electron affinity refers to the attraction between electrons and isolated atoms. Electronegativity refers to the attraction between bonding electrons and an atom in a covalent compound.

Exercise 54

(a) (i) Electronegativity increases across a period.

(ii) Electronegativity decreases down a group.

(b) Small atoms tend to attract electrons more strongly than large atoms, so that decreasing atomic radius tends to give greater electronegativity. Atomic radius (whether covalent, metallic or van der Waals) decreases across a period and increases down a group.

Exercise 55

(a) B is more electronegative than A. Anions that are readily polarized have a charge cloud which is readily distorted and attracted towards a cation, tending to form covalent bonds. Thus, elements with readily polarized anions have a low electronegativity (relative to F^- - of course, elements with very low electronegativity do not form anions at all!).

(b) C is more electronegative than D. Cations that have high polarizing power distort and attract the charge cloud of neighbouring anions, tending to form covalent bonds. These elements therefore have high electronegativity (relative to Cs^+ - of course, elements with very high electronegativity do not form cations at all!).

Exercise 56

(a) Nitrogen and chlorine have roughly the same electronegativity, 3.0. (The values are slightly different on some scales.)

(b) Since the two atoms have roughly the same electronegativity, the bonding electrons would be more or less equally shared.

(c) Bonding between nitrogen and chlorine can be regarded as almost purely covalent, with little or no ionic character.

(d) Nitrogen trichloride would not be expected to have to have a significant dipole moment, because the bonds are practically non-polar.

Exercise 57

(a) The difference in electronegativity is 3.5 - 0.8 = 2.7.

(b) In a covalent bond between rubidium and oxygen, the bonding electrons would be drawn very strongly towards the oxygen atom.

(c) F with elements in Groups I and II (except Be) - differences range from 3.3 for Cs and F, to 2.8 for Mg and F. Also O and Cs (3.5 - 0.7 = 2.8).

(d) The difference in electronegativity is so great that the electrons in any covalent bond would be drawn so strongly towards the oxygen atom as to result in the formation of separate ions. The bonding would therefore be described as almost purely ionic, with hardly any covalent character.

Exercise 58

(a) KF - almost pure ionic. 4.0 - 0.8 = 3.2

(b) CuO - partly covalent and partly ionic. 3.5 - 1.9 = 1.6

(c) CS_2 - almost pure covalent. 2.5 - 2.5 = 0

(d) NaCl - predominantly ionic. 3.0 - 0.9 = 2.1

(e) PBr_3 - predominantly covalent. 2.8 - 2.1 = 0.7

[% ionic character may be calculated as follows, using an electronegativity difference of 3.3 to indicate 100%.

(a) KF: $\frac{3.2}{3.3} \times 100 = 97\%$ (d) NaCl: $\frac{2.1}{3.3} \times 100 = 64\%$

(b) CuO: $\frac{1.6}{3.3} \times 100 = 48\%$ (e) PBr_3: $\frac{0.7}{3.3} \times 100 = 21\%$

(c) CS_2: $\frac{0}{3.3} \times 100 = 0\%$

Note that a more complex calculation is used to obtain the slightly different values you may find in some data books.]

Exercise 59

(a) (Experimental values - theoretical values) / kJ mol^{-1} are as follows:

NaCl,17; NaBr,15; NaI,22;

CsCl, 2; CsBr,-1; CsI, 4;

AgCl,51; AgBr,74; AgI,81.

(b) (i) Caesium halides show the best agreement.

(ii) Silver halides show the poorest agreement.

Note that, strictly speaking, % differences should be compared. However, in this exercise it is not necessary because all the lattice energies are of similar magnitude.

(c) The iodides show the poorest agreement.

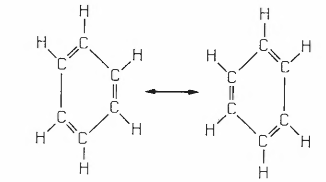
(d) The calculated values depend on the assumption that ions are discrete charged spheres. The greater the electronegativity difference for two elements, the more nearly the assumption is true.

Caesium has the lowest electronegativity of the three metals and therefore the electronegativity difference is greatest for the caesium halides. However, silver has the highest electronegativity, so that the difference is least for the silver halides and distortion of the spherical shape of the ions (polarization) leads to a significant degree of covalent bonding.

If the ions are not discrete spheres, the calculation of lattice energy is based on a false assumption and therefore gives an inaccurate result. Iodine has the lowest electronegativity of the halogens, its ions are readily distorted (polarized) and so the calculated lattice energies are inaccurate.

Exercise 60

(a)

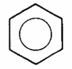


(b) C—C bond lengths are usually 0.154 nm

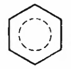
C=C bond lengths are usually 0.134 nm

In benzene, all the carbon-carbon bond lengths are the same, i.e. 0.139 nm.

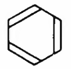
(c)



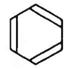
1



2



3



4

1 and 2 are the best representations, with 1 most commonly used. However, you may find 3 or 4 in some textbooks.

Exercise 61

(a)

$$\begin{tikzcd}
\boxed{6C(g) + 6H(g)} \arrow[rr, "\Delta H_1"] & & \boxed{C_6H_6(g)} \\
& \boxed{6C(s) + 3H_2(g)} \arrow[ul, "\Delta H_2"'] \arrow[ur, "\Delta H_3"] &
\end{tikzcd}$$

$$\Delta H_1 = -\Delta H_2 + \Delta H_3 = -\left(6\Delta H^{\ominus}_{at}(C) + 6\Delta H^{\ominus}_{at}(H)\right) + \Delta H^{\ominus}_f(\text{benzene } \underline{\text{vapour}})$$

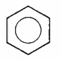
$$= \left(-(6 \times 715) + (6 \times 218) + 82.9\right)\text{kJ mol}^{-1} = \boxed{-5515 \text{ kJ mol}^{-1}}$$

(b)
$$\Delta H^{\ominus} = -\left(6\bar{E}(C—H) + 3\bar{E}(C—C) + 3\bar{E}(C=C)\right)$$

$$= -\left((6 \times 412) + (3 \times 348) + (3 \times 612)\text{kJ mol}^{-1} = \boxed{-5352 \text{ kJ mol}^{-1}}\right.$$

(c) The formation of the Kekulé structure would release less energy than the formation of the actual structure. The actual structure is, therefore at a lower energy level and is energetically more stable.

The stabilization energy is (5515 - 5352) kJ mol^{-1} = $\boxed{163 \text{ kJ mol}^{-1}}$

(d) 6C(g) + 6H(g) →  (g); $\Delta H^{\ominus} = -5515 \text{ kJ mol}^{-1}$

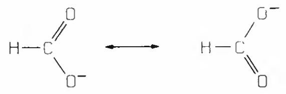
But also $\Delta H^{\ominus} = -6\bar{E}(C—H) - 6\bar{E}(C\overset{\cdots}{—}C)$

$$\therefore\ \bar{E}(C\overset{\cdots}{—}C) = \tfrac{1}{6}\left(-\Delta H^{\ominus} - 6\bar{E}(C—H)\right)$$

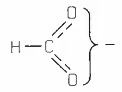
$$= \tfrac{1}{6}\left(5515 - (6 \times 412)\right)\text{kJ mol}^{-1} = \boxed{507 \text{ kJ mol}^{-1}}$$

This value is intermediate between $\bar{E}(C—C)$ and $\bar{E}(C=C)$, 348 and 612 kJ mol^{-1}.

Exercise 62

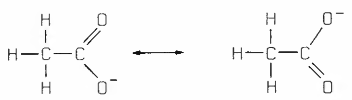


Note that a single structure can be drawn:

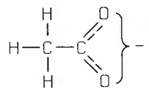


Exercise 63

The ethanoate ion has a structure intermediate between the two electron pair structures shown below:

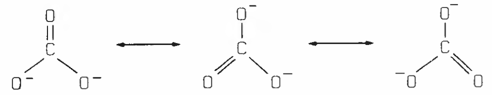


Note that a single structure can be drawn:

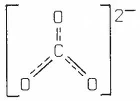


The C—O bond lengths would be equal at 0.127 nm just as they are in the methanoate ion.

Exercise 64

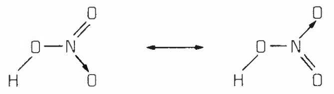


Note that a single structure can be drawn:

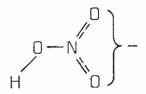


Exercise 65

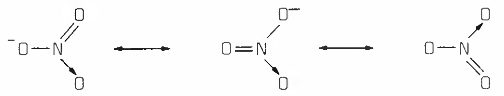
(a)



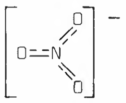
Note that a single structure can be drawn:



(b)



Note that a single structure can be drawn:

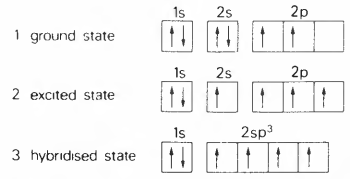


(c) In HNO_3, there would be two different N—O bond lengths. One of these, involving the oxygen atom attached to hydrogen, would be the 'normal' single bond length. The other two N—O bonds would be equal, but shorter than the single bond length. (Bond order $1\frac{1}{2}$.)

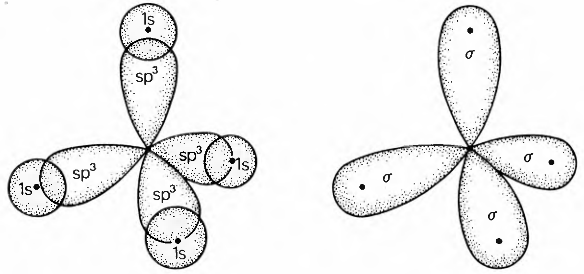
In NO_3^-, all bond lengths would be equal, and shorter than the N—O single bond length. (Bond order $1\frac{1}{3}$)

Exercise 66

(a)

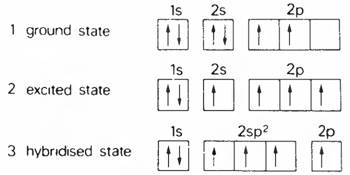


(b)

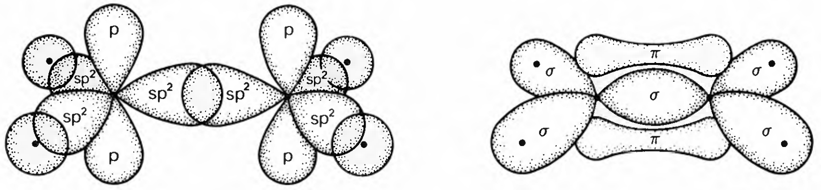


Exercise 67

(a)



(b)



(c) The dashed line indicates overlap of two *p*-orbitals.

Exercise 68

(a) $\overline{E}(\sigma\text{-bond}) = 348\ \text{kJ mol}^{-1}$

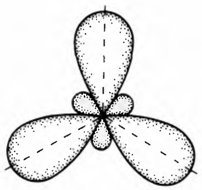
$\overline{E}(\pi\text{-bond}) = (612 - 348)\text{kJ mol}^{-1} = 264\ \text{kJ mol}^{-1}$

The π-bond is considerably weaker than the σ-bond.

(b) We assume that the σ-bonds in ethane, C_2H_6, and in ethene, C_2H_4, are almost identical.

Exercise 69

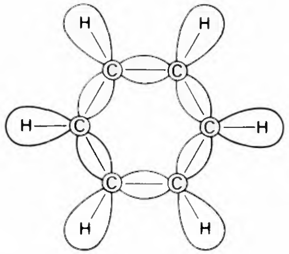
(a)



(The small lobes are sometimes omitted for simplicity.)

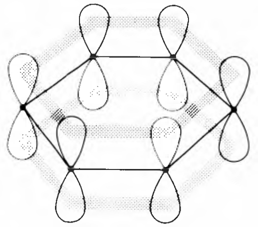
(b) The sp^2 hybrid orbitals lie in directions at 120° to each other. 120° is the internal angle of a regular hexagon.

(c)



(d) One $2p$-orbital for each carbon atom is not used in the σ-bonding. It lies at right angles to all the sp^2-hybrids with one lobe on each side of the hexagon.

(e)



Note that this sketch is not to scale. The p-orbitals should be much closer together - but this makes drawing more difficult.

(f) The six electrons in the ring-shaped orbitals are said to be delocalized because they cannot be allocated in pairs to particular bonds.

(g) Graphite has a hexagonal layer structure which involves sp^2 hybridization and delocalization of electrons not merely over six carbon atoms but over the whole layer.

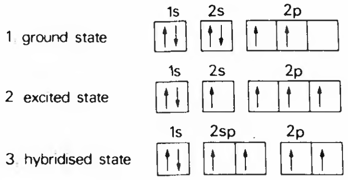
Exercise 70

(a) A conjugated system is one in which the electron pair structure contains alternate single and double bonds.

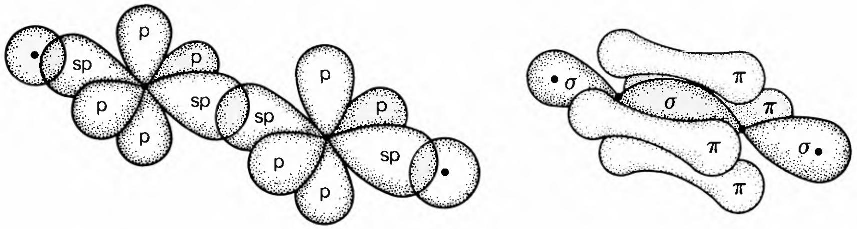
(b) Each area labelled A represents a σ-orbital containing a pair of electrons bonding a carbon atom to a hydrogen atom. Each area labelled B represents a σ-orbital containing a pair of electrons bonding two carbon atoms. The areas labelled C represent π-orbitals - the two lobes together contain two pairs of electrons (not necessarily one pair in each). The electrons in the π-orbitals are delocalized because they cannot be allocated in pairs to particular bonds.

Exercise 71

(a)



(b)



(c) The π-electron charge cloud is cylindrical in shape. It is symmetrical around the σ-bond.

Exercise 72

(a) Argon and neon would experience the same type of attractive force - that due to temporary dipoles. Argon has more electrons so the dipoles are stronger, the attractive force greater and the boiling point higher.

(b) HF has a higher boiling point than HCl despite having fewer electrons. This is because hydrogen bonding occurs between HF molecules, but not between HCl molecules.

(c) Butane has the higher boiling point, for the same reason as given in (a).

Exercise 73

(a) +1 (b) -2 (c) +3 (d) +1 (e) -1

Exercise 74

(a) KCl is ionic $K^+ + Cl^-$ $Ox(K) = +1$ $Ox(Cl) = -1$

(b) Na_2O is ionic $2Na^+ + O^{2-}$ $Ox(Na) = +1$ $Ox(O) = -2$

(c) BaF_2 is ionic $Ba^{2+} + 2F^-$ $Ox(Ba) = +2$ $Ox(F) = -1$

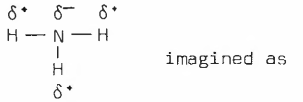
(d) Na_3P is ionic $3Na^+ + P^{3-}$ $Ox(Na) = +1$ $Ox(P) = -3$

(e) Mg_3N_2 is ionic $3Mg^{2+} + 2N^{3-}$ $Ox(Mg) = +2$ $Ox(N) = -3$

(f) CsH is ionic $Cs^+ + H^-$ $Ox(Cs) = +1$ $Ox(H) = -1$

Exercise 75

(a) N is more electronegative than H



$\overset{\delta+}{H}-\overset{\delta-}{N}(-\overset{\delta+}{H})-\overset{\delta+}{H}$ imagined as $H^+ \quad N^{3-} \quad H^+ \quad H^+$

$\therefore \quad Ox(N) = -3, \quad Ox(H) = +1$

(b) O is more electronegative than Cl

$\overset{\delta+}{Cl}-\overset{\delta-}{O}-\overset{\delta+}{Cl}$ imagined as $Cl^+ \quad O^{2-} \quad Cl^+$

$\therefore \quad Ox(O) = -2, \quad Ox(Cl) = +1$

Exercise 76

(a) The O—O bond is non-polar, i.e. neither oxygen atom can be regarded as having gained or lost an electron with respect to the other. However, the O—H bonds are polar, and each oxygen atom is regarded as having gained an electron from a hydrogen atom.

$\overset{\delta+}{H}-\overset{\delta-}{O}-\overset{\delta-}{O}-\overset{\delta+}{H}$ imagined as $H^+ \quad O^- \quad O^- \quad H^+$

$\therefore \quad Ox(O) = -1, \quad Ox(H) = +1$

(b) Fluorine is more electronegative than oxygen.

$\overset{\delta-}{F}-\overset{\delta+}{O}-\overset{\delta-}{F}$ imagined as $F^- \quad O^{2+} \quad F^-$

$\therefore \quad Ox(O) = +2, \quad Ox(F) = -1$

Exercise 77

(a) $Ox(As) + Ox(\text{all other atoms}) = 0$

$\therefore \quad Ox(As) = -Ox(\text{all other atoms}) = -\left(3Ox(H) + 4Ox(O)\right)$

$= -\left(3(+1) + 4(-2)\right) = -3 + 8 = \boxed{+5}$

(b) $2Ox(Cr) + Ox(\text{all other atoms}) = -1$

$\therefore \quad 2Ox(Cr) = -1 - Ox(\text{all other atoms}) = -1 - \left(Ox(H) + 7Ox(O)\right)$

$= -1 - \left(+1 + 7(-2)\right) = -1 - (-13) = +12$

$\therefore \quad Ox(Cr) = \boxed{+6}$

Exercise 78

(a) $2Ox(Cr) + Ox(\text{all other atoms}) = 0$

$\therefore \quad Ox(Cr) = -\tfrac{1}{2}Ox(\text{all other atoms})$

$= -\tfrac{1}{2}\left(2Ox(K) + 7Ox(O)\right) = -\tfrac{1}{2}\left(2(+1) + 7(-2)\right) = \boxed{+6}$

(b) $PbSO_4$ contains the SO_4^{2-} ion

$\therefore \quad Ox(S) + 4Ox(O) = -2$

$\therefore \quad Ox(S) = -2 - 4Ox(O) = -2 - 4(-2) = -2 + 8 = \boxed{+6}$

(c) $Ox(N) = -\left(Ox(H) + 3Ox(O)\right) = -\left(+1 + 3(-2)\right) = -(1 - 6) = \boxed{+5}$

(d) $Ox(S) = -\tfrac{1}{2}\left(2Ox(Na) + 3Ox(O)\right) = -\tfrac{1}{2}\left(2(+1) + 3(-2)\right) = -\tfrac{1}{2}(2 - 6) = \boxed{+2}$

(e) $Ox(C) = -\left(Ox(Ca) + 3Ox(O)\right) = -\left(+2 + 3(-2)\right) = -(2 - 6) = \boxed{+4}$

(f) $Ox(Ta) = -\tfrac{1}{6}\left(8Ox(Na) + 19Ox(O)\right) = -\tfrac{1}{6}\left(8(+1) + 19(-2)\right) = -\tfrac{1}{6}(8 - 38) = \boxed{+5}$

(g) There are two methods, depending on whether we consider the formula as one entity or as two ions.

(i) Considering the whole formula:

$Ox(N) = -\tfrac{1}{2}\left(4Ox(H) + 3Ox(O)\right) = -\tfrac{1}{2}\left(4(+1) + 3(-2)\right) = -\tfrac{1}{2}(4 - 6) = \boxed{+1}$

(ii) Considering the ion NH_4^+:

$Ox(N) + 4Ox(H) = +1$

$\therefore \quad Ox(N) = +1 - 4Ox(H) = +1 - 4(+1) = \boxed{-3}$

Considering the ion NO_3^-:

$Ox(N) + 3Ox(O) = -1$

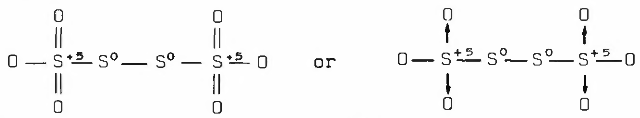
$\therefore \quad Ox(N) = -1 - 3Ox(O) = -1 - 3(-2) = \boxed{+5}$

Since the oxidation number concept is merely a 'book-keeping' device, both methods and, therefore, both answers may be considered correct. However, since the substance is known to be ionic, the second method is preferred. Note that the first answer is the mean of the second pair of answers. $\left(+1 = \tfrac{1}{2}(-3 + 5)\right)$

(h) $Ox(S) = -\tfrac{1}{4}\left(2Ox(Na) + 6Ox(O)\right) = -\tfrac{1}{4}\left(2(+1) + 6(-2)\right) = -\tfrac{1}{4}(2 - 12) = \boxed{2\tfrac{1}{2}}$

Note that the fractional oxidation numbers sometimes appear in these calculations. This is usually because some atoms of the element concerned have one integral oxidation number and other atoms have another integral oxidation *number*.

Only if the structure is known can these integral oxidation numbers be allotted. In this case, the structure of the $S_4O_6^{2-}$ ion, with individual oxidation numbers added, is



(i) $Ox(Fe) = -\tfrac{1}{3}\left(4Ox(O)\right) = -\tfrac{1}{3}\left(4(-2)\right) = \boxed{\tfrac{8}{3}}$

This fraction arises because Fe_3O_4 contains both Fe^{2+} and Fe^{3+} ions - Fe^{2+}, $2Fe^{3+}$, $4O^{2-}$.

The sum of the oxidation numbers for the three iron atoms is $+2 + 2 + 3 = 8$. The mean $Ox(Fe)$ is therefore $\tfrac{8}{3}$.

Exercise 79

(a) $\underset{0}{Fe(s)} + \underset{+2}{CuSO_4(aq)} \rightarrow \underset{+2}{FeSO_4(aq)} + \underset{0}{Cu(s)}$

Iron is oxidised from Fe(0) to Fe(II)
Copper is reduced from Cu(II) to Cu(0)

∴ Reaction is redox

(b) $\underset{+1\ -1}{2KBr(aq)} + \underset{0}{Cl_2(aq)} \rightarrow \underset{+1\ -1}{2KCl(aq)} + \underset{0}{Br_2(aq)}$

Bromine is oxidised from Br(-I) to Br(0)
Chlorine is reduced from Cl(0) to Cl(-I)

∴ Reaction is redox

(c) $\underset{+2}{CuSO_4(aq)} + \underset{+2}{Pb(NO_3)_2(aq)} \rightarrow \underset{+2}{Cu(NO_3)_2(aq)} + \underset{+2}{PbSO_4(s)}$

No oxidation or reduction, i.e. reaction is not redox.

(d) $\underset{-2\ +1}{C_2H_4(g)} + \underset{0}{H_2(g)} \rightarrow \underset{-3\ +1}{C_2H_6(g)}$

Some hydrogen is oxidised from H(0) to H(+I)
Carbon is reduced from C(-II) to C(-III)

∴ Reaction is redox.

Note that the oxidation number concept is not generally useful in organic chemistry except in the simplest compounds.

(e) $\underset{+7}{MnO_4^-(aq)} + \underset{+2}{5Fe^{2+}(aq)} + 8H^+(aq) \rightarrow \underset{+2}{Mn^{2+}(aq)} + \underset{+3}{5Fe^{3+}(aq)} + 4H_2O(l)$

Iron is oxidised from Fe(II) to Fe(III)
Manganese is reduced from Mn(VII) to Mn(II)

∴ Reaction is redox.

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The following schools and colleges took part in the trials of the Independent Learning Project for Advanced Chemistry. The Inner London Education Authority wishes to thank the teachers in these schools and their students for their help.

Abbey Wood School
Acland Burghley School
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P4 Intermolecular Forces and Solvation
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O1 Hydrocarbons
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O3 More Functional Groups
O4 Big Molecules

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I2 The Halogens
I3 The Periodic Table
I4 Group IV Elements
I5 Transition Elements
I6 Selected p-Block Elements

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