CHEMICAL BONDING

4

Achemical bond is an interaction between atoms or ions that results in a reduction in the potential energy of the system which hence becomes more stable. The formation of a chemical bond between atoms involves the interaction of the electrons in the valence shells of the atoms. There are three idealised types of chemical bond, namely ionic, covalent and metallic, though there are examples of bonds intermediate between these. The bond type depends on the extent to which the atoms involved attract the bonding electrons, that is, on their **electronegativities**. If the elements have very different electronegativities then ionic bonding results. If they both have quite high electronegativities then the bonding will be covalent, whereas if they both have low electronegativities they form a metallic bond. Each type of bonding gives rise to distinctive physical properties of the substance formed.

4.1 IONIC BONDING

4.1.1   Describe the ionic bond as the result of electron transfer leading to attraction between oppositely charged ions.

4.1.2   Determine which ions will be formed when metals in groups 1, 2 and 3 lose electrons.

4.1.3   Determine which ions will be formed when elements in groups 6 and 7 gain electrons.

4.1.4   State that transition metals can form more than one ion.

4.1.5   Predict whether a compound of two elements would be mainly ionic or mainly covalent from the position of the elements in the periodic table, or from their electronegativity values.

4.1.6   Deduce the formula and state the name of an ionic compound formed from a group 1, 2 or 3 metal and a group 5, 6 or 7 non-metal.

4.1.7   State the formula of common polyatomic ions formed by non-metals in periods 2 and 3.

4.1.8   Describe the lattice structure of ionic compounds.

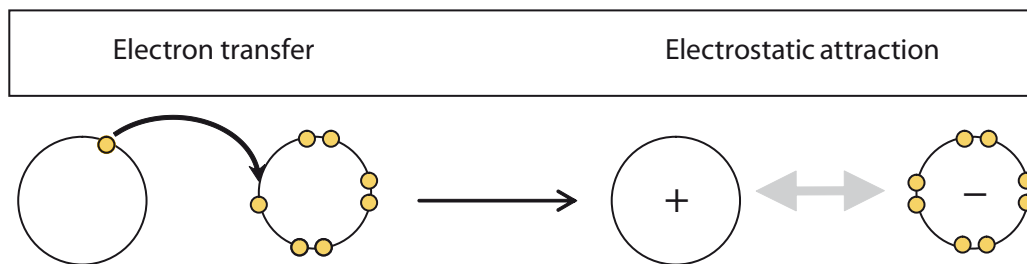Electron transfer   Electrostatic attraction

Figure 401   Ionic bonding

Ionic bonding occurs between elements that have a large difference in electronegativity. In ionic bonding a metal atom with a low electronegativity loses electrons to form a positively charged ion, or **cation** and a non-metal atom with a high electronegativity gains electrons to form a negatively charged ion, or **anion**. As a result there is an electrostatic attraction between these ions which results in ionic bonding as illustrated in Figure 401.

This means that we can predict that the bonding in barium selenide is ionic because barium (Ba) is a metal (in Group 2) and selenium (Se) is a non-metal (in Group 6). Almost all metal compounds are ionic. They are made up of a regular array of positively and negatively charged particles, called ions, held together by electrostatic attraction. In simple cases these ions are isoelectronic with (that is they have the same electronic structure as) the noble gases. The three dimensional arrangement between cations and anions of opposite charges in ionic crystals accounts, resulting in very strong electrostatic attractions, for the high melting points and stability of ionic solids.

In ionic bonding the number of electrons lost varies from metal to metal, but the elements in the s-block of the periodic table lose all of the electrons in their **valence level**. Sodium, which has an electronic structure 2,8,1, therefore loses just its one outer electron to give a sodium ion, with an electronic structure 2,8 (isoelectronic with Ne). This carries a single positive charge because it has one more proton than electron (11 p^+ compared to 10 e^-).

$$Na \longrightarrow Na^+ + e^-$$

(2,8,1)   (2,8)
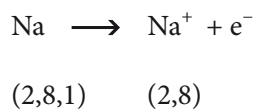
Similarly calcium has two valence electrons (2,8,8,2) and so it forms an ion with an electronic structure 2,8,8 (isoelectronic with Ar) that has two positive charges.

The number of electrons lost by metals outside of the s-block is less easy to predict, especially in the case of the transition metals, and a particular metal can form stable ions with different charges, for example iron can form

both Fe^{2+} (the iron(II) ion) and Fe^{3+} (the iron(III) ion). This means that the charges on the ions must be learnt and those most commonly met are given in Figure 404, from which it can be seen that a 2+ charge is by far the most common.

Non-metals usually gain electrons to fill the valence level of the atom. Chlorine therefore, with an electronic structure 2,8,7, requires one electron to fill its valence level, so it forms an ion with an electronic structure 2,8,8 (isoelectronic with Ar), which carries a single negative charge because it has one more electron than proton (18 e^- compared to 17 p^+).

$$Cl + e^- \longrightarrow Cl^-$$

(2,8,7)   (2,8,8)
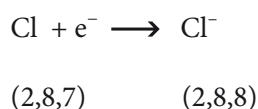
Similarly oxygen (2,6) requires two electrons to fill its valence level and so it forms an ion with an electronic structure 2,8 (isoelectronic with Ne) that has two negative charges.

Hence in forming sodium chloride the sodium atom can be considered to have transferred an electron to the chlorine atom. Similarly in forming calcium oxide the calcium atom transfers two electrons to the oxygen atom. No electron sharing occurs between the ions in ionic bonding.

The anions and cations have opposite electrical charges and are attracted together into a **crystal lattice** in which each anion is surrounded by cations and *vice versa*. A single layer of such a lattice, formed by ions of equal charge, is shown in Figure 402.

The lattice naturally extends in three dimensions, so that there would be an anion above and below each cation and *vice versa* as illustrated in Figure 403.

An ionic substance is therefore held together by strong electrostatic attractions in all three dimensions. This means that there are no molecules present in ionic
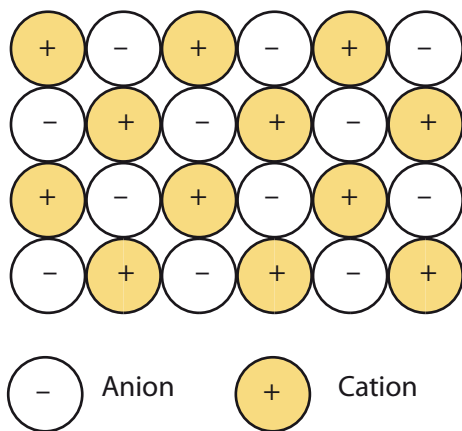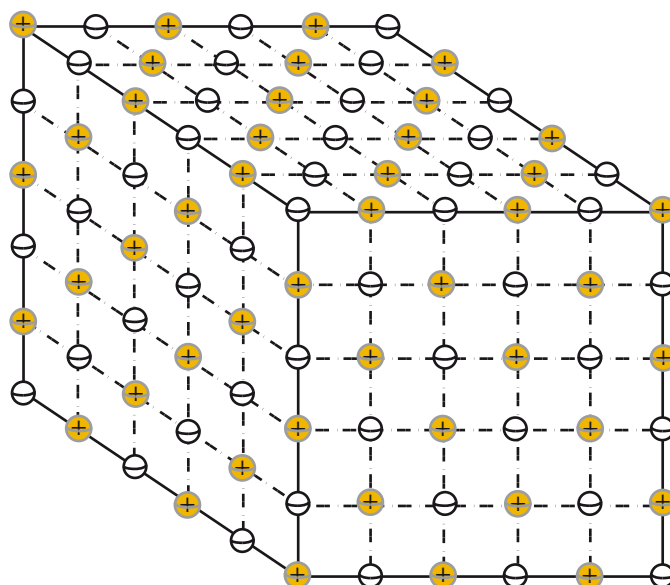
Figure 402   A layer of an ionic lattice

Anion   Cation

Figure 403   A representation of cations ond anions
in a three dimensional crystal lattice

Anion

Cation

substances. Because of the way in which bonding occurs, ionic compounds have distinctive physical properties:

- Hard, brittle crystalline solids.
- Relatively high melting and boiling points.
- Do not conduct electricity when solid, but do when molten or in aqueous solution.
- Are more soluble in water than other solvents.

Groups of atoms, joined together by covalent bonds can also have an electrical charge and so form compounds with ions of the opposite charge by ionic bonding. The sulfate ion (SO_4^{2-}), for example, consists of a sulfur atom and four oxygen atoms, joined by covalent bonds, which has gained two extra electrons to give a charge of 2–. Table 404 gives the electrical charges carried by common anions and cations. Note:

- Simple anions change the ending of the names of the atoms to -ide, e.g. chlorine gives the chloride ion.
- Anions that end in -ate contain oxygen e.g. sulfate.

Ionically bonded compounds are simply named according to the names of the two ions involved, the cation being given first, so that Al_2O_3 is aluminum oxide and $Cr(OH)_3$ is chromium(III) hydroxide. Note that the bracketed Roman numerals are used for transition metals, which have multiple oxidation states, to give the oxidation number of the metal in the compound, which is usually equal to the charge on the cation.

Converting from the name to the formula requires a knowledge of the ratio that the ions combine in. Ionic compounds must contain cations and the anions in such a ratio that their charges cancel each other to give an electrically neutral compound. If they have equal, but opposite charges, as for example with zinc and sulfide ions, then this requires just an equal number of each, so the formula of zinc sulfide is simply ZnS. In other cases the formula must give the ratio of the different ions, so that copper(II) fluoride is CuF_2, because for each doubly charged copper(II) ion there must be two singly charged fluoride ions. When multiplying groups of atoms, they must be enclosed in brackets, so that ammonium sulfate has the formula $(NH_4)_2SO_4$.

A simple way of predicting the formula of an ionic compound is to 'swap' the numbers of the charges on the ions involved. For example, the formula of calcium phosphate can be predicted as $Ca_3(PO_4)_2$, by 'swapping' the bold numbers of the charges on the ions - Ca^{2+} and PO_4^{3-}, that is, the '**2**' charge for the calcium becomes the phosphate subscript and *vice versa*. The formulas of acids can be predicted by combining the hydrogen ion (H^+) with the appropriate anion, hence nitric acid (H^+ and NO_3^-) has the formula HNO_3. However, it must be remembered that the pure acids contain covalently bonded molecules.

CORE

Anions			Cations			
1−	2−	3−	1+	← 2+ →		3+
Fluoride F^-	Oxide O^{2-}	Nitride N^{3-}	Hydrogen H^+	Magnesium Mg^{2+}	Calcium Ca^{2+}	Aluminium Al^{3+}
Chloride Cl^-	Sulfide S^{2-}		Sodium Na^+	Manganese Mn^{2+}	Iron(II) Fe^{2+}	Chromium(III) Cr^{3+}
Bromide Br^-			Potassium K^+	Cobalt Co^{2+}	Nickel Ni^{2+}	Iron(III) Fe^{3+}
Iodide I^-			Copper(I) Cu^+	Copper(II) Cu^{2+}	Zinc Zn^{2+}	
			Silver Ag^+	Lead Pb^{2+}	Tin Sn^{2+}	
Hydroxide OH^-	Carbonate CO_3^{2-}	Phosphate PO_4^{3-}	Ammonium NH_4^+			
Nitrate NO_3^-	Sulfate SO_4^{2-}					

Figure 404   The charges on common anions and cations

Using Lewis structures, a pair of electrons can be represented by dots,
crosses, a combination of dots and crosses or by a
line. For example, a chlorine molecule can be shown as:

Note: Cl — Cl   is not a Lewis structure

Figure 405   Lewis structure for Cl_2

Exercise 4.1

1. An element has an atomic number of 16. What will be the charge on the ions that it forms?

   A   +2
   B   +1
   C   −1
   D   −2

2. The electronic structures of five elements are given below. Which one of these will be most likely to form an ion with a charge of 2+?

   A   2,1
   B   2,4
   C   2,6
   D   2,8,2

3. Which one of the following elements is most likely to be capable of forming cations with different charges?

   A   Be
   B   V
   C   Sr
   D   Cs

4. Name the following compounds:

   a) KBr   b) Li_3N c) BaS
   d) AlI_3 e) BeO

5. The table below gives the electronic structures of pairs of elements, A and B. On the basis of these electronic structures, predict the ions that these elements would form and hence the formula of the compound that would result.

	Element A	Element B
a)	2,1	2,8,7
b)	2,6	2,8,8,2
c)	2,8,1	2,8,6
d)	2,8,3	2,7
e)	2,5	2,8,2

4.2 COVALENT BONDING

4.2.1 Describe the covalent bond as the electrostatic attraction between a pair of electrons and positively charged nuclei.

4.2.2 Describe how the covalent bond is formed as a result of electron sharing.

4.2.3 Deduce the Lewis (electron dot) structures of molecules and ions for up to four electron pairs on each atom.

4.2.4 State and explain the relationship between the number of bonds, bond length and bond strength.

4.2.5 Predict whether a compound of two elements would be covalent from the position of the elements in the periodic table, or from their electronegativity values.

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Covalent bonding occurs between atoms that have quite high electronegativities, that is usually between non-metals (under some circumstances metals in high oxidation states can also form covalent bonds). In covalent bonding the two atoms involved share some of their valence electrons since neither element loses electrons easily. The attraction of the two positively charged nuclei for these shared pairs of electrons results in the two atoms being bonded together as illustrated in Figure 406.
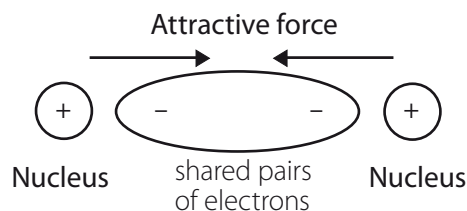

Figure 406   Covalent bonding as a result of electron pair sharing

In contrast to ionic bonding and metallic bonding, the interaction involves two specific atoms. A single covalent bond consists of a shared pair of electrons, a double bond two shared pairs and a triple bond three. Usually each atom involved contributes one electron, but in some circumstances one atom can donate both electrons. In this case the bond is known as a **dative covalent bond** (refer

to the end of this page). When forming covalent bonds, the atoms involved usually fill their valence level, so that the number of bonds formed is equal to the number of electrons needed for this. As a result the noble gases, which have filled valence shells, rarely form compounds. It also means that atoms in compounds (except for hydrogen) usually have eight electrons in their valence shell. This is often known as the **octet rule**. Carbon has an electronic structure of 2,4 and so requires four more electrons to fill its valence level. It therefore forms four bonds, as shown in Figure 406.
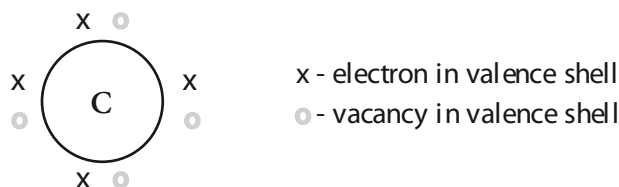
Figure 406   The valence level in carbon, showing vacancies

Similarly fluorine, (which has an electronic structure 2,7) and hydrogen (1) both require just one electron to fill their valence levels and so form just one bond. Oxygen (2,6) requires two electrons and normally forms 2 bonds, whilst nitrogen (2,5) forms 3 bonds.

If carbon and fluorine form a compound, because carbon forms four bonds and fluorine only forms one, four fluorines are required for each carbon and so the formula is CF_4. This can be represented as a **structural formula**, in which each covalent bond is shown as a line joining the atoms involved, or as a **Lewis structure** (electron dot diagram), which shows all the valence electrons of the atoms involved, or as a combination of these in which each electron pair is represented by a line (or a pair of crosses or

a combination of a pair of dots, crosses and lines). These representations of CF_4 are given in Figure 407, with two styles of Lewis electron structure on the lower line. The Lewis structure shows that the atoms involved all have filled valence shells in the molecule.
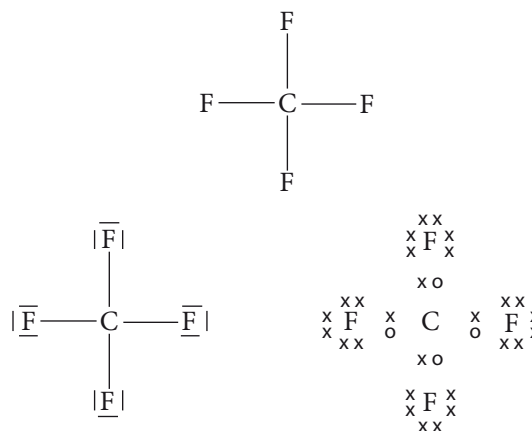

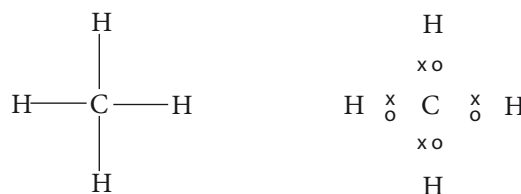*Figure 407 Bonding in carbon tetrafluoride*

Figure 408   Bonding in methane

Figure 408 shows the bonding in CH_4 illustrated as both a structural formula (left), which in this case is the same as the simple Lewis structure, and the "dot & cross" Lewis structure.
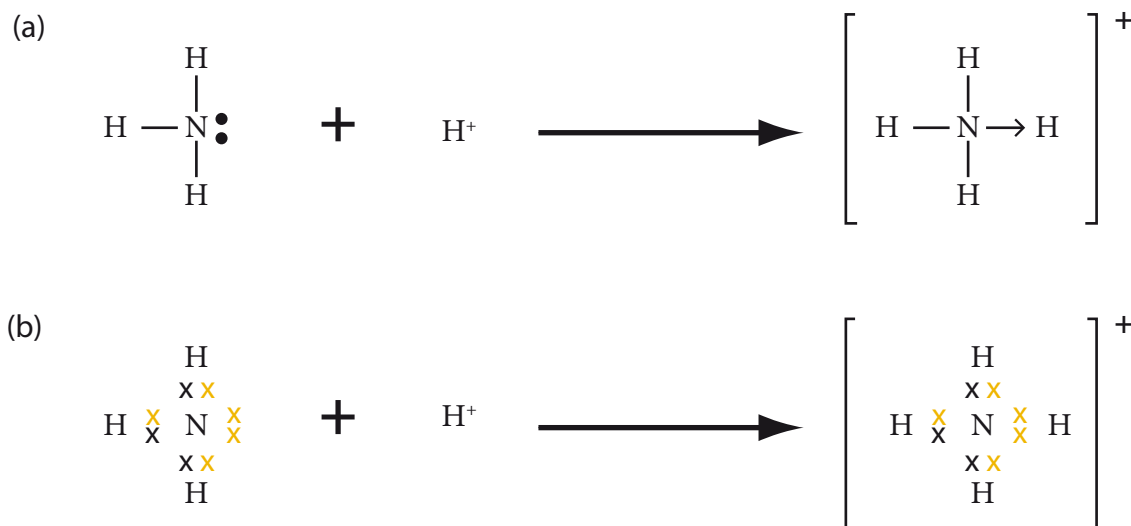

Figure 409   Bonding in the Ammonium ion

Sometimes in a covalent bond both of the electrons that form the bond originate from the same atom. A bond of this type is known as **dative bond**, though it is also sometimes referred to as a **coordinate bond**, or as a donor-acceptor bond. It is however equivalent to a normal covalent bond in every way apart from the origin of the electrons. The simplest example of a bond of this type is the bond formed between an ammonia molecule (NH_3) and a hydrogen ion to form the ammonium ion (NH_4^+), illustrated in Figure 409. In structural formulas a dative bond is often indicated by an arrow pointing in the direction the electron pair is donated and this is illustrated in Figure 409(a) whilst 409(b) shows it as a Lewis diagram. Dative bonds also occur in the triple bond formed in carbon monoxide, in all acid base interactions and in all ligand metal ion interactions

If two pairs of electrons are shared a double bond is formed, which joins the atoms more tightly and closer together than a single bond (as there are now two electron pairs pulling the two nuclei closer together). Carbon forms four bonds and oxygen forms two bonds, so that two oxygens are needed for each carbon, giving carbon dioxide. The oxygen and carbon atoms are joined by double bonds, which are represented as double lines in the structural formula. The diagrams for these are given in Figure 410.
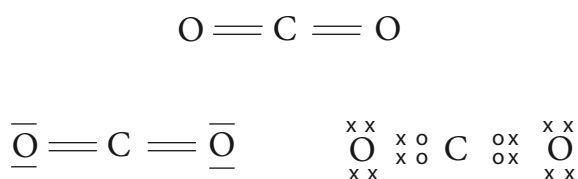
$$O = C = O$$

Figure 410   The bonding In CO_2

Figure 410 shows the bonding in CO_2 illustrated as both a structural formula (top) and two styles of Lewis diagram (lower line)

Again notice that the valence shells of both the carbon and oxygen are filled. Ethene is an example of an organic molecule that contains a double bond, and is an example of an unsaturated molecule. Its structural formula is given in Figure 414.

Two atoms can also share three pairs of electrons giving an even stronger triple bond. A nitrogen atom has five electrons in its valence level (electronic structure 2,5) and so requires three more electrons to fill it. In a nitrogen molecule therefore, the two nitrogen atoms are held together by a triple bond to form a nitrogen molecule, as shown in Figure 411.
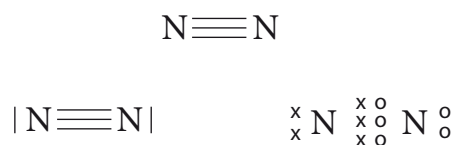
$$N \equiv N$$

Figure 411   The bonding in N_2

Figure 411 shows the bonding in N_2 illustrated as both a structural formula (top) and two styles of Lewis diagram (lower line).

Again note that the valence shells of both nitrogen atoms are filled. Ethyne is an example of an unsaturated organic molecule containing a triple bond (See Figure 414).

The types of diagrams above represent three of the stages involved in drawing a "dot & cross" Lewis diagram:

1   Decide how many bonds each atom involved forms. For many simple molecules this equals the number of electrons required to fill the outer electron shell, for more complicated cases see "Molecules with more or less than four electron pairs" under Section 14.1).

2   Decide on which is/are the central atom(s) (i.e. the one that has most bonds) and join the atoms together with bonds, so that all the atoms have the required number of bonds - this gives the structural formula. (n.b. if more than one structural formula is possible then the species most likely displays delocalised bonding, refer to Section 4.7).

3   Each bond will involve one electron from each of the atoms it joins (unless it is a dative bond). Subtract these from the total number of electrons in the valence shell of each atom to calculate the number of electrons present as non-bonding electrons. Draw a line to represent each of these pairs - this gives a simple Lewis diagram. If the species is an ion, then show the charge on the atoms with unpaired electrons.

4   To produce a "dot and cross" (sometimes referred to as an "electron dot") Lewis structure, replace each bond and each line by an electron pair. The electrons may be all represented by 'x's, or preferably a mixture of 'x's and 'o's can be used to indicate which atom the electron originally came from.

5   If the species is an ion rather than a molecule then one electron needs to be added for each negative charge and one removed for each positive charge. The

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Hydrogen cyanide	Methanoate ion
Carbon (2,4) forms four bonds, nitrogen (2,5) three and hydrogen (1) one in order to complete their valence shells.	Carbon (2,4) forms four bonds, oxygen (2,6) two and hydrogen (1) one in order to complete their valence shells.
The structural formula accounts for all of the carbon and hydrogen valence electrons, as the carbon has eight in its valence shell and the hydrogen one. The structural formula however only accounts for three of nitrogen's five valence electrons, so it must have a non- bonding pair. The simple Lewis diagram is therefore: H−C≡N|	The structural formula accounts for two electrons around the hydrogen and eight electrons around the carbon. The double bonded to the oxygen only accounts for two of its six electrons so there must also be two non-bonding pairs. The single bond to the other oxygen only accounts for one of its electrons so there are five more valence electrons to account for, two pairs and an unpaired electron*. |O| ‖ H−C−O̅•
There is one pair of electrons in the C−H bond and three pairs of electrons in the triple C≡N bond, so the "dot & cross" Lewis structure is: H ⚬ C ⚬ N ⚬	Replacing each bond by a pair of electrons, replacing the lines by non-bonding pairs and taking into account the unpaired electron on the oxygen, is the first stage in producing the "electron dot" Lewis structure.
Hydrogen cyanide is a neutral molecule so there is no need to add or remove electrons.	Finally the electron that causes the negative charge needs to be shown in the Lewis structure and the overall charge shown outside the square brackets: $\left[\text{H} \overset{\times}{\underset{\circ}{\cdot}} \text{C} \cdots \text{O} \cdots \right]^{-}$

* Note for the methanoate ion that a second structure could be drawn in whih the bonding to the oxygens is interchanged. This indicates that delocalised bounding probably occurs see Section 4.7

Figure 412   Constructing Lewis diagrams for hydrogen cyanide molecule and methanoate ion

electrons should be added/removed so as to give full valence shells of paired electrons. It may be useful to indicate such electrons by a '□' or '●'

This process is illustrated for the hydrogen cyanide molecule (HCN) and the methanoate ion (HCO_2^-) in Figure 412:

An alternative way to determine the Lewis structure, if each atom has an octet of electrons surrounding it (as is the case with C, N and O), is to follow the following procedure:

1. Count the total number of valence electrons from the group the atoms are in, accounting for any charge(s) present (add one for each "−" and subtract one for each "+").

2. Count the number of atoms requiring octets and hence calculate the resulting number of electrons needed (ignore hydrogens as their electrons all comprise part of other octets).

3. Take the difference between these two figures and add the number of electrons involved in bonds (as they are counted in two octets) to give the number of electrons in lone pairs (x). Hence there are $\frac{x}{2}$ lone pairs.

Using, the carbonate ion, CO_3^{2-} as an example:

1. Number of valence $e^- = 4 + (3 \times 6) + 2$ (added for 2− charge) = $24e^-$

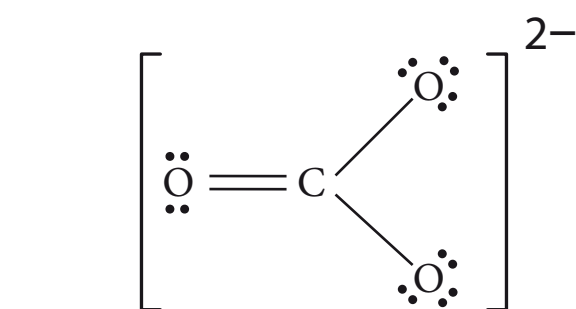2. Number of octets required = 4; ∴ number of electrons needed = $4 \times 8 = 32e^-$

Figure 413 The Lewis structure for CO_3^{2-}

3. Number of e^- short = $(32 – 24) = 8e^-$; plus 8e⁻ in bonds to give a total of 16e⁻; thus 8lone pairs required.

Now to produce the Lewis diagram, draw a double bond between C and (any) O, and single bond between C and the other two oxygens.

Carbon with 4 bonds now has its octet complete

Draw lone e^- pairs around the other oxygen atoms to complete their octet.

Show the 2⁻ charge on the ion [in square brackets] as in Figure 413.

Organic molecules, such as ethane, ethene and ethyne show the effect of single, double and triple bonding on the length and strength of the carbon-carbon bond as shown in Figure 414:

Covalent bonding can lead to two very different types of structures. Usually, as in all the examples so far considered,

	Ethane (single C–C bond)	Ethene (double C–C bond)	Ethyne (triple C–C bond)
Structural formula			H—C≡C—H
Lewis diagram			
C–C bond length (pm)	154	134	121
C–C bond energy (kJ mol⁻¹)	346	598	837

Figure 414   The structure of some simple hydrocarbons

the covalent bonds hold a small number of atoms together to form discrete units called **molecules**. Although the covalent bonds holding the molecule together are strong, the forces between molecules are much weaker (refer to Section 4.8), so that individual molecules are easily separated from each other. As a result molecular covalent solids have characteristic physical properties, such as being quite soft in the solid state, not conducting electricity, being more soluble in non-polar solvents than in water and having low melting and boiling points (often existing as liquids or gases at room temperature and pressure). This too is discussed in more detail in Section 4.8.

Sometimes, the whole lattice of a solid can be held together by strong covalent bonds. These 'covalent network', or 'giant covalent' structures are very different, being very hard and having very high melting and boiling points (again refer to Section 4.8) .

Exercise 4.2

1. An element forms a covalently bonded compound with hydrogen, that has the formula XH_3, where X is the element. In which group of the periodic table would you expect to find X?

    A   Group 1
    B   Group 14
    C   Group 15
    D   Group 17

2. "Two atoms each provide two electrons that are shared by the two atoms". This is a description of a

    A   single covalent bond.
    B   double covalent bond.
    C   triple covalent bond
    D   quadruple covalent bond.

3. A non-metal usually forms two covalent bonds in its compounds. How many electrons will it have in its valence level?

    A   2
    B   4
    C   6
    D   8

4. The noble gases do not usually form chemical compounds because

    A   they have very stable nuclei.
    B   the bonds between their atoms are very strong.
    C   they already have complete valence electron levels.
    D   they are not polar.

5. Which one of the following compounds contains both ionic and covalent bonds?

    A SiO_2
    B BaF_2
    C Na_2CO_3
    D Cl_2O

6. From the electronic structures of the following pairs elements deduce the numbers of covalent bonds, if any, that each would normally form, and hence predict the formulaes of the compound you would expect to result.

    a) helium and sulfur
    b) chlorine and hydrogen
    c) nitrogen and chlorine
    d) silicon and fluorine
    e) phosphorus and oxygen

7. From the electronic structures of the pairs of elements given, predict the type of bonding that you would expect in the compound they form.

    a) 2,4 and 1
    b) 2,8,5 and 2,8,7
    c) 2,1 and 2,8,6
    d) 2,6 and 2,7
    e) 2,8 and 3,2,6

8. Draw Lewis diagrams of the following molecules:

    a) HCl   b) O_2 c) PH_3

    d) F_2O e) H_2CO

4.2.7 Predict the shape and bond angles for species with four, three and two negative charge centres on the central atom using the valence shell electron pair repulsion theory (VSEPR).

4.2.8 Predict whether or not a molecule is polar from its molecular shape and bond polarities.

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SHAPES OF MOLECULES AND IONS

Molecules with 4 electron pairs

Covalent molecules all have distinct shapes. The shape of a molecule is determined by repulsion between the electron pairs in the valence shell. This is known as Valence Shell Electron Pair Repulsion (**VSEPR**) **theory**. Most common molecules have filled valence levels that contain four pairs of electrons. In order to be as widely separated as possible and hence minimise their potential energy, these electron pairs distribute themselves so that they are pointing towards the corners of a tetrahedron (a regular triangular based pyramid) with angles of 109.5°. If all of the electron pairs are bonding pairs, as for example in methane, CH_4, then this is also the shape of the molecule (See Figure 415).

Some molecules also contain non-bonding, or 'lone' pairs of electrons and these affect the shape of the molecule. In order to determine this it is vital to draw a correct Lewis structure for the species before any attempt is made to predict its shape. In ammonia, NH_3, if there were only the three pairs of bonding electrons, then these would point to the corners of an equilateral triangle with the nitrogen atom at its centre and angles would be 120°. The pair of electrons on the nitrogen that is not involved in the bonding (the lone pair or non-bonding pair), repels the bonding electrons so the molecule has the shape of a triangular pyramid. Similarly, if it were not for its two pairs of non-bonding electrons, the water molecule would be linear and not bent. The basic shapes of these common molecules is summarised in Figure 415.
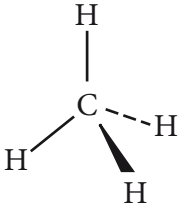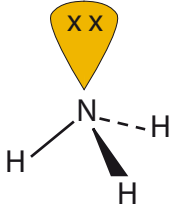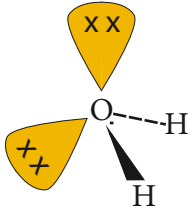
Number of non-bonding electron pairs	Example	Lewis diagram	Shape and bond angle
None	Methane		Tetrahedral 109.5°
One	Ammonia		Trigonal pyramidal 107°
Two	Water		Non-linear ('bent') 'angular' or 'V-shaped'. 104°

Figure 415 The shapes of common molecules

In all of these structures, the angles between all of the bonds might be expected to be the tetrahedral angle of 109.5° and this is the angle that is found in methane and other molecules that contain just four bonding pairs. The repulsion between a lone pair and a bonding pair is however greater than that between two bonding pairs. As a result the presence of a lone pair distorts the geometry, causing a slight reduction in the bond angle. If there is just one lone pair, as in ammonia, the bond angle is about 107°, whilst the presence of two lone pairs, as in water, reduces the bond angle to about 104°.

Note that in describing the shape of the molecule only the atoms and not the lone pairs are considered so that even though water has four regions of high electron density that have approximate tetrahedral orientation, its shape is described as non-linear (bent, angular or V-shaped) because that is the orientation of the atoms. It is important to indicate the angle as other non-linear molecules (such as ozone, O_3) can have angles of about 120°.

Molecules with less than four electron pairs

As discussed above, the shape of a molecule is determined by repulsion between the regions of high electron density in the valence level, that is, covalent bonds and non-bonding (or 'lone') electron pairs. The former arises when elements in groups 2 and 3/13 form covalent bonds, or when elements in the later groups form multiple bonds (which with regard to the shape of the molecule are the same as single ones) and hence have a reduced number of electron dense regions close to the nucleus. Ethene and ethyne (see Figure 4.15) are good examples of this.

If there are two regions of high electron density, then the result will be a linear molecule with 180° bond angle, as is found in gaseous beryllium chloride ($BeCl_2$) and in carbon dioxide. If there are three regions of high electron density then these will point towards the corners of an equilateral triangle with angles of 120°. If they are all bonding pairs then a trigonal planar molecule results, such as boron trifluoride. If one is a non-bonding pair, as in sulfur dioxide or ozone, then a bent (V-shaped; angular) molecule results. As would be expected from their effect in ammonia and water, the presence of the lone pair in sulfur dioxide reduces the bond angles to ~117° (less than 120°). These structures are given in Figure 416.

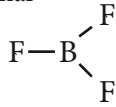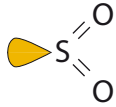| Nunber of regions of high electron density	Number of non-bonding electron pairs	Example	Shape and bond angle
Two	None	Carbon dioxide	Linear 180˚ O=C=O
Three	None	Boron trifluoride	Trigonal planar 120˚ F—B with F, F
Three	One	Sulfur dioxide	Non-linear (V-shaped) 117˚ S with O, O

Figure 416   The shapes of common molecules with less than four regions of high electron density
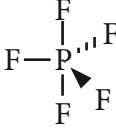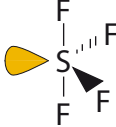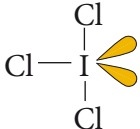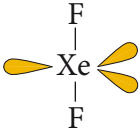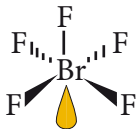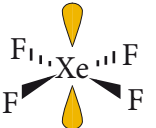
Number of regions of high electron density	Number. of non-bonding electron pairs	Example	Shape and bond angle(s)
Five	None	Phosphorus pentafluoride	Trigonal bipyramidal — 90° & 120°
Five	One	Sulfur tetrafluoride	'Saw horse' — 90° & ≈ 117°
Five	Two	Iodine trichloride	T-shaped — 90°
Five	Three	Xenon difluoride	Linear — 180°
Six	None	Sulfur hexafluoride	Octahedral — 90°
Six	One	Bromine pentafluoride	Square pyramid — ≈ 88°
Six	Two	Xenon tetrafluoride	Square planar — 90°

Figure 418   The shapes of common molecules with more than four regions of high electron density

HIGHER LEVEL

14.1 SHAPES OF MOLECULES AND IONS (AHL)

14.1.1 Predict the shape and bond angles for species with five and six negative charge centres using the VSEPR theory.

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MOLECULES WITH MORE THAN FOUR

ELECTRON PAIRS

Molecules with more than four negative charge centres arise because elements in the third (Al to Ar) and lower periods of the p-block can 'promote' one or more electron from a doubly filled s- or p-orbital into an unfilled low energy d-orbital. This increases the number of unpaired electrons available, and hence the number of bonds that can be formed by two for each electron promoted. Phosphorus ([Ne] $3s^2 3p^3$) for example usually has three unpaired electrons and forms the chloride PCl_3. By promoting one of its s-electrons it can take on the electron configuration ([Ne] $3s^1 3p^3 3d^1$) which has five unpaired electrons and so can form the chloride PCl_5. Molecules of this kind have more than eight outer electrons and so are said to have an **expanded valence shell**. This usually occurs only when the element forms strong polar covalent bonds (which in practice means to very electronegative elements) to small atoms (so that they can fit around the central atom without severe repulsion). As a result in many molecules with expanded valence shells the central atom is bonded to fluorine, oxygen or chlorine, especially fluorine. For example sulfur forms SF_6 and iodine IF_7.

In some molecules with expanded valence shells, there may be five or six regions of high electron density. Application of VSEPR theory shows that these will give molecular shapes based on the trigonal bipyramid (5 negative regions) and the octahedron or square bipyramid (6 negative regions). The trigonal bipyramid has two types of electron rich regions, two axial ones (each at 90° to three other pairs and at 180° to the fourth) and three equatorial ones (each at 90° to two other pairs and at 120° to the remaining two). Non-bonding electron pairs always occupy the equatorial positions, presumably because this minimises electron-electron repulsion. In the octahedral or square bipyramid arrangement, all of the positions are equal, but if there are two non-bonding pairs in an octahedral arrangement then these take positions opposite to each other to give a square planar shape (for example in XeF_4) so that they are separated as far as possible. It is of course vital to draw correct Lewis structures to determine the geometry of a molecule or ion, so as to find the number of lone pairs. As with tetrahedral based shapes, the presence of a lone pair causes slight distortion of the bond angles. Note that in all these cases, the central atom has more than an octet of electrons. These basic shapes and some common examples are summarised in Figure 418.

SHAPES OF MOLECULES WITH MULTIPLE

AND DELOCALISED BONDS

As will be seen later, quite a number of molecules and ions involve π-bonds (refer to Section 4.6) and delocalised bonds (refer to Section 4.7). When predicting the shape of these, exactly the same theory applies. The shape is dictated by the σ-bonds and the non-bonding electron pairs. π-bonds do not affect the shape of the molecule and hence it does not matter whether the delocalised structure or one of the resonance structures derived from a Lewis diagram is considered, as both give identical answers. This is illustrated below for the nitrate ion, which has three regions of high electron density (charge centres, or centres of negative charge) around the nitrogen and hence is trigonal planar and has bond angles of 120°.
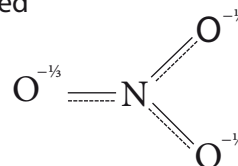

Resonance structure
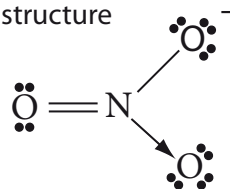
Delocalised

Figure 417   Nitrate structures

Consider for example the shapes of the three species NO_2^+, NO_2 and NO_2^-. Oxygen will normally form two bonds and nitrogen three, so the requirements of simple bonding theory cannot be satisfied in NO_2 which has

an odd number of electrons (each oxygen has 6 valence electrons and nitrogen has 5). Oxygen can however also accept an electron pair to form a dative bond and this does meet the bonding requirements, except that it will be noted that there is a single unpaired electron on the nitrogen atom. (Species with unpaired valence electrons are called free radicals and are usually very reactive. NO_2 by being relatively stable is a notable exception. Further details of free radicals are given later). In NO_2^+ this unpaired electron is lost and in NO_2^- an additional electron has been gained to give a non-bonding electron pair on the nitrogen. The Lewis structures are therefore:
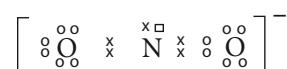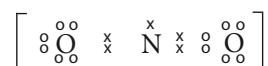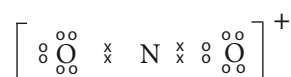

Figure 419   Lewis Structures of NO₂ species

It can therefore be seen that, because it has only two regions of negative charge around the nucleus, NO_2^+ will be linear with a bond angle of 180° and that NO_2^- with three centers of electron charge (one of which is a lone electron pair) will be trigonal planar with a bond angle of just less than 120°, probably about 117°. In the case of NO_2 because there is only a single lone electron rather than a lone pair, it is likely that it will be non-linear, but because the repulsion caused by a single electron will be less than that from a pair of electrons, the bond angle will be between 120° and 180° (it is in fact 134°). It is an arbitrary decision in all of these structures which of the oxygen atoms to join with a single bond and which with a double. This gives a clear indication that they are resonance structures, so that the actual species will involve delocalised π-bonds and be a resonance hybrid of the possible resonance structures (refer to Section 4.7). Similar considerations show that the carbonate ion (CO_3^{2-}) is trigonal planar.

Exercise   14.1

1. (AHL) Which one of the following molecules would you not expect to be planar?

    A SCl_4
    B C_2H_4
    C BCl_3
    D XeF_4

2. If a molecule has a trigonal pyramid shape, how many non-bonding pairs of electrons are there in the valence level of the central atom?

    A   1
    B   2
    C   3
    D   4

3. What shapes would you predict for the following molecules?

    a) SiF_4
    b) PCl_3
    c) H_2S
    d) NF_3
    e) CCl_4

4. Draw Lewis diagrams for and hence predict the shape, giving approximate bond angles, for $^+CH_3$, $^-CH_3$ and $\bullet CH_3$ (i.e. a methyl radical).

5. Sketch the shapes and predict the bond angles in each of the following species:

    a)   H—CO—OH
    b) CH_3—NH_2
    c)   H—CN
    d) ICl_2^- (AHL)

POLARITY

Polarity in covalent bonding and molecules

In covalent bonding, the bonds consist of electrons shared between the atoms. This sharing is not equal, unless the two atoms involved are identical (such as the two chlorine atoms in a Cl_2 molecule), because different atoms have different **electronegativities**, that is, have different attraction for electrons in a covalent bond (the most commonly met electronegativity scale is the Pauling electronegativity, used here, which assigns a value between 0 and 4 to indicate how strongly an atom will attract electron pairs in a covalent bond – the larger the number the greater the attracting power). The more electronegative atom will attract the electrons more strongly than the less electronegative one and that will result in it having a slight negative charge. The less electronegative atom will therefore be slightly deficient in electrons and so will have a slight positive charge. A covalent bond in which the atoms have fractional electrical charges (referred to as delta plus and delta minus and shown as δ+ and δ-) is known as a **polar bond**. In hydrogen chloride, for example, the chlorine atom is more electronegative than the hydrogen, which has the lowest electronegativity of all the common non-metals, and so the chlorine attracts the shared electrons more strongly. The hydrogen therefore has a slight positive charge and the chlorine a slight negative charge, as illustrated in Figure 420.

$$H^{\delta+} \quad Cl^{\delta-}$$

Figure 420   Illustrating a polar bond in hydrogen chloride

The **electronegativity** of an element can be judged from its position in the periodic table. All of the elements that form covalent bonds have quite high electronegativities, otherwise they would bond in a different way. The electronegativity of atoms increases across a period of the periodic table and also increases going up a group, so that the electronegativities fall into a series:

B & Si < P & H < C & S & I < Br < Cl & N < O < F

High   Very high   Extremely high

The greater the difference in electronegativity of the atoms involved, the greater the polarity of the bond and hence the electrical charges on the atoms involved. For example compared to the H–Cl the bond, the H–F bond is more polar and the H–I bond less polar. In the extreme case of very large electronegativity differences (e.g. sodium and chlorine) the electron can be considered to have been transferred, resulting in ionic bonding.

In some cases, such as hydrogen chloride, the polar bonds result in the molecule having a resultant dipole, that is, there is a positive and a negative end to the molecule. In carbon dioxide, even though the carbon-oxygen bonds are polar, their effects cancel out because of the symmetry of the molecule. The centres of positive and negative charge are in the same place, so that there is no overall **dipole**. In other molecules, such as water, because the shape is not so symmetrical, the effects of the polar bonds do not cancel, so that the molecule does have an overall dipole. Carbon dioxide and water molecules are compared in Figure 421.
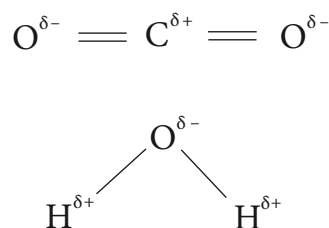
$$O^{\delta-} = C^{\delta+} = O^{\delta-}$$

$$H^{\delta+} \quad O^{\delta-} \quad H^{\delta+}$$

Figure 421   Comparing a non-polar molecule (Carbon Dioxide) with a polar molecule (Water)

In summary, for a molecule to be polar:
- it must contain polar bonds, and
- its shape must be such that the centres of positive and negative charges are not in the same place.

The **dipole moment** is a measure of the polarity of a molecule. Non-polar molecules have a zero dipole moment. For other molecules the more polar the molecule, the greater the dipole moment. Methane for example has a dipole moment of zero, hydrogen iodide has a value of 0.42 Debye, hydrogen chloride 1.05 Debye and hydrogen fluoride a value of 1.91 Debye.

Another way to represent the polarity of a bond is by means of arrows drawn next to the bond (with the head pointing to the more electronegative element). If because of symmetry the arrows on the various bonds in a molecule cancel each other out (that is, their vector sum is zero, so that when when placed head-to tail, these arrows return to the same point) then the molecule will be non-polar

(for example, CO_2). If they do not then the molecule will be polar and the vector sum of the polar bonds will give the molecular dipole (for example in H_2O). Molecular polarity can be indicated by an arrow drawn next to the molecule. By convention the head of the arrow points in the direction of the partial negative charge. This is illustrated below for polar trichloromethane ($CHCl_3$) and non-polar tetrachloromethane (CCl_4), both of which are tetrahedral:
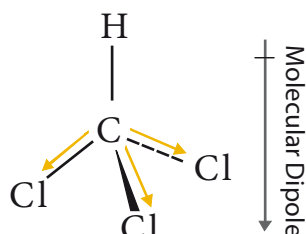
Trichloromethane, polar bonds do not cancel, so it is a polar molecule. (Note: the C—H bond has a low polarity and is generally ignored.)
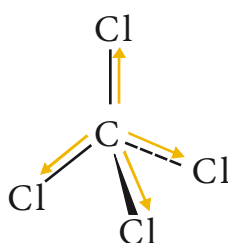
Tetrachloromethane, polar bonds cancel (equal and symmetrical) so it is a non-polar molecule.

Figure 422   Using bond polarity vectors to predict molecular polarity

Similar consideration of the polar bonds in symmetrical molecules such as methane (CH_4) and ethene (C_2H_4) will indicate that these are non-polar, whereas less symmetrical molecules such as ammonia (NH_3), chloromethane (CH_3Cl) and dichloromethane (CH_2Cl_2) are polar.

Experimentally, it is easy to tell if a liquid is polar or not by bringing an electrostatically charged rod close to a jet of liquid running out of a burette. If it is polar (such as $CHCl_3$, C_2H_5OH or $(CH_3)_2CO$) the stream of liquid will be attracted to the rod, if non-polar (such as CCl_4 or hexane, C_6H_{14}) it will be unaffected. This occurs because, in the electrical field produced by the rod, the molecules orientate themselves so that the end closest to the rod has the opposite charge to the rod, meaning that the electrostatic force of attraction is greater than the force of repulsion.

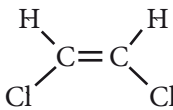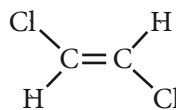1. Which one of the following bonds would be the most polar?

    A   C—N
    B   S—O
    C   Si—F
    D   P—Cl

2. Carbon and chlorine form a series of compounds: CH_4; CH_3Cl; CH_2Cl_2; $CHCl_3$; CCl_4. Which of these will be polar molecules?

    A CCl_4 only
    B CH_3Cl and $CHCl_3$ only
    C CH_3Cl, CH_2Cl_2 and $CHCl_3$ only
    D CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 only

3. State whether you would expect the molecules below to be polar or non-polar.

    a) SiF_4 b) PCl_3 c) H_2S
    d) NF_3 e) CCl_4

4. Which atom in the following bonds would you expect to carry a partial negative charge?

    a) H—N   b) O—P   c) C—F
    d) S—S   e) B—O

5. Two molecules are shown below

    A)   B)

    a)   In the molecules there are three kinds of bonds (C=C, C—Cl and C—H). Which would you expect to be the most polar and which the least?
    b)   Which one of these molecules would you expect to be polar and which non- polar? Explain why.
    c)   Given unlabelled samples of the two liquids, how could you use this property to identify them. Say exactly what you would do and what result you would expect in each case.

6. For each of the following species :

    i)   draw the Lewis structure, including all non-bonding electrons.

ii) give a sketch of the shape (including bond angles) of the molecule.

iii) state whether it would be polar or non-polar.

a) $BeCl_2$ (g)
b) H_2CO
c) N_2F_2 (2 isomeric forms exist)
d) ICl_4^- (AHL)
e) PF_4^- (AHL)

HIGHER LEVEL

14.2 HYBRIDIZATION (AHL)

14.2.2 Explain hybridization in terms of the mixing of atomic orbitals to form new orbitals for bonding.

14.2.3 Identify and explain the relationships between Lewis structures, molecular shapes and types of hybridization (sp, sp^2 and sp^3).

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When carbon and hydrogen form methane (CH_4), a perfectly tetrahedal molecule in which carbon bonds to four hydrogens results. How can this be explained when carbon has only two unpaired electrons with which to form bonds in its ground state? Firstly one of the pair of electrons in the s-orbital is 'promoted' to the vacant p-orbital to produce a carbon atom in an excited state which has four unpaired electrons (see below, this is similar to the electron promotion in valence shell expansion). One of these is however an s-electron and the others are p-electrons, and it seems most unlikely that these would produce four entirely equivalent bonds with hydrogen

atoms. Similarly, consider the oxygen atom ($1s^2 2s^2 2p^4$). Since electrons go singly into p orbitals before pairing begins, the oxygen atom has one paired and two unpaired electrons ($2p_x^2$, $2p_y^1$, $2p_z^1$). If only the p_y and p_z orbitals are involved in the bonding then the bond angle in H_2O should be 90° (since the p_y orbital is at 90° to the p_z orbital). This is not the case in water and again some explanation is required.

The theory used to explain these is **hybridization** which states that when an atom bonds the atomic orbitals involved in forming the σ-bonds, or accommodating the lone pairs of electrons, interact with each other to form an equal number of highly directional **hybrid orbitals** of equal energy. In the cases above this results in four equivalent sp^3 hybrid orbitals, as illustrated for carbon in figure 424:

Note that the total energy has not changed, it has just been redistributed equally amongst the four new hybrid orbitals. Because of electron-electron repulsion these hybrid orbitals are directed towards the corners of a regular tetrahedron.

In other words, when atoms join together to form molecules (except in the case of hydrogen), their outer atomic orbitals interact with each other to produce hybrid orbitals. This process of hybridization gives the same number of hybrid orbitals as the atomic orbitals involved, but these orbitals are all of the same energy, are symmetrically arranged around the atom and are more directional so as to produce greater interaction with the orbitals of the other atoms. The precise type of hybridization that occurs depends on the number of σ-bonds and non-bonding electron pairs that have to be accommodated about the atom. If there are two of these, then the hybridization will involve one s-orbital and one p-orbital and so is known as sp hybridization. This produces two hybrid orbitals at 180° to each other (as for example in CO_2 and C_2H_2). If three electron pairs are to be accommodated, then it involves one s-orbital and two p-orbitals to give sp^2 hybridization, with a trigonal planar symmetry (as for example in BF_3 and $H_2C=O$), and if four
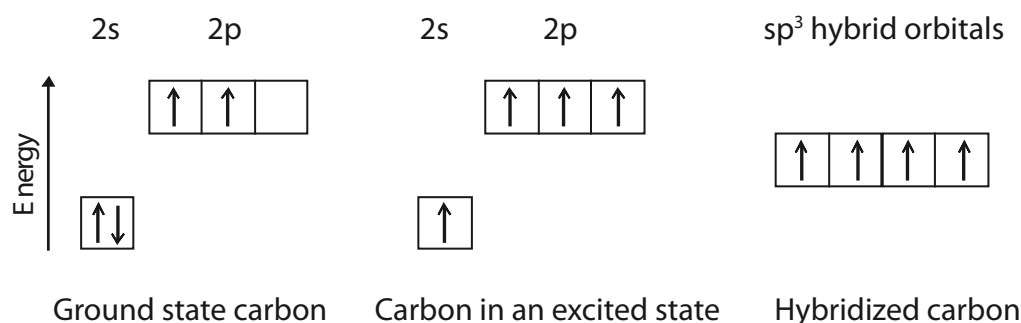

Figure 424   *sp^3 hybrid orbitals*

TOK   Is hybridization a real process or a mathematical device?

Now the person who wrote this sounds just like my friends who, when I tell them of my plans for the future, say to me "Get real!" I suppose that "really" gets to the heart of things. What is reality? I suppose first of all you have to agree there is a reality – an external universe outside of my head (no, not your head, my head because you only exist in there). Once that is over, the question must then what attributes would something have to have for me to be sure that it was part of this physical world – we mulled over this a bit with regard to atoms and sub-atomic particles, but perhaps hybridisation is a little bit different – it's not supposed to be an object, but a process and what do we mean by a process being real.

Do we actually need it? What does it help us to explain? It is useful and are there simpler alternatives? I suppose that what it helps to explain is how all of these different shaped atomic orbitals (and again it's interesting to reflect on the evidence for these) can give rise to equal bonds in molecules like methane. So hybridisation is a bit like saying you take a large, green wine bottle, along with 3 small, colourless beer bottles, melt them and use the glass to make four identical pale green bottles for fizzy water. Isn't it enough to say in the atom there were atomic orbitals and in the molecule there are molecular orbitals and we don't really need to know a lot about how one became the other? This is the basis of the "molecular orbital" approach which youhave started to meet through σ-bonds and π-bonds.Hybridization

seems to work mathematically, meaning that if you put in the atomic wave functions and carry out some fancy mathematical transformations, lo and behold out come things with a similar symmetry to common molecular shapes. Perhaps it's a bit like saying that long division is real (whatever that might mean) because if I have148 pieces of candy to share out amongst the 13 students in my class I can calculate I'll have to eat five myself (or maybe 18?). Again I'm just not sure that it helps my understanding of anything.

The contrast between mathematical devices and reality in the statement is an interesting one, Just like the first part of Bertrand Russell's famous quotation about "Mathematics is a subject in which people never know what they are talking about and never know whether it is true." Is what they are talking about the real world? Is mathematics discovered, in which case it is part of the real world (Didn't somebody once say that God was the great geometer, so maybe we are all part of a mathematical device?), or invented, in which case it is a product of human imagination and no more real than that may be. Anyway the statement seems to have prejudged the issue. Can't something be both? The Laws of Physics seem to be very well expressed in mathematical terms, so maybe all of mathematics is real? If so can both Euclidean and non-Euclidean geometry be real at the same time? I think I'll go off to find out more about imaginary numbers, and don't dare tell me that they're real!

such regions then an s-orbital and three p-orbitals interact to give four tetrahedrally orientated sp^3 hybrid orbitals (as for example in CCl_4 and C_2H_6). These hybrid orbitals are shown in Figure 425:

It can be seen that the shapes of these hybrid orbitals correspond to the shapes found for molecules according to electron repulsion theory (refder to the VSEPR theory in section 4.3) and the best way to determine the hybridization around an atom is by considering the shape of the molecule.

In ethyne (C_2H_2) for example, we can conclude that the carbon atoms are sp hybridized because of the linear shape of the molecule.

$$H-C\equiv C-H \qquad \text{Linear}$$

Note that hybrid orbitals can just form σ-bonds; π-bonds are only produced by the sideways interaction of unhybridized p-orbitals. (For an explanation of σ- and π-bonds refer to Section 4.6) The hybridization process of the carbons in this case are represented in Figure 426.
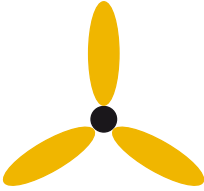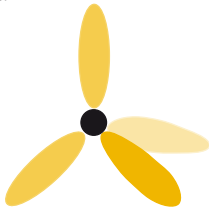
No. of orbitals	Hybridization	Shape
2	sp	Linear
3	sp^2	Trigonal planar
4	sp^3	Tetrahedral

Figure 425   The shapes of hybrid orbitals

2s   2p   2s   2p   sp hybrid orbitals form σ-bonds   2p orbitals form π-bonds

Ground state carbon   Carbon in an excited state   Hybridized carbon
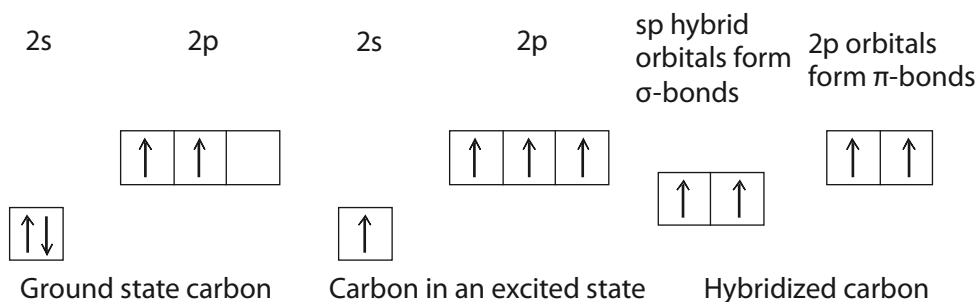
Figure 426   Hybridization of carbon in ethyne

Another example is ammonia, which has sp^3 hybridization because its trigonal pyramid shape can only result from a tetrahedral geometry. In this case however the sp^3 hybrid orbitals are not all used for bonding as one accommodates a lone pair of electrons. The hybridization can be represented as:

2s   2p   sp³ hybrid orbitals, 1 non-bonding, 3 bonding

Ground state nitrogen   Hybridized nitrogen
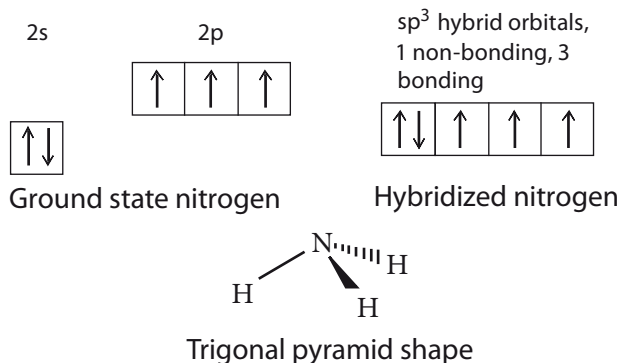
Trigonal pyramid shape

Figure 427   Hybridisation in ammonia

Another way to predict the hybridization present is from the Lewis structure. In this case the number of orbitals required around the central atom will be equal to the sum of the number of bonds (single, double or triple all count as one as each only involves one σ-bond) and the number of lone pairs. In water for example, there are two bonds and two lone pairs so that four orbitals are required, hence the hybridization will be sp^3. A second example would be the carbon atom in ethene which must be sp^2 hybridized in order to form bonds to three other atoms with no lone pairs. The relevant Lewis structures are gien in figure 428
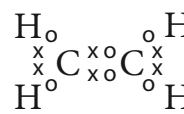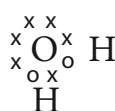
Figure 428   The Lewis structures of the molecules whose hybridization is discussed above

14.2.1 Describe σ and π bonds.

Exercise 14.2

1. The carbon atoms in ethane (C_2H_6), ethene (C_2H_4) and ethyne (C_2H_2) provide examples of the three common types of hybridization. In the order given above the type of hybridization corresponds to

   A   sp, sp^2, sp^3
   B   sp, sp^3, sp^2
   C sp^3, sp^2, sp
   D sp^3, sp, sp^2

2. The hybridization of the boron atom in boron trifluoride is described as sp^2.

   a) Use this example to explain what is meant by the term 'hybridization'.
   b) Why may we conclude that this kind of hybridization occurs in boron trifluoride?
   c) Boron trifluoride can react with a fluoride ion to give the tetrahedral BF_4^- ion. What type of hybridization would you expect the boron in this to have?

MULTIPLE BONDS

When a double bond forms between two atoms, the two bonds are not identical. The first bond is formed by the "end on" interaction of electrons in a s-orbital, or more commonly a hybrid orbital (see Section 4.5). When they interact they produce a bond in which the electron density is at its greatest on the inter-nuclear axis (an imaginary line joining the two nuclei) and is symmetrical about it. Bonds of this type are called σ (pronounced sigma) bonds.

The second bond in a double bond is formed by the "side on" interaction of electrons in p-orbitals at right-angles to the inter-nuclear axis. This bond has a low electron density on the inter-nuclear axis, but regions of high electron density on opposite sides of it. Bonds of this type are called π (pronounced pi) bonds. The formation of sigma and pi bonds is shown in Figure 429.

Single bonds are always σ-bonds, double bonds are always made up of one σ-bond plus one π-bond, whereas triple bonds are one σ-bond plus two π-bonds, with the π- bonds being at 90° to each other (that is, one with high electron density above and below the inter-nuclear axis, the other with high electron density in front of and behind it as you view the page). This is illustrated in Figure 430.
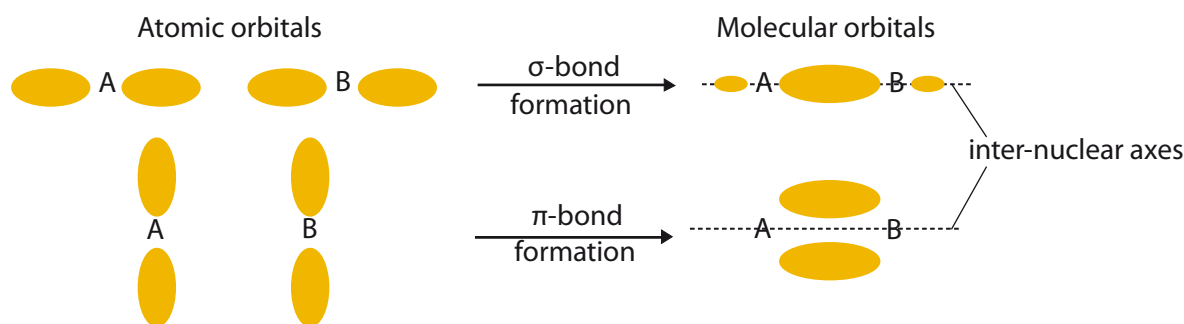
AHL

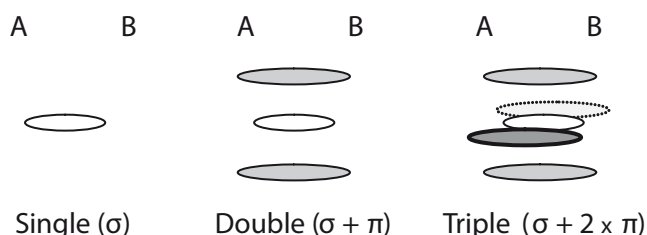Figure 429   The formation of σ-bonds and π-bonds from the interaction of atomic orbitals

Figure 430   The molecular orbitals comprising single, double and triple bonds

Because there are more electrons between the two nuclei, double and triple bonds result in them being more strongly bonded than single bonds, so pulling the atoms closer together. This means that going from single to double to triple bonds the bond energies increase and the bond lengths decrease, as shown in Figure 431 using carbon-carbon bonds as examples.

Bond type	Bond energy - kJ mol^{-1}	Bond length pm
Single (C—C)	348	154
Double (C=C)	612	134
Triple (C≡C)	837	120

Figure 431   The bond energies and bond lengths of carbon-carbon bonds

This is also true for other types of bonds. For example ethanoic acid contains two carbon-oxygen bonds, one single and one double, and it is found that the double bond is significantly shorter and stronger than the single. Similarly in the second period of the periodic table, the bond energy decreases going from nitrogen (N≡N, 944 kJ mol^{-1}, one of the strongest covalent bonds), through oxygen (O=O, 496 kJ mol^{-1}) to fluorine (F—F, 158 kJ mol^{-1}, one of the weakest covalent bonds).

Exercise   14.2

1.   Which one of the following correctly describes a π-bond?

   A   It is formed by the interaction of s-orbitals and has a high electron density on the internuclear axis.

   B   It is formed by the interaction of s-orbitals and has a low electron density on the internuclear axis.

   C   It is formed by the interaction of p-orbitals and has a high electron density on the internuclear axis.

   D   It is formed by the interaction of p-orbitals and has a low electron density on the internuclear axis.

2.   Carbon and oxygen can bond either by a single bond (as in CH_3—OH), a double bond (as in O=C=O), or a triple bond (as in C≡O).

   a)   Describe these three types of bonds in terms of σ-bonds and π-bonds.

   b)   How would you expect the length of the carbon-oxygen bond to vary in the three examples given?
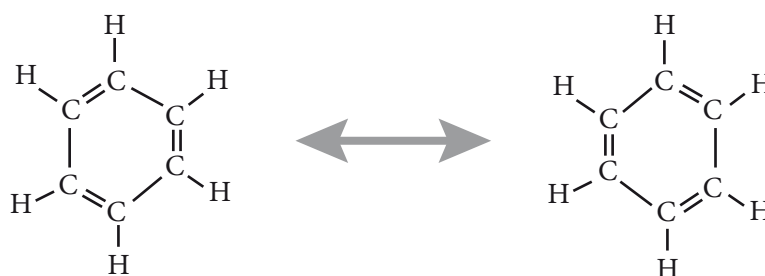
14.3.1 Describe the delocalization of π electrons and explain how this can account for the structures of some species.
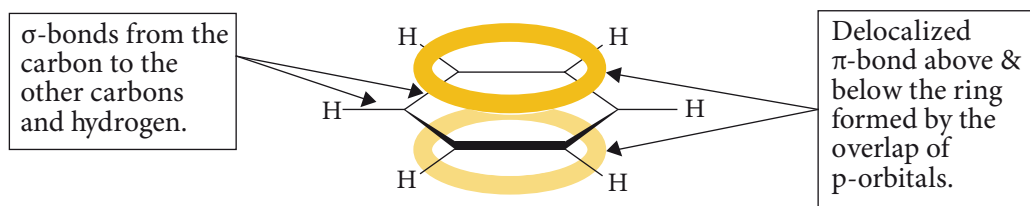
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14.3 DELOCALIZATION OF ELECTRONS (AHL)

A π-bond results from the "sideways" interaction of p-orbitals on two atoms, each containing one electron. On some occasions this interaction can involve more that two atoms and the p-orbitals on these atoms may contain differing numbers of electrons. This results in what is known as a **delocalized π-bond**. Delocalization in poly-atomic species allows the π electrons to spread over more than two nuclei (i.e. the π valence electrons provided by an individual atoms are not held around that atom but are mobile and shared by a number of atoms). This spreading out of the electrons that gives the species a lower potential energy (making it more stable) than it would have if it were composed of simple double and single bonds. Delocalization can hence be used to explain observations that are not readily accounted for in other ways.

The best known occurrence of delocalization is in benzene, C_6H_6, which is a planar, regular hexagonal shaped molecule, in which all of the carbon-carbon bond lengths and angles are equal. Simple bonding theory would predict that the carbon-carbon bonds in the ring would be alternately double and single (see Figure 432 a). This however would not lead to a regular hexagonal shape, as double bonds are shorter than single ones. The description involving delocalization is that each carbon atom in benzene is sp^2 hybridized. One of these orbitals forms a σ-bond to the hydrogen atom it is attached to, the other two form σ-bonds to the carbons on either side. The remaining electron (carbon has four valence electrons, three of which have been used to form the three σ-bonds) is in a p-orbital perpendicular to the plane of the σ-bonds. These p-orbitals on each carbon atom interact to produce a delocalized π-bond, which gives rings of high electron density above and below the ring of carbon atoms (see Figure 432 b).

AHL

(a) Possible "resonance" structures in terms of localized single and double bonds

σ-bonds from the carbon to the other carbons and hydrogen.	Delocalized π-bond above & below the ring formed by the overlap of p-orbitals.

(b) Delocalized description

Figure 432   Some descriptions of the bonding in benzene

An alternative approach (the "valence bond" model as opposed to the "molecular orbital" model above) is to consider the bonding in relation to the possible Lewis structures. If there are two or more equivalent structures that can be drawn for a molecule, as shown for benzene in Figure 432 (a), then what actually occurs will be mid-way between these various possibilities. The equivalent simple structures are called "resonance structures" and the actual species that exists is referred to as a "resonance hybrid" of these structures, because the species cannot be described adequately by a single structure involving just single and double bonds. Resonance structures have the same sigma bonds but differ in the arrangement of the pi bonds.

The "bond order" is the average of the number of bonds of the different resonance structures. In the case of benzene each bond is single in one resonance structure and double in the other, so the bond order is 1½. The resonance hybrid is always more stable than any of the resonance structures, the difference in stability being known as the resonance energy (the terms delocalisation energy and stabilisation energy are also sometimes used). This means that, for example, thermochemical calculations based on resonance structures give incorrect results.

Cyclohexene reacts with hydrogen to form cyclohexane and this reaction releases 119 kJ mol^{-1} of heat energy. If benzene contained three double bonds (i.e. it was 1,3,5-cyclohexatriene) then it would be reasonable to expect it to release three times this amount of energy (i.e. 357 kJ mol^{-1}).

In fact only 207 kJ mol^{-1} of heat energy is released when benzene is fully hydrogenated so that the delocalization of the π-bonds results in benzene being more stable by about 150 kJ mol^{-1}. This is illustrated in Figure 433.
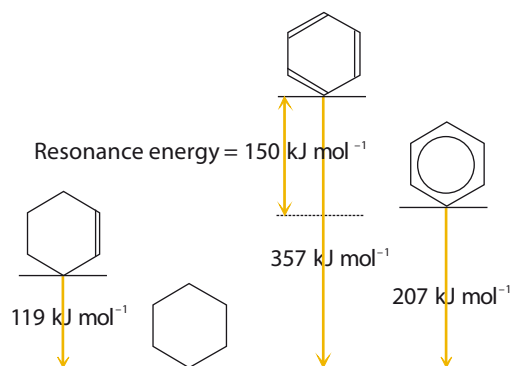
Figure 433   The hydrogenation of benzene

Graphite, an allotrope of carbon, has bonding that is very similar to that in benzene. The hydrogens on benzene are replaced by other carbons, so that each carbon is bonded to three other carbons by σ-bonds, formed by sp^2 hybrid orbitals, and the p-orbitals on the carbon atoms interact to form a delocalized π-bond that extends in two dimensions throughout the layer of the graphite crystal. This gives a carbon-carbon bond order (the average of the bonds between the atoms) of 1⅓. The structure of graphite is shown in Figure 454.

Another example of delocalized bonding is the carbonate ion shown in Figure 434. There are three equivalent resonance structures that can be drawn for this. Note the use of the double headed arrow ($\longleftrightarrow$) used to join resonance structures. This should never be confused with, or substituted for, the equilibrium arrow ($\rightleftharpoons$). The resonance hybrid has all the carbon–oxygen bonds part way between single and double bonds (specifically, the bond order is 1⅓ as each is a double bond in one of the three resonance structures), with the negative charge equally distributed over all of the oxygens (to be more precise each oxygen has a ⅔– charge as it carries a negative charge in two of the three resonance structures). The description of the carbonate ion in terms of delocalized bonding would be that the central carbon is sp² hybridized and that it forms σ-bonds to the three oxygens. There is then a delocalized π-bond formed by the four p-orbitals on the carbon and the three oxygens that also accommodates the extra electrons which give the ion its negative charge.

It is sometimes difficult deciding exactly when delocalization is likely to occur. Ethanoic acid and its anion, the ethanoate ion, are very similar however delocalization occurs in the anion, but not in the acid. The way that this may be predicted is from the fact that only one valid Lewis structure can be drawn for the acid, but there are two valid equivalent Lewis structures for the anion (see Figure 435). The evidence that this interpretation is correct is that in the acid the two carbon–oxygen bond lengths are different, but in the anion the two bonds are equal and their length is between the lengths of the bonds in the acid.
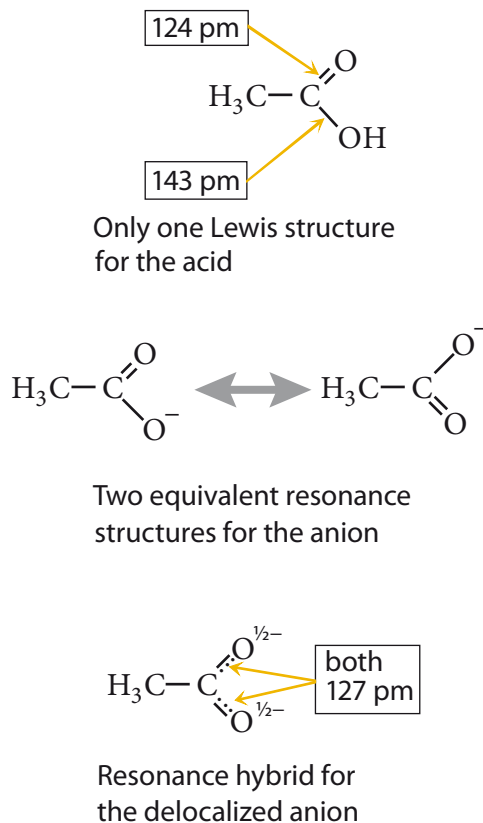
124 pm

143 pm

Only one Lewis structure
for the acid

Two equivalent resonance
structures for the anion

Resonance hybrid for
the delocalized anion

both
127 pm

Figure 435   Bonding in ethanoic acid and the ethanoate ion

Two other examples of common species in which delocalization occurs are ozone (O_3) and the nitrite ion (NO_2^-, also known as the nitrate(III) ion). In ozone the contributing resonance structures each have the central atom forming a dative single bond to one oxygen and a double bond to the other. A delocalized π-bond description would be that the oxygens all have sp² hybridization and the p-orbitals perpendicular to this interact to form a delocalized π -bond above and below the plane of the oxygen atoms, giving a bond order of 1½ in ozone.

Resonance structures
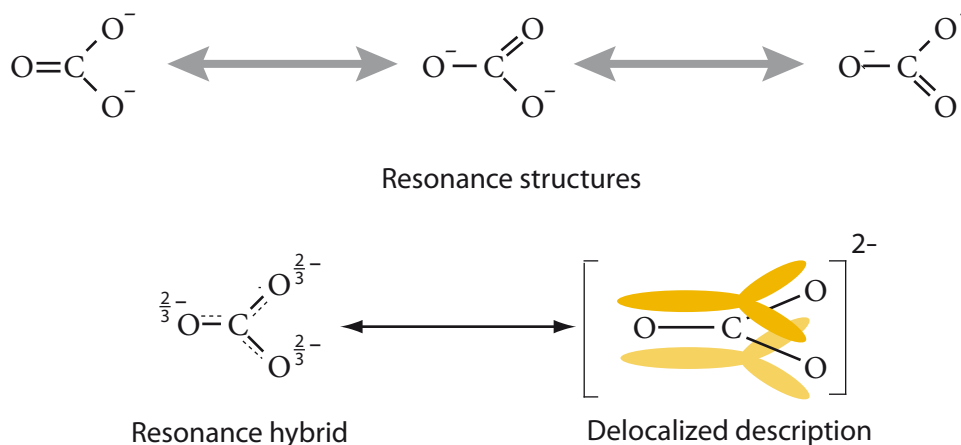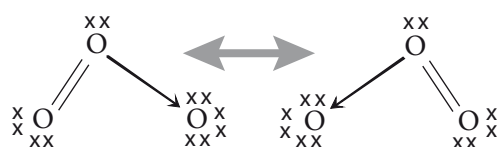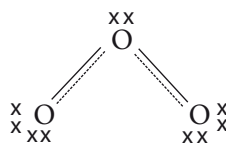
Resonance hybrid

Delocalized description

Figure 434   Delocalization in the carbonate ion
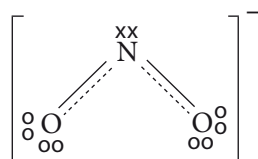
Resonance structures

Resonance hybrid

Figure 436   Resonance structures

This predicts that the oxygen-oxygen bond length will be part way between the single bond found in hydrogen peroxide (HO—OH, 146 pm) and the double bond in the oxygen molecule (O=O, 121 pm). The **empirically** determined value of 128 pm fits with this prediction. Lewis diagrams for the possible resonance structures for the nitrite ion, which is isoelectronic with ozone, are shown below along with the resonance hybrid:

Resonance structures

Resonance hybrid

Figure 437   Resonance Lewis structures

Note that the predicted nitrogen-oxygen bond order is 1½ and that the charge is shared equally over the two oxygen atoms. A similar approach can be used to predict the bonding in the nitrate(V) ion (see question 2 in Exercise 4.7).

Exercise	14.3

1.   Which one of the following species cannot be adequately described by a single Lewis diagram?

      A NH_4^+
      B HCO_3^-
      C C_2H_2
      D OH^-

2.   a)   Draw a Lewis diagram for the nitrate(V) ion.

      b)   Explain how this fails to adequately describe the shape of the nitrate(V) ion.

      c)   How is the bonding better described using the concept of delocalization?

      d)   Describe how the atomic orbitals interact to produce a delocalized bond.

      e)   What bond order would you expect for the N—O bond in the nitrate(V) ion and what charge would you expect each oxygen atom to carry?

      f)   How would you expect the lengths of the N—O bonds in nitric(V) acid (HNO_3)to compare with those in the nitrate(V) ion?

4.3 INTERMOLECULAR FORCES

Covalent bonding between atoms can result in either a giant structure such as diamond, or in a simple molecular structure such as methane. In the latter weak forces exist between the molecules. If it were not for these then molecular covalent compounds would never condense to liquids and solids when cooled. There are three types of these intermolecular forces that will be dealt with in order of increasing strength.

VAN DER WAALS' FORCES

These forces are also sometimes referred to as **London forces** (after the Polish physicist *Fritz London*), or dispersion forces. They exist between all species as a result of the fact that a temporary dipole on one molecule resulting from the random movements of the electrons, especially in the valence shell, has an inductive effect on the neighbouring molecules. Thus, if one end of a molecule has an instantaneous negative charge then the electrons in a neighbouring molecule will be repelled from that end of the molecule resulting in an instantaneous positive charge. The net result is that the attractive forces between molecules are on average stronger than the repulsive forces, as illustrated in Figure 438.
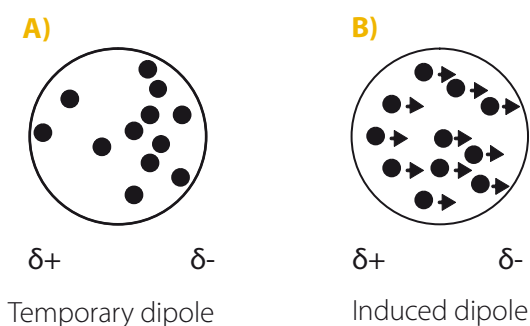

Figure 438   Illustrating van der Waals' forces

At this moment in time in "A" there are, by chance, more electrons on the right hand side than on the left hand side, which results in the right hand side of "A" having a temporary partial negative charge. This repels the electrons in "B", as shown, inducing the left hand side of B to acquire a positive charge, resulting in an attractive force. This however does not last owing to the random, independent movement of electrons.

The strength of this force increases with the molar mass of the molecule, owing to an increase in the number of electrons and hence the size of the instantaneous dipoles. This effect can be seen, for example in the noble gases (helium boils at 4 K, xenon at 165 K) and the alkanes (methane boils at 111 K, hexane at 341 K). Another example of this trend is the halogens which all exist as non-polar diatomic molecules. As the molar mass of the molecules increases, so does the boiling point as shown in Figure 439:
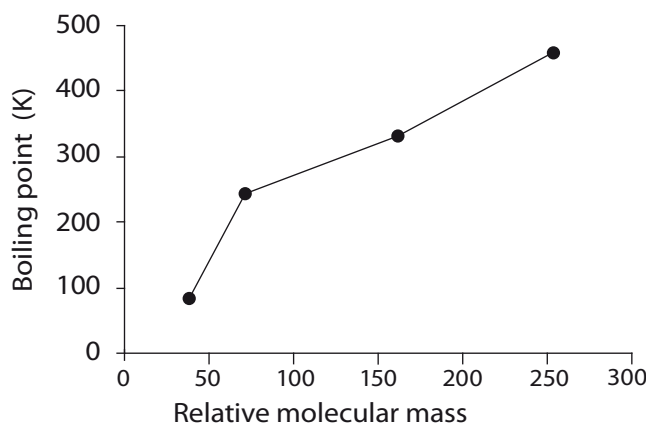
Figure 439   The variation of boiling point of the halogens with molar mass

These forces are only effective over a short range and so they are very dependent on the surface area of the molecules that come into close contact with each other. The more elongated the molecule, the stronger the van der Waals' forces and the higher the boiling point. Pentane, $CH_3-CH_2-CH_2-CH_2-CH_3$ boils at 309 K, whereas its almost spherical isomer, dimethylpropane, $(CH_3)_4C$ boils at 283 K. Under certain circumstances **van der Waals' forces** can become quite strong, such as those between polymer chains in some common plastics, such as polythene. These long thin molecules have both a high molar mass and a very large surface area.

DIPOLE-DIPOLE FORCES

These occur because of the electrostatic attraction between molecules with permanent dipoles.

Electrostatic attraction

$$H^{\delta+}—Cl^{\delta-} ||||||||||||||||||||| H^{\delta+}—Cl^{\delta-}$$

These are significantly stronger than van der Waals' forces in molecules of a similar size, so that, even though both have similar molar masses, the boiling point of polar hydrogen chloride (188 K) is significantly higher than that of non-polar fluorine (85 K). Similarly, as shown in Figure 440, the boiling points of the non-polar noble gases (Ar, Kr and Xe) are considerably lower than the polar hydrogen halides of a similar molar mass (HCl, HBr and HI), because both will have van der Waals' forces between their particles, but in addition to these the hydrogen halides will have **dipole-dipole forces**:
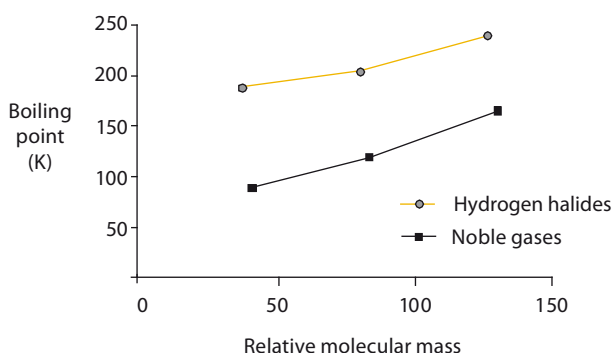

Figure 440   A comparison of the boiling points of polar and non-polar substances

HYDROGEN BONDING

This occurs most markedly in molecules that contain hydrogen bonded to highly electronegative and small nitrogen, oxygen or fluorine atoms. It occurs as a result of the interaction of a non-bonding electron pair on one of these atoms with a hydrogen atom that is carrying a relatively high partial positive charge, as a result of being bonded to another of these small, very electronegative atoms. As such it may be thought of as being part way between a dipole-dipole bond and a dative covalent bond. In the hydrogen bond, for maximum strength, the two atoms and the hydrogen should all be in a straight line. The **hydrogen bonding** interaction is illustrated in Figure 441 (in which X and Y are N, O or F).
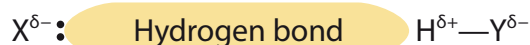
Figure 441   An illustration of hydrogen bonding

Hydrogen bonding is usually considerably stronger than other intermolecular forces and has a large effect on the physical properties of the substances in which it occurs (refer to Section 4.10). Hydrogen peroxide (H_2O_2), of a similar molar mass to fluorine and hydrogen chloride mentioned above, has a boiling point of 431 K (158 °C) - an increase of > 250 °C over hydrogen chloride. Another set of examples is that propane C_3H_8 ($M_r = 44$), which has only van der Waals' forces, boils at 231 K, ethanal $CH_3–CO–H$ ($M_r = 44$) which is polar but cannot hydrogen bond, boils at 294 K, whereas ethanol CH_3CH_2OH ($M_r = 46$), which has intermolecular hydrogen bonds, boils at 352 K.

Hydrogen bonding has a profound effect on the boiling points of the hydrides of nitrogen (NH_3), oxygen (H_2O) and fluorine (HF) when compared to those of other

Figure 442   The effect of hydrogen bonding on the boiling points of some hydrides

elements in the same group of the periodic table. This is shown in Figure 442.

In the case of the group 4/14 compounds, the hydrides are tetrahedral and hence non-polar, so that the only forces between them are van der Waals' forces. As a result they are always the compounds with the lowest boiling points. All of the other hydrides are less symmetrical and so will have some resultant dipole and hence a degree of dipole-dipole interaction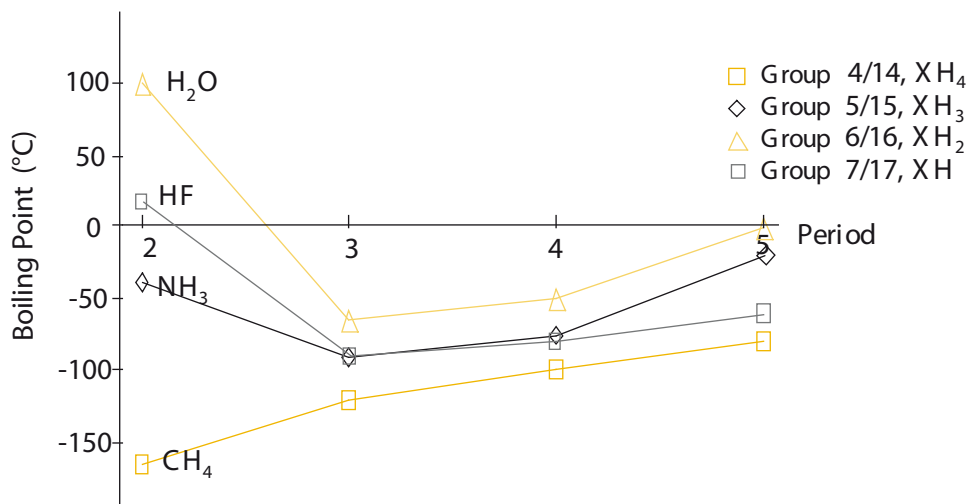 as well as the van der Waals' forces. It can be seen that going from period 5 to period 4 to period 3 the boiling points decrease in all of the groups, because of the reduction in the strength of the van der Waals' forces with decreasing molar mass. In group 4/14 this trend continues into period 2, with methane (CH_4) but in the other groups there is a sharp increase in boiling point on going from period 3 to period 2. This is explained by the existence of hydrogen bonding between molecules of ammonia (NH_3), water (H_2O) and hydrogen fluoride (HF), as well as van der Waals' forces. The deviation is most marked for water because each water molecule has two hydrogen atoms and two non-bonding electron pairs,which allows it to form two hydrogen bonds per molecule. Ammonia has only one non-bonding electron pair and hydrogen fluoride has only one hydrogen atom, so in both cases they can form only one hydrogen bond per molecule, as illustrated in Figure 443.
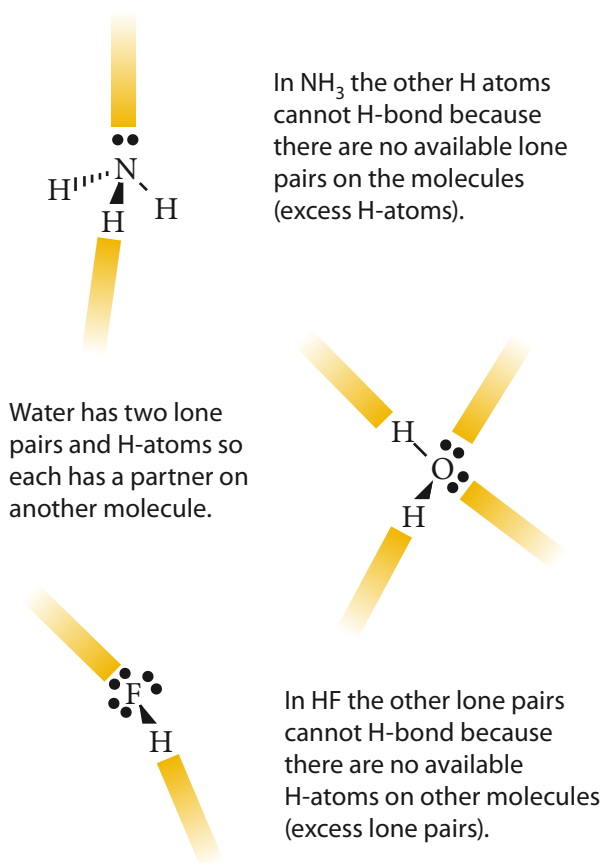
Water is one of the most strongly hydrogen bonded substances and this affects many other physical properties, such as the molar enthalpy of fusion (6.0 kJ mol^{-1} for H_2O and only 2.4 kJ mol^{-1} for H_2S) and molar enthalpy of vaporization (41 kJ mol^{-1} for H_2O and only 19 kJ mol^{-1} for H_2S). It also accounts for many of its anomalous physical properties, such as ice having a density less than that of water. Because each water molecule can form four hydrogen bonds, ice has a structure in which each water molecule is hydrogen bonded to four others with tetrahedral symmetry.

This produces a structure very similar to the diamond structure, but with hydrogen bonds instead of covalent bonds, compare that of ice in Figure 444 below with that of diamond in Figure 452. This is a very open structure with large empty spaces enclosed in it, hence the low density. Thus ponds and lakes freeze from the surface downwards. As the water cools at the surface, it becomes less dense and stays on top until it freezes. The layer of ice on the surface helps to insulate the water underneath from further heat loss and fish and plants survive under the ice. Even when ice melts, this structure persists to some extent, which is why the density of liquid water increases when heated from 0 °C to 4 °C, the exact opposite of the effect of temperature on density in almost all other liquids.

In NH$_3$ the other H atoms cannot H-bond because there are no available lone pairs on the molecules (excess H-atoms).

Water has two lone pairs and H-atoms so each has a partner on another molecule.

In HF the other lone pairs cannot H-bond because there are no available H-atoms on other molecules (excess lone pairs).

Figure 443   The number of hydrogen bonds formed by some common hydrides

Figure 444   The structure of ice

The properties of many organic compounds are affected by the fact that hydrogen bonding can occur between their molecules, for example ethanoic acid (CH_3–CO–OH, M_r = 60, b.p. 391 K) is a liquid at room temperature and pressure, whereas butane (CH_3–CH_2–CH_2–CH_3, M_r = 58, b.p. 273 K) is a gas. Even in the gaseous state or in non-aqueous solution, the hydrogen bonding between pairs of ethanoic acid molecules persists, as shown below, so that its relative molecular mass appears to be ≈ 120.
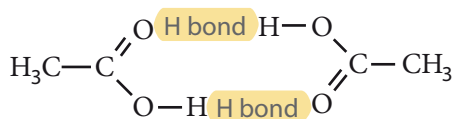
*Figure 445   Hydrogen bonding in **dimers** of ethanoic acid*

Butane and other substances that cannot hydrogen bond are insoluble in water, because their presence would disrupt the hydrogen bonding between water molecules, whereas ethanoic acid can form its own hydrogen bonds to water and hence is fully miscible. Indeed ethanoic acid is even more strongly hydrogen bonded in aqueous solution than compounds such as ethanol because it has two oxygen atoms ($>C=O$ and $—O—H$) that can form hydrogen bonds to water molecules. Water solubility even extends to compounds such as propanone ($CH_3—CO—CH_3$), which cannot form hydrogen bonds to other propanone molecules (it has no suitable hydrogen atom), but which can hydrogen bond to water molecules (the $>C=O$ oxygen bonds to the hydrogen atom of a water).

Hydrogen bonding is also of great biological importance. It provides the basis for the pairing of bases in DNA and the α-helix and β-sheet secondary structures of protein molecules. The α-helix is in fact an example of intra-molecular hydrogen bonding, i.e. hydrogen bonding within a molecule. This type of bonding can also occur in much simpler molecules and explains why the boiling point of 2-nitrophenol (216 °C), which mainly bonds intra-molecularly and hence has weaker intermolecular forces, is significantly lower than that of 4-nitrophenol (279 °C), which mainly bonds inter-molecularly, as shown in Figure 446.
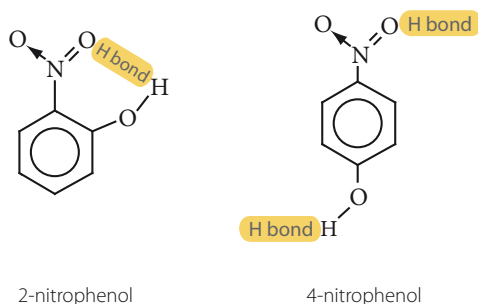

2-nitrophenol   4-nitrophenol

Figure 446   Hydrogen bonding in nitrophenols

In brief the consequences of hydrogen bonding for a substance are:
*   Higher boiling point and lower volatility,
*   Greater solubility in water,
*   Higher viscosity.

1. In which one of the following compounds would hydrogen bonding occur?

    A $COCl_2$
    B PH_3
    C H_2CO
    D CH_3OH

2. Which one of the following molecules would you expect to have the highest boiling point?

    A $CH_3–CH_2–CH_2–CH_2–CH_2–CH_3$
    B $CH_3–CH(CH_3)–CH_2–CH_2–CH_3$
    C $CH_3–CH_2–CH(CH_3)–CH_2–CH_3$
    D $CH_3–C(CH_3)_2–CH_2–CH_3$

3. In which of the following substances would there be the strongest forces between the molecules?

    A SiH_4
    B $H_2C=O$
    C $CH_3–CH_3$
    D O_2

4. Which one of the following usually produces the weakest interaction between particles of similar molar mass?

    A   Hydrogen bonding
    B   Covalent bonds
    C   Dipole-dipole forces
    D   Van der Waals' forces

5. In which one of the following substances is hydrogen bonding **not** significant?

    A   Ice
    B   Polythene (polyethene)
    C   DNA
    D   Protein

6. Explain the following observations in terms of the intermolecular forces that exist.

    a)   At room temperature and pressure chlorine is a gas, bromine a liquid and iodine a solid.
    b)   Water is a liquid at room temperature and pressure, but hydrogen sulfide is a gas.
    c)   Ethanol (CH_3CH_2OH) has a much higher boiling point than its isomer methoxymethane (CH_3OCH_3).

d)   Pentan-1-ol boils at 137 °C, whereas pentan-3-ol boils at 116 °C.

e)   The boiling point of sulfur dioxide is 24 °C higher than that of chlorine.

7.   Explain why the boiling points of hydrogen fluoride, water and ammonia are significantly higher than those of the analogous compounds in the next period. What other effects on physical properties occur as a consequence of the bonding you describe? Give specific examples.

4.4 METALLIC BONDING

4.4.1   Describe the metallic bond as the electrostatic attraction between a lattice of positive ions and delocalized electrons.

4.4.2   Explain the electrical conductivity and malleability of metals.

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Metallic bonding occurs between atoms which all have low electronegativities. In a metal the atoms are all packed together as closely as possible in three dimensions - like oranges packed into a box. A regular arrangement of this type is known as a **close-packed lattice**. Because the metal atoms have low ionization energies and many low energy unfilled orbitals, the valence electrons are delocalized amongst (that is, shared by) all the atoms, so that no valence electron belongs to any particular atom, and they are free to move throughout the metal. The atoms, having lost their valence electrons, are positively charged and are therefore better described as being cations. The attraction of these positive ions for the mobile electrons provides the

+ positive ion

− electron

Figure 447   Bonding in metals

force which holds the structure together. Thus a metallic structure is often described as consisting of a lattice of positive ions filled by a mobile 'sea' of valence electrons, as illustrated in Figure 447.

The attraction is between the ions and the mobile electrons and not between the ions themselves, so that the layers of ions can slide past each other without the need to break the bonds in the metal. This means that metals are **malleable** and **ductile**. If an atom of a different size is introduced (for example, carbon in steel) then it is less easy for the planes to slide, hence alloys (metals containing more than one type of atom) are usually harder than pure metals.

The delocalized electrons are free to move from one side of the lattice to the other when a potential difference is applied, so that they can carry an electric current. Metals are therefore good conductors of electricity. These mobile electrons also make them good conductors of heat and their interaction with light produces the lustre characteristic of metals, at least when freshly cut.

The strength of the bond between the metal atoms depends on how many electrons each atom shares with the others. For example, the melting point of potassium (one valence electron per atom) is 337 K, calcium (two valence electrons per atom) is 1123 K and scandium (three valence electrons per atom) is 1703 K. It also depends on how far from the positive nucleus the electrons in the 'sea' are (i.e. depends on the ionic radius). For example, going down group 1 the melting point decreases from lithium (454 K), through sodium (371 K) to potassium (337 K). In some cases, such as sodium, the metallic bonding is quite weak, so that the substance is soft and has low melting and boiling points. In most cases however metallic bonding is strong, so that the solid is quite hard, though still malleable, and has high melting and boiling points. Mercury, a metal that is one of two elements that is a liquid at room temperature and pressure (bromine is the other), is an obvious exception.
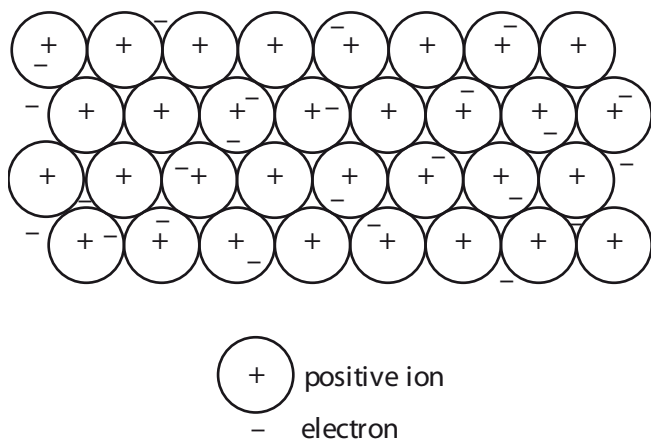
Exercise   4.4

1.   Use the commonly accepted model of metallic bonding to explain why:

a)   the boiling points of the metals in the third period increase from sodium to magnesium to aluminium.

b)   most metals are malleable.

c)   all metals conduct electricity in the solid state.

4.5 PHYSICAL PROPERTIES

The physical properties of a substance depend on the forces between the particles of the chemical species that it is composed of. The stronger the bonding between these particles, the harder the substance and the higher the melting and boiling points, though the melting point is also very dependent on the extent to which the bonding depends on the existence of a regular lattice structure. The presence of impurities in a substance disrupts the regular lattice that its particles adopt in the solid state, weakening the bonding. Hence the presence of impurities always lowers (and broadens) the melting point of a substance. For this reason, melting point determination is often used to check the purity of molecular covalent compounds. Similarly, alloys have lower melting points than the weighted mean of their component metals. The volatility, that is, how easily the substance is converted to a gas, also depends on the strength of forces between particles. Electrical conductivity depends on whether the substance contains electrically charged particles that are free to move through it when a potential difference is applied. Dissolving involves the intimate mixing of the particles of two substances (the **solute** and **solvent**). In order for one substance to dissolve in another the forces between the two types of particles in the mixture must be as strong, or stronger, than that between the particles in the two pure substances, though entropy changes also play an important role in determining solubility.

In metals the hardness, **volatility**, melting point and boiling point all depend upon the number of valence electrons that the individual metal atom contributes to the delocalized electrons. It is the mobility of these delocalized electrons that allows metals to conduct electricity in all physical states.

The malleability and ductility of metals results from the fact that the bonding is between the metal ions and these electrons, and not between the ions themselves. This allows one layer of the lattice to slide over another without the need to break the bonding.

The forces between metal atoms are often quite strong and metal atoms cannot form bonds of comparable strength to substances that are held together by bonding of a different type (that is, ionic or covalent). As a result metals do not

dissolve in other substances unless they react with them chemically (for example, sodium in water). Metals can however dissolve in other metals to form mixtures of variable composition called alloys, for example brass is an alloy of copper and zinc. Mercury, as a liquid metal, forms a wide range of alloys, known as amalgams. To a limited extent non-metals can also be dissolved into metals to form alloys, the most common example being steel, which is iron with a small percentage of dissolved carbon. Alloys usually retain metallic properties, though an alloy is generally less malleable and ductile than the pure metal because the varying size of atoms in the lattice means that it is less easy for the layers to slide over each other as shown in Figure 448.
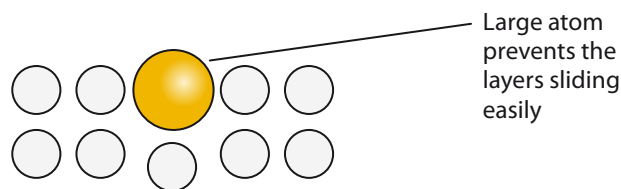

Large atom prevents the layers sliding easily

Figure 448   The lattice structure of an alloy

The ions in an ionic compound are held together by strong electrostatic forces operating in all three dimensions (see Figure 402 & 403), so that they are non-volatile, with high melting points and high boiling points. Hence they are all solids at room temperature and pressure. If one layer moves a fraction then ions of the same charge will come next to each other and so repulsion rather than attraction will result. This causes the substance to break, hence ionic solids as well as being hard, are also brittle.

The particles that make up an ionic solid are electrically charged ions. In the solid however, these are firmly held in place and cannot move to carry an electric current. However when the substance is molten, or in solution, the ions can move freely and carry an electric current. Ionic compounds therefore conduct when molten and in solution, but not in the solid state.

The strong forces between the ions mean that ionic substances are insoluble in most solvents. Water however is a highly polar molecule; hence water molecules can bond to both anions and cations because of the attraction between the partial charge on the atoms of the water molecule and the charge on the ion. The interaction between ions and the polar water molecules, known as ion-dipole interactions, is illustrated in Figure 449.
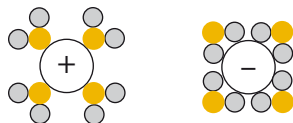
● The oxygen atoms carry a slight negative charge

○ The hydrogen atoms carry a slight positive charge

Figure 449   The hydration of anions and cations by polar water molecules

As a result of this hydration of the ions, ionic substances are more soluble in water than in non-polar solvents. If however the forces between the ions are very strong, then the ionic substance will not even dissolve in water. There are definite patterns to the solubility of ionic compounds and the **solubility** of most ionic substances can be correctly predicted using a few simple solubility rules:

- All nitrates are soluble.
- All sodium, potassium and ammonium compounds are soluble.
- All sulphates are soluble, except $BaSO_4$ and $PbSO_4$; $CaSO_4$ is only sparingly soluble.
- All chlorides, bromides and iodides are soluble, except those of silver. Lead halides are sparingly soluble in cold water, but quite soluble in boiling water.
- All other compounds are insoluble, though some, such as $Ba(OH)_2$ and $Ca(OH)_2$ are sparingly soluble.

The hydration enthalpy (that is, the enthalpy change when one mole of gaseous ions is converted to one mole of hydrated ions) is a measure of the strength of the interaction of the water molecule with the ion. It depends on the charge to size ratio (its charge density): this increases with the charge on the ion and decreases with the size of the ion. It is also greater for cations than for anions as a result of their smaller size and the angular shape of the water molecule giving better packing. As a result the hydration energy is greatest for small, highly charged cations such as the aluminium ion Al^{3+}.

In the substances of the two kinds described above the bonding is uniform throughout the substance and this kind of structure is described as a 'giant' structure. Covalent bonding can lead to two very different structures. The first of these is a giant covalent structure (also known as network covalent or macromolecular structure) such as in diamond and silica, SiO_2. In these, all of the atoms in the lattice are joined to each other by strong covalent bonds, so that giant covalent substances are very hard and have very high melting and boiling points. The strong forces holding the substance together also means that giant covalent substances are solids at room temperature and pressure, and insoluble in all solvents. All of the electrons are usually firmly held in the covalent bonds so the substance does not conduct electricity (with the exception of graphite, see Figure 455).

By contrast, in the second type of covalent structure, known as a molecular covalent structure, there are strong covalent bonds (intramolecular forces) between the atoms making up the molecule, but only weak intermolecular forces between these molecules (refer to Section 4.9). Because the bonds between one molecule and another are so weak, molecular covalent substances are often liquids or gases at room temperature and pressure, whereas the other structure types almost always give rise to solids.

The physical state depends on the strength of the intermolecular forces. In the case of the halogens, as the molar mass and hence the strength of the van der Waals' forces increases (refer to Section 4.9) the state of the element (at room temperature and pressure) changes from gas (F_2 and Cl_2) to liquid (Br_2) to solid (I_2).

Molecular covalent substances are usually quite soft as a result of the weak forces between the molecules of the solid. They will often dissolve in non- polar solvents, such as hexane, which also have weak van der Waals' forces between the molecules, but are insoluble in very polar solvents like water. This is because water is very strongly hydrogen bonded, so that inclusion of a non-polar molecule into its structure would require the breaking of these bonds. Substances that dissociate to form ions in water, such as hydrogen chloride are an exception to this, as are substances which can form hydrogen bonds to water. As with giant covalent substances, the electrons in molecular covalent substances are firmly held in the covalent bonds and so they do not conduct electricity. The bonding in a molecular covalent substance is illustrated in Figure 450.
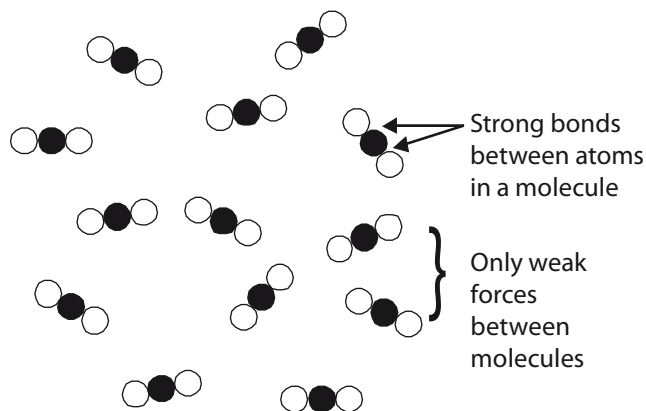

Figure 450   An illustration of molecular covalent bonding

Hydrogen bonding can however have a large effect on the properties of molecular covalent substances. These forces are much stronger than other intermolecular forces so that hydrogen bonded substances have much higher melting and boiling points than molecules of a similar molar mass that cannot hydrogen bond. For example, at room temperature and pressure ethanol (CH_3–CH_2–OH) is a liquid (b.p. = 351 K), whereas its isomer methoxymethane (CH_3–O–CH_3), which is unable to form hydrogen bonds, is a gas (b.p. = 248 K). In solids, hydrogen bonding can often result in the crystals being harder, and more brittle, than those solids with other types of intermolecular forces. Sucrose (sugar) would be a good example of such a substance. Molecules that can hydrogen bond, such as ethanol and sucrose, are usually quite soluble in water. This is because the molecule can form hydrogen bonds to the water molecules to compensate

for the water-water hydrogen bonds that are broken. In alcohols the hydroxyl (—OH) group forms hydrogen bonds, but the hydrocarbon chain disrupts the hydrogen bonding in the water. This means that as the length of the hydrocarbon chain increases, the solubility of the alcohol in water decreases. This also explains why ethanoic acid (CH_3–CO–OH) is fully miscible with water, but hexanoic acid (C_5H_{11}–CO–OH) and benzoic acid (C_6H_5–CO–OH) are only sparingly soluble.

The physical properties associated with different types of structure are summarised in Figure 451, along with some typical examples.

	Giant Metallic	Giant Ionic	Giant Covalent	Molecular Covalent
Hardness and malleability	Variable hardness, malleable rather than brittle	Hard, but brittle	Very hard, but brittle	Usually soft and malleable unless hydrogen bonded
Melting and boiling points	Very variable, dependent on number of valence electrons, but generally high	High: melting point usually over 500 °C	Very high melting point, usually over 1000 °C	Low melting point, usually under 200 °C. Liquids and gases are molecular covalent
Electrical and thermal conductivity	Good as solids and liquids	Do not conduct as solids, but do conduct when molten or in solution	Do not conduct in any state (graphite is an exception)	Do not conduct in any state
Solubility	Insoluble, except in other metals to form alloys	More soluble in water than other solvents	Insoluble in all solvents	More soluble in non-aqueous solvents, unless they can hydrogen bond to water or react with it
Examples	Iron, copper, lead, mercury, brass	Sodium chloride, calcium oxide	Carbon (diamond) silicon dioxide (quartz, sand)	Carbon dioxide, ethanol, iodine

Figure 451   Structural types and physical properties - a summary

CORE

4.2 COVALENT BONDING (CONT)

4.2.9 Describe and compare the structure and bonding in the three allotropes of carbon (diamond, graphite and C_{60} fullerene).

4.2.10 Describe the structure of and bonding in silicon and silicon dioxide.

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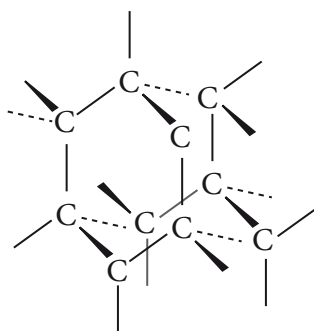## CARBON AND SILICON

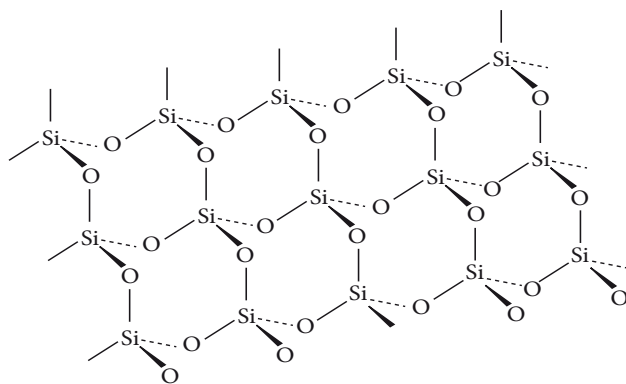*Figure 452   The covalent structure of diamond*

Figure 453   The bonding in silicon dioxide

Diamond is the most common example of a substance that has a giant three dimensional covalent structure. Each carbon atom in diamond is sp^3 hybridised and is joined to four others arranged tetrahedrally, so that there is strong bonding in all three dimensions. The arrangement of carbon atoms in diamond is illustrated in Figure 452. This explains why crystals of diamond are exceptionally hard and why it has very high melting and boiling points. Diamond is probably the best example of a **giant covalent structure**.

Silicon, also forming four covalent bonds, has an almost identical crystal structure to diamond. The sideways overlap between the p-orbitals of the larger atoms is less so other allotropes that involve π-bonding do not occur. Silicon dioxide (SiO_2, sometimes called silica), which occurs commonly as quartz and (in a less pure form) sand, has a very similar structure to silicon and diamond, except that each carbon is replaced by a silicon and the C-C bonds are replaced by an oxygen 'bridging' between the silicon atoms. A two dimensional diagram of the bonding is shown in Figure 453 below."

Graphite is another **allotrope** of carbon. Allotropes are different forms of an element that exist in the same physical state (ozone and diatomic oxygen molecules are another example of allotropes). It is unusual in that it comprises a giant covalent network in two dimensions, but has only weak van der Waals' forces between these sheets of carbon atoms, see Figure 454. There is a delocalized π-bond between all of the sp^2 hybridized carbon atoms in a given sheet, so that the bond order of the carbon-carbon bonds is 1⅓, hence the carbon–carbon bond length is slightly less than that found in diamond. The distance between the sheets is quite large and the forces between them quite small, hence they can easily slide over each other. This results in graphite having a lower density than diamond, being a soft solid used as a lubricant and, as layers of carbon are easily rubbed off on to paper, it is used in 'lead' pencils. The delocalized electrons between the layers are free to move so that graphite can conduct electricity in two dimensions.

The **fullerenes** are a recently discovered allotrope of pure carbon. They contain approximately spherical molecules made up of five- and six- membered carbon rings. The fullerene that has been most completely investigated is C_{60} (whose shape resembles a soccer ball), illustrated in Figure 455. In fullerenes each sp^2 hybridised carbon is bonded by sigma bonds to three other carbons, but because the surface of the sphere is not planar, there is only a little delocalization of the unpaired bonding electrons (contrast to graphite) and electrons cannot flow easily from one C_{60} molecule to the next. Hence the electrical conductivity,
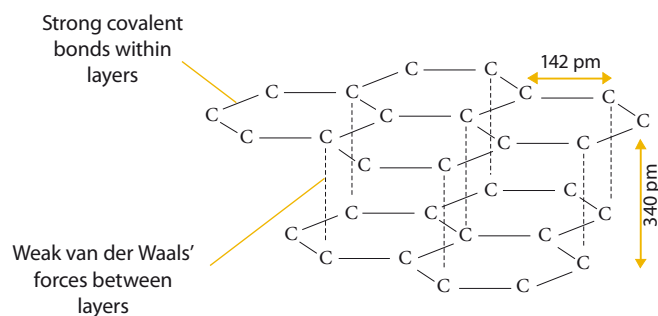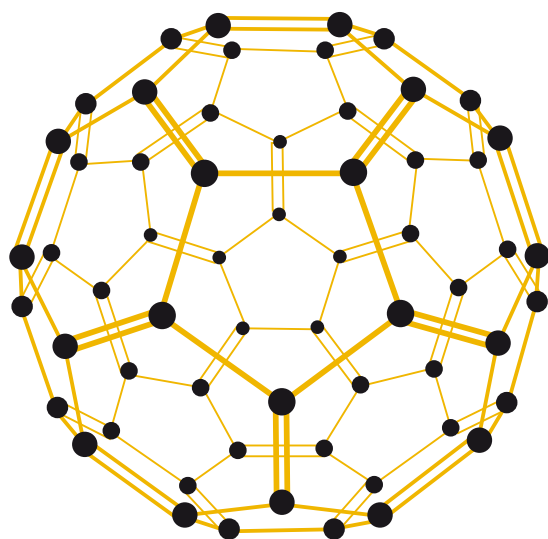
Strong covalent bonds within layers

142 pm

340 pm

Weak van der Waals' forces between layers

Figure 454   The structure of graphite

Figure 455   The structure of fullerene-60 (C_{60})

whilst greater than that of diamond, is much less than that of graphite and some fullerene derivatives, for example $C_{60}K_3$, have unusual electrical properties. Chemically C_{60} behaves as an electron deficient molecule readily accepting electrons from reducing agents to form anions with a variety of charges. Addition reactions, similar to those found in alkenes, can also occur. Unlike diamond and graphite, fullerenes are molecular, hence they will dissolve in non-polar solvents and have comparitively low melting points. For example C_{60} is moderately soluble in non-polar solvents, such as methylbenzene, and sublimes at about 800 K. With such open, spherical molecules, fullerenes have interesting compressibility properties. Closely related to the fullerenes are the nanotubes, which comprise capped cylinders of carbon atoms bonded in a very similar manner to the fullerenes.

Exercise   4.2

1.   A substance that is a gas at standard temperature and pressure is likely to

    A   have a molecular covalent structure.
    B   be a compound of a metal.
    C   have a giant covalent structure.
    D   have its atoms held together by metallic bonds.

2.   If an element in group 2 of the periodic table formed a compound with an element in group 7/17 of the periodic table, the compound formed is likely to

    A   conduct electricity in the solid state.
    B   have a low boiling point.
    C   dissolve in non-polar solvents.
    D   be a crystalline solid.

3.   Ethanol (C_2H_5OH) is a molecular covalent compound. When pure ethanol boils the gas consists of

    A   a mixture of carbon dioxide and water.
    B   carbon, hydrogen and oxygen.
    C   water and ethanol.
    D   ethanol only.

4.   Which one of the following substances would you expect to have the lowest boiling point?

    A   CsCl
    B $SrSO_4$
    C Sc_2O_3
    D $AsCl_3$

5.   Which one of the following would not conduct an electric current?

    A   Solid sodium chloride
    B   Liquid sodium chloride
    C   Aqueous sodium chloride
    D   Solid mercury

6.   Which one of the following substances would you expect to be most soluble in water?

    A $CH_3–CH_2–CH_2–CH_2–CH_2–CH_3$
    B $H_2N–CH_2–CH_2–CH_2–CH_2–NH_2$
    C $Cl–CH_2–CH_2–CH_2–CH_2–Cl$
    D $CH_3–CH_2–CH_2–O–CH_2–CH_2–CH_3$

7. Molten lead and molten lead(II) bromide both conduct electricity. Which one of the following statements relating to this is true?

    A   Both undergo a chemical change when they conduct.

    B   Both conduct by the movement of charged particles.

    C   Both will also conduct in the solid state.

    D   Both contain mobile electrons.

8. Rubidium chloride (RbCl) is an ionic compound, naphthalene (C_6H_8) is a molecular covalent solid, scandium (Sc) is a metal and silicon carbide (SiC)by has a giant covalent structure.

a) Which of these substances would you expect to have the highest melting point?

b) Which of these substances would you expect to have the lowest melting point?

c) Which of these substances would you expect to be soluble in water?

d) Which of these substances would you expect to conduct electricity as a solid?

e) Which of these substances would you expect to be soluble in a non-polar solvent, such as hexane?

f) Which of these substances would you expect to conduct electricity only when molten, or in solution?

g) Which of these substances would you expect to be malleable?

h) Which of these substances is an element rather than a compound?

i) Which of these substances would you expect to be the hardest solid?

j) Which of these substances contains charged particles?

9. Magnesium is a silver-grey metal, iodine a black crystalline non-metal. Under suitable conditions, they will react together to form a white compound, magnesium iodide.

a) Give two physical properties that you would expect to be different for magnesium and iodine.

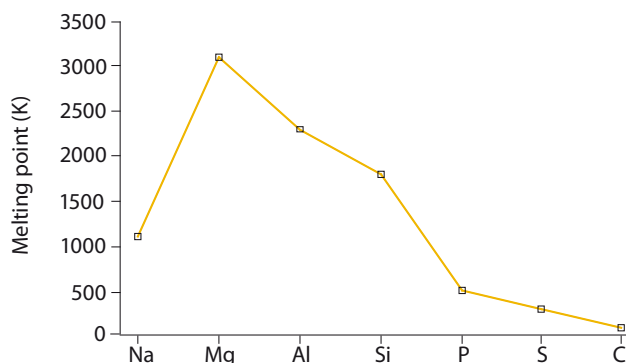b) How would the appearance of a mixture of magnesium and iodine compare with that of their compound?

c) What is the formula of the compound that they form? What kind of bonding is present in it?

d) How would you expect the behaviour of magnesium iodide to compare with that of a mixture of magnesium and iodine if both were shaken with water?

e) Describe how a non-polar solvent, such as tetrachloromethane could be used to separate the mixture of magnesium and iodine into its components.

10. In cookery class Anita expresses surprise that sugar melts so much more easily than salt, when in many other ways they are similar. Her friend Jenny, wanting to show off the fact that she is taking science, says

"That's because sugar has covalent bonds and salt has ionic bonds. Ionic bonds are stronger than covalent ones"

As is often the case, there is some truth in what Jenny says. Using suitable examples, explain why this statement as it stands is not accurate and then express more accurately what Jenny meant.

11. Ethanoic acid (CH_3-CO-OH) reacts with sodium hydroxide to form sodium ethanoate (CH_3–CO–O⁻ Na⁺) and with ethanol to form ethyl ethanoate (CH_3–CO–O–CH_2–CH_3). Explain why ethanoic acid and sodium ethanoate both dissolve in water, but ethyl ethanoate does not.

12. The graph below shows the melting points of representative oxides of the elements in the third period of the periodic table. Explain how the type of bonding present in these compounds varies across the period and how this is reflected in the graph.

CRYSTAL TYPE	PARTICLES IN CRYSTAL	PRINCIPAL ATTRACTIVE FORCES BETWEEN PARTICLES	MELTING POINTS and BOILING POINTS	ELECTRICAL CONDUCTIVITY OF LIQUID (IN MOLTEN STATE)	CHARACTERISTICS OF THE CRYSTALS	CONDITIONS FOR FORMATION	EXAMPLES
IONIC NETWORK CRYSTALS	Positive and negative ions due to electron transfer from active metal to active non-metal, e.g., $Na^+ \dots Cl^-$, NaCl $Ca^{2+} \dots O^{2-}$, CaO $2K^+ \dots SO_4^{2-}$, K_2SO_4	Attractions between oppositely charged ions. Strong ionic bonding.	High. Non-volatile due to three dimensional arrangement of anions and cations.	High. Electrolyte in molten form or in aqueous solution. Non-electrolytes as solids.	Solid. Hard, brittle. Most dissolve in polar solvents e.g. H_2O.	Metal - non-metal combination. Formed between atoms of greatly differing electronegativity (between elements of Groups 1, 2 and 3 and 6 and 7).	NaCl, CaO, K_2SO_4, KCl, CaF_2, Cs_2S, MgO
COVALENT NETWORK CRYSTALS / NETWORK SOLIDS / GIANT STRUCTURES, OR MACRO-MOLECULAR	Non-metal atoms	Covalent bonds (i.e., electron sharing) throughout the whole crystal. Very strong.	Very high. Non-volatile due to 3D network arrangement.	Diamond: nil Graphite solid: moderate conductor; Fullerene: poor conductor.	Solids. Very hard. Insoluble in most ordinary liquids.	Most are formed by two elements of Group 4, e.g. C, Si	Diamond, Si, SiO_2, graphite. Fullerene-60
METAL NETWORK CRYSTALS	Lattice of positive ions surrounded by delocalized / mobile valence electrons.	Metallic bonding. Attraction of mobile valence electrons by positive nuclei. Strong.	Most are medium to high. Non-volatile.	Very high due to presence of mobile valence electrons.	Usually solids. Most are hard yet malleable, ductile. High thermal conductivity. Insoluble in liquids. Usually soluble in molten metals.	Formed by electropositive metallic elements with low electronegativity.	Na, Cu, Ca (¾ of the periodic table elements are metals)

Figure 463   Characteristics of Crystalline Solids - A Summary

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CRYSTAL TYPE	PARTICLES IN CRYSTAL	PRINCIPAL ATTRACTIVE FORCES BETWEEN PARTICLES	MELTING POINTS and BOILING POINTS	ELECTRICAL CONDUCTIVITY OF LIQUID (IN MOLTEN STATE)	CHARACTERISTICS OF THE CRYSTALS	CONDITIONS FOR FORMATION	EXAMPLES
(SIMPLE) MOLECULAR CRYSTALS (a) POLAR	Polar molecules containing elements of high electronegativity (i.e. non-metals).	Electrostatic attraction between dipoles. Intermediate strength.	Intermediate-low molar mass compounds tend to be volatile.	Very low or non-conductors when solids, liquids and in aqueous solution. A few (e.g. HCl) react with H_2O to form electrolyte.	Many polar substances are soluble in polar solvents.	Formed from asymmetrical distribution of electron cloud containing polar covalent bonds. Such bonds are formed between atoms having a moderate difference in electronegativity.	ICl, SO_2, HCl
(b) H-BONDING	H bonded to N, O, or F	Strengthened by hydrogen bonding if H is bonded to O, F or N.	Hydrogen-bonding increases boiling and melting points.		Most small hydrogen bonded substances are soluble in polar solvents.	Hydrogen-bonding if H is bonded to F, N, O.	Hydrogen bonding in: H_2O, H_2O_2, HF, NH_3, alcohols, amines, organic acids.
(c) NON-POLAR	Non-polar molecules or atoms (in the case of noble gases).	Strong covalent bonds between atoms. van der Waals' forces (weak, temporary, instantaneous dipoles) between molecules.	Low; Volatile	Non-conductors when solid and as liquid.	Soft. Usually gases or volatile liquids. Most are soluble in non-polar or slightly polar solvents. Insoluble in polar water.	Formed between atoms or from symmetrical molecules containing covalent bonds between like atoms or atoms having a small difference in electronegativity.	H_2, Cl_2, S_8, C_6H_6, CH_4, N_2, CO_2, CCl_4, I_2. Noble gases: simple atomic substances.