

By the end of this chapter, you will have an understanding of the covalent bonds formed by the attraction of two non-metal atoms. When non-metals bond, their atoms share electrons to gain stable outer shells. Covalent bonding results in non-metal atoms being arranged into either discrete molecules or three-dimensional lattice structures.

You will become familiar with the valence shell electron pair repulsion (VSEPR) theory and use the theory to predict the shape and polarity of molecules. You will then use these predictions to determine the types of intermolecular forces found between molecules—dispersion forces, dipole–dipole attraction and hydrogen bonding. You will examine the factors that influence the strength of these intermolecular forces, and how this impacts physical properties such as the melting and boiling points of substances.

Finally, you will look at the structure of diamond and graphite and relate this to their properties.

Key knowledge

- the use of Lewis (electron dot) structures, structural formulas and molecular formulas to model the following molecules: hydrogen, oxygen, chlorine, nitrogen, hydrogen chloride, carbon dioxide, water, ammonia, methane, ethane and ethene **3.1**
- shapes of molecules (linear, bent, pyramidal, and tetrahedral, excluding bond angles) as determined by the repulsion of electron pairs according to valence shell electron pair repulsion (VSEPR) theory **3.2**
- polar and non-polar character with reference to the shape of the molecule **3.3**
- the relative strengths of intramolecular bonding (covalent bonding) and intermolecular forces (dispersion forces, dipole-dipole attraction and hydrogen bonding) **3.4**
- physical properties of molecular substances (including melting points and boiling points and non-conduction of electricity) with reference to their structure **3.4**
- the structure and bonding of diamond and graphite that explain their properties (including heat conductivity and electrical conductivity and hardness) and their suitability for diverse applications. **3.5**

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3.1 Covalent bonding model

In this section, you will look at the chemical bonding that occurs when atoms of non-metals combine with each other. By examining a series of simple molecules, you will be introduced to the concept of a covalent bond, which is formed when non-metallic atoms share electrons. Using your knowledge of the valence shell electron arrangements of non-metallic atoms, you will be able to predict the molecules that different elements can form.

COVALENT BONDS

Many atoms become more stable if they obtain an outer shell of eight electrons by combining with other atoms (the **octet rule**).

Commonly, when atoms of non-metals combine, electrons are shared so that each atom has eight electrons in its outer shell. **Molecules** formed in this way are more stable than the separate atoms. A molecule is a discrete (individually separate) group of atoms of known formula, bonded together. Molecular substances are neutral overall. As they contain no free moving charged particles, they are unable to conduct electricity.

Non-metallic atoms have a relatively high number of electrons in their outer shells and they tend to share rather than to transfer electrons. Covalent bonding occurs when electrons are shared between atoms. The **covalent bonds** formed between atoms within a molecule are generally called **intramolecular bonds** (bonds within a molecule).

Single covalent bonds

When atoms share two electrons, one from each atom, the covalent bond formed is called a **single covalent bond**. Two examples of substances that contain single bonds are hydrogen and chlorine.

Example 1: Hydrogen

Hydrogen atoms have one electron. The outer shell for a hydrogen atom can hold a maximum of two electrons. A hydrogen atom can bond to another hydrogen atom to form a molecule of H_2 , as shown in Figure 3.1.1.

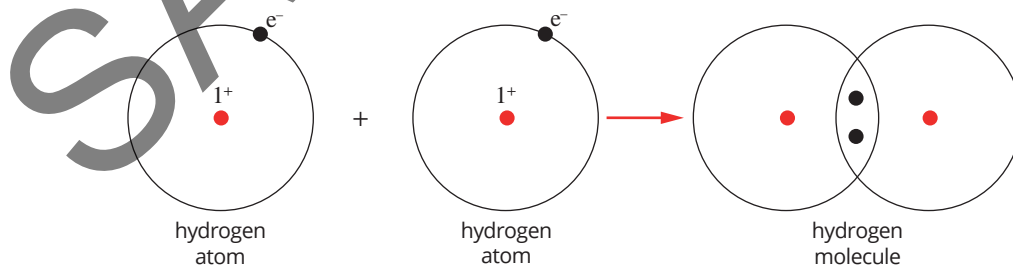


FIGURE 3.1.1 A covalent bond is formed when two hydrogen atoms share two electrons, one from each atom.

i The molecular formula indicates the number and type of atoms found in a molecule. For example, H_2O indicates there are two hydrogen and one oxygen atoms in a molecule of water.

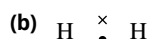
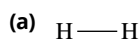


FIGURE 3.1.2 The single covalent bond in a hydrogen molecule can be represented by (a) a straight line or (b) a dot and cross.

In the molecule that is formed:

- two hydrogen atoms each share one electron to form a single covalent bond
- the atoms of hydrogen are now strongly bonded together by two electrons (an electron pair) in their outer shells.

The hydrogen molecule can be represented by the **molecular formula**, H_2 . Molecules like these that contain two atoms are called **diatomic molecules**.

Two alternative ways of representing a hydrogen molecule are shown in Figure 3.1.2.

In a hydrogen molecule, the electron of each atom is attracted to the proton within the neighbouring atom, as well as to their own proton. This means the two electrons will spend most of their time between the two nuclei instead of orbiting their own nuclei. Even though the protons in the two nuclei still repel each other

(remember, like charges repel), the electrostatic attraction to the electrons (which are closer) holds the molecule together.

Hydrogen is an example of a covalent molecular substance.

Example 2: Chlorine

A chlorine atom has an electronic configuration of 2,8,7. It requires one more electron to achieve eight electrons in its outer shell.

One chlorine atom can share an electron with another chlorine atom to form a molecule of chlorine with a single covalent bond. As a result, both atoms gain outer shells of eight electrons as shown in Figure 3.1.3. This is an example of the application of the octet rule.

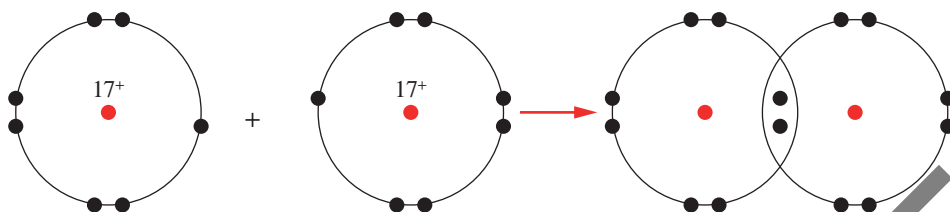


FIGURE 3.1.3 Two chlorine atoms share one electron each to form a chlorine molecule. Note that only outer-shell electrons are shown in these diagrams.

Lewis structures

Chemists often use **Lewis structures** (also known as electron dot structures) to represent molecules.

Lewis structures show the valence shell electrons of an atom, as only these electrons are involved in bonding.

Lewis structures also allow you to distinguish between bonding electrons and non-bonding electrons. A chlorine molecule has one pair of bonding electrons. The outer-shell electrons that are not involved in bonding are called the **non-bonding electrons**. Each chlorine atom has six non-bonding electrons, grouped into three pairs. Pairs of non-bonding electrons are also known as lone pairs.

Figure 3.1.4 shows examples of the Lewis structure for a molecule of chlorine. Electrons can be represented by dots, crosses, lines or a combination of all three.

Double covalent bonds

In a **double covalent bond**, two pairs of electrons are shared between the atoms.

The oxygen molecule contains a double covalent bond. The electronic configuration of an oxygen atom is 2,6. Each oxygen atom requires two electrons to gain a stable outer shell containing eight electrons. Therefore, when one oxygen atom bonds to another, each atom shares two of its electrons.

As you can see in Figure 3.1.5, each oxygen atom in the molecule now has eight valence electrons. Four of these are bonding electrons and four are non-bonding electrons.

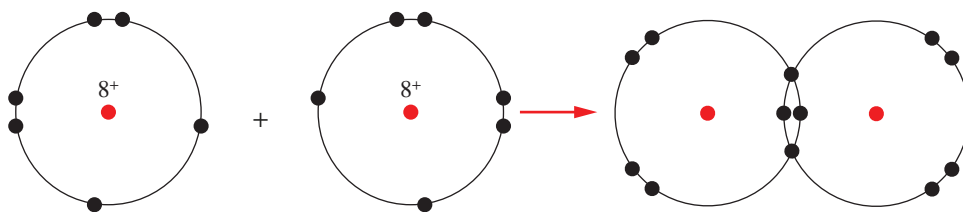


FIGURE 3.1.5 In oxygen molecules, each oxygen atom contributes two electrons to the bond between the atoms.

In Figure 3.1.6, you can see the Lewis structure of an oxygen molecule.

CHEMFILE

Hydrogen airships

Hydrogen has a low density. This was once thought to make it suitable for use in airships. Zeppelins were a type of rigid airship that was used as a mode of transport during the early 1900s. However, their popularity as a way of travel decreased after the hydrogen gas in the zeppelin Hindenburg (see figure below) caught fire in 1937, killing many on board.



The German passenger zeppelin Hindenburg exploded during its attempt to dock at the Lakehurst Naval Air Station in the United States.

i In Lewis structures, electrons can be represented by dots, crosses, lines or a combination of all three.

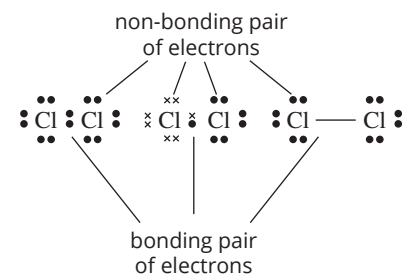


FIGURE 3.1.4 Three examples of Lewis structures for a chlorine molecule showing the bonding and non-bonding pairs of electrons

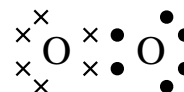


FIGURE 3.1.6 The Lewis structure shows that O_2 has a double covalent bond. Four electrons are shared and each oxygen has two non-bonding electron pairs.

CHEMFILE

The strong triple covalent bond in N_2

The triple covalent bond in nitrogen gas (N_2) is relatively strong and not easily broken. This means that nitrogen gas is relatively unreactive. Nitrogen is an essential element in living organisms because it is a major component of proteins and other biological molecules. Even though 78% of air is nitrogen gas, very few organisms can make use of the nitrogen because it is so unreactive. Nitrogen-fixing microorganisms are able to convert nitrogen gas into soluble nitrogen-containing compounds. These compounds are then absorbed by plants, allowing nitrogen to then be passed up the food chain.

In the early twentieth century, German chemist Fritz Haber invented a process for converting nitrogen gas and hydrogen gas into ammonia, which is used to make synthetic fertilisers (see figure). This allowed humans to grow more food to feed a growing world population.



Urea is used in synthetic fertilisers, which have allowed humans to grow more food to feed a growing world population.

Triple covalent bonds

A **triple covalent bond** occurs when three electron pairs are shared between two atoms. The nitrogen molecule contains a triple covalent bond. The electronic configuration of nitrogen is 2,5. A nitrogen atom requires three electrons to achieve eight electrons in its outer shell. When it bonds to another nitrogen atom, each atom contributes three electrons to the bond that forms, as shown in Figure 3.1.7. The Lewis structure of the nitrogen molecule is shown in Figure 3.1.8.

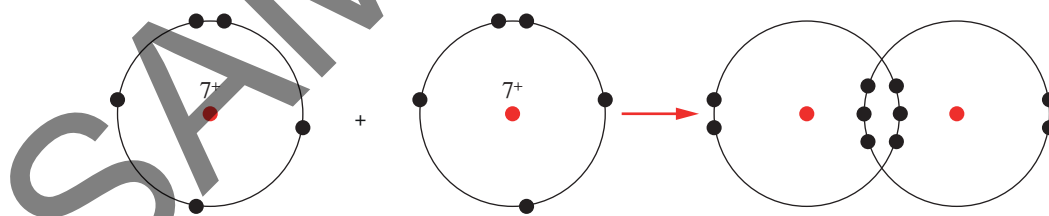


FIGURE 3.1.7 Each nitrogen atom contributes three electrons to form a triple covalent bond in a molecule of N_2 .



FIGURE 3.1.8 A Lewis structure for N_2

MOLECULAR COMPOUNDS

A diatomic molecule contains two atoms. The molecules discussed so far have been diatomic molecules that contain atoms of the same element.

Covalent bonds can also form between atoms of different elements. Hydrogen chloride (HCl) is a simple example (Figure 3.1.9). A hydrogen atom requires one electron to gain a stable outer shell, as does a chlorine atom. They can share an electron each and form a single covalent bond.

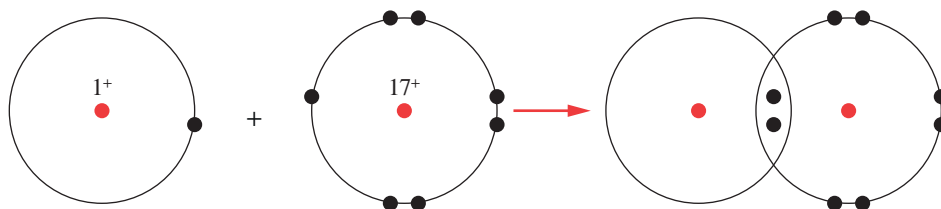


FIGURE 3.1.9 A pair of electrons is shared in the formation of a molecule of HCl.

POLYATOMIC MOLECULES

Molecules made up of more than two atoms are called **polyatomic molecules**. Three examples of polyatomic molecules are water, methane and ethene.

Example 1: Water

When a compound forms between hydrogen and oxygen, an oxygen atom bonds with two hydrogen atoms. The oxygen atom shares one electron with each hydrogen atom. Each hydrogen atom shares one electron with the oxygen atom.

As you can see in the Lewis structure (Figure 3.1.10), a water molecule contains:

- two single covalent bonds, each containing a shared electron pair
- two non-bonding pairs of electrons on the oxygen atom.



FIGURE 3.1.10 A water molecule has two single covalent bonds and two non-bonding pairs of electrons.

Example 2: Methane

When a compound forms between carbon and hydrogen, four hydrogen atoms are needed to provide the four electrons required to have eight electrons in the outer shell of a carbon atom (Figure 3.1.11). The molecule is called methane and has a molecular formula of CH_4 .

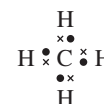


FIGURE 3.1.11 In a methane molecule, a carbon atom shares one electron with each of four hydrogen atoms to gain eight electrons in its outer shell.

Example 3: Ethene

Ethene (C_2H_4) is another example of a compound containing carbon and hydrogen. Each carbon atom shares two electrons with the other carbon atom, forming a double covalent bond. Two hydrogen atoms each share one electron with each carbon atom, forming two single covalent bonds. Figure 3.1.12 shows the Lewis structure of ethene.

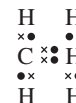


FIGURE 3.1.12 The Lewis structure of ethene contains a double covalent bond.

Worked example 3.1.1

LEWIS STRUCTURES

Draw the Lewis structure of hydrogen sulfide (H_2S).	
Thinking	Working
Write the shell electronic configuration of the atoms in the molecule.	S electronic configuration: 2,8,6 H electronic configuration: 1
Determine how many electrons each atom requires for a stable outer shell.	S requires 2 electrons H requires 1 electron
Draw a Lewis structure of the likely molecule, ensuring that each atom has a stable outer shell. Electrons not involved in bonding will be in non-bonding pairs.	Draw a Lewis structure of the molecule.

Worked example: Try yourself 3.1.1

LEWIS STRUCTURES

Draw the Lewis structure of ammonia (NH_3).



CASE STUDY

Historical development of bonding in molecules

Before the twentieth century, chemists had a limited understanding of the bonds formed between atoms in molecules. A very early theory was that some atoms had 'hooks' and others had 'eyes' and a bond formed when one atom hooked onto another (Figure 3.1.13).



FIGURE 3.1.13 Hydrogen atoms with 'hooks' looped in the 'eyes' of the oxygen atom

By the nineteenth century, chemists understood that atoms of elements combined together in set proportions. For example, two hydrogen atoms combined with one oxygen atom to form a water molecule. In the mid-nineteenth century, German chemist Friedrich August Kekulé and Scottish chemist Archibald Couper proposed that carbon formed four bonds. Kekulé is known for first proposing the structure for benzene (C_6H_6) (Figure 3.1.14). However, these chemists were far from understanding how atoms bonded together.

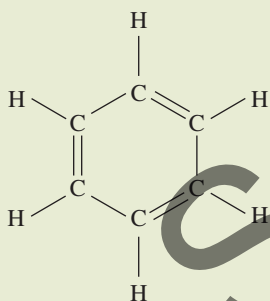


FIGURE 3.1.14 Kekulé structure for benzene

In the early twentieth century, the Bohr model of the atom was developed (see Chapter 2) that proposed that electrons were found in 'shells' around the nucleus of an atom. Gilbert Newton Lewis was an American chemist who in his lectures to his university students used dots to represent the electrons in atoms. He is the one who proposed the octet rule. Atoms were pictured as having electrons located in the corners of a cube. Cubes could combine in a way to satisfy the octet rule. For example, a single bond was formed when two atoms shared two electrons along an edge (Figure 3.1.15a) or a double bond was formed when atoms shared four electrons on a face (Figure 3.1.15b). These ideas were shared in a 1916 article called 'The atom and the molecule' which also contained the first examples of Lewis structures.

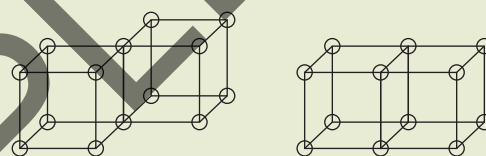


FIGURE 3.1.15 Reproductions of Lewis's cubic atoms from the 1916 article 'The atom and the molecule'. (a) A single bond formed from two atoms sharing an edge. (b) A double bond formed from two atoms sharing a face.

3.1 Review



SUMMARY

- Covalent bonds form between non-metallic atoms, often enabling the atoms to obtain outer shells containing eight electrons (except hydrogen, which obtains an outer shell containing two electrons).
- A covalent bond involves the sharing of electrons.
- A single covalent bond forms when two atoms share a pair of electrons.
- A double covalent bond forms when two atoms share two pairs of electrons.
- A triple covalent bond forms when two atoms share three pairs of electrons.
- Valence electrons that are not involved in bonding are called non-bonding pairs.
- Lewis structures show the valence electron arrangements of atoms in a molecule.

KEY QUESTIONS

Knowledge and understanding

- 1 Define the term 'molecule'.
- 2 How many covalent bonds are formed between atoms in these diatomic molecules?
 - a H_2
 - b N_2
 - c O_2
 - d F_2
- 3 What is the maximum number of covalent bonds formed by an atom of each of the following elements?
 - a H
 - b S
 - c P
 - d Si
 - e Br
 - f Ar
- 5 When oxygen forms covalent molecular compounds with other non-metals, the Lewis structures that represent the molecules of these compounds all show each oxygen atom with two non-bonding pairs of electrons. Why are there always two non-bonding pairs?
- 6 Suggest the most likely molecular formula of the compound formed between the following pairs of elements.
 - a C, F
 - b P, Cl
 - c C, S
 - d Si, H
 - e N, Br

Analysis

- 4 Draw Lewis structures for each of the following molecules.
 - a fluorine (F_2)
 - b hydrogen fluoride (HF)
 - c water (H_2O)
 - d tetrachloromethane (CCl_4)
 - e phosphine (PH_3)
 - f carbon dioxide (CO_2).

3.2 Shapes of molecules



FIGURE 3.2.1 Water (H_2O) molecules have a distinctive shape that is responsible for many of its properties. The valence shell electron pair repulsion theory accurately predicts the shape of water molecules.

i An electron group can either be covalent bonds or a non-bonding electron pair.

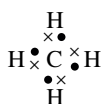


FIGURE 3.2.2 This Lewis structure of a methane (CH_4) molecule shows the four electron pairs surrounding the central carbon.

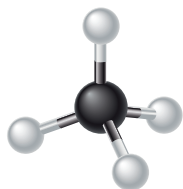


FIGURE 3.2.3 In a methane (CH_4) molecule, the four electron groups repel each other. The repulsion forces the single covalent bonds as far apart as possible, leading to a tetrahedral molecular shape.

The shapes of molecules are critical in determining many physical properties of covalent molecular substances. In particular, molecular shape affects melting point, boiling point, hardness and solubility. This is because the shape of a molecule determines how it interacts with other molecules.

The shape of small molecules can be predicted using a relatively simple model known as the **valence shell electron pair repulsion (VSEPR) theory**. In this section, you will see how VSEPR theory can be used to predict the shape of molecules such as the water molecule shown in Figure 3.2.1.

VALENCE SHELL ELECTRON PAIR REPULSION THEORY

Lewis structures represent the arrangement of valence electrons in the atoms of a molecule. As the name suggests, the VSEPR theory uses the arrangement of the valence electrons as shown in Lewis structures to predict the shape of the molecule. These valence electrons can be arranged into **electron groups**—either as different types of covalent bonds or as non-bonding pairs. The VSEPR theory is based on the principle that negatively charged electron groups around an atom repel each other. As a consequence, these electron groups are arranged as far away from each other as possible.

ELECTRON GROUP REPULSION

From the previous section, you learnt that atoms in covalent molecules are most stable when they have eight electrons in their valence shell. This is known as the octet rule. These eight electrons are arranged into four pairs of electrons.

Using the Lewis structure of methane (CH_4) as an example (Figure 3.2.2), you can see the carbon atom shares a pair of electrons with each hydrogen atom.

Each single covalent bond is an example of an electron group. The VSEPR theory states that the electron groups in methane repel each other so that they are as far apart as possible. This repulsion between the electron groups results in a **tetrahedral** shape as shown in Figure 3.2.3.

Non-bonding pairs of electrons

In the VSEPR theory, non-bonding pairs of electrons are considered another type of electron group.

In the ammonia molecule shown in Figure 3.2.4, the nitrogen atom has a stable octet made up of one non-bonding pair of electrons and three single bonds. The four electron groups repel each other to form a tetrahedral arrangement. However, the shape of the molecule is only determined by the position of the single bonds (and hence the position of the atoms). The non-bonding pair of electrons influences the shape but is not a part of it. The three hydrogen atoms are described as forming a **pyramidal** shape with the nitrogen atom.

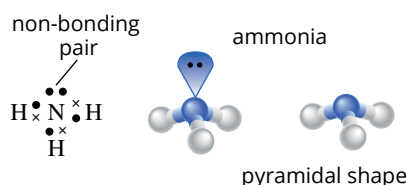


FIGURE 3.2.4 The Lewis structure of an ammonia (NH_3) molecule shows that the nitrogen atom has one non-bonding pair of electrons and three single bonds. These four electron groups repel each other to form a tetrahedral arrangement around the nitrogen atom. The result is a pyramidal shaped molecule.

In water molecules, the oxygen atom has a stable octet made up of two non-bonding pairs and two single bonds. The four electron groups repel each other to form a tetrahedral arrangement. This causes the two hydrogen atoms to form a bent arrangement with the oxygen atom, as shown in Figure 3.2.5.

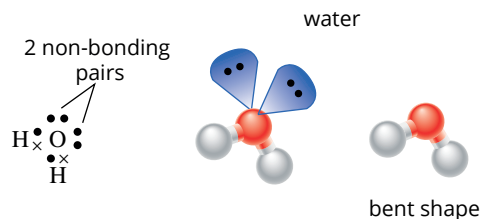


FIGURE 3.2.5 The Lewis structure of a water (H_2O) molecule shows that the oxygen atom has two non-bonding pairs of electrons and two single bonds. These four electron groups repel each other to form a tetrahedral arrangement around the oxygen atom. The result is a bent shaped molecule.

In a hydrogen fluoride molecule, the fluorine atom has a stable octet made up of three non-bonding pairs and one single bond. The four electron groups repel each other to form a tetrahedral arrangement. The hydrogen and fluorine atoms form a linear molecule, as you can see in Figure 3.2.6.

i Non-bonding pairs of electrons influence a molecule's shape but are not considered a part of the shape.

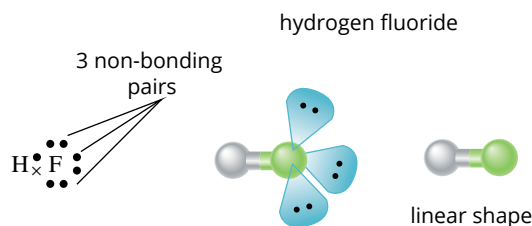


FIGURE 3.2.6 The Lewis structure of a hydrogen fluoride (HF) molecule shows that the fluorine atom has three non-bonding pairs of electrons and one single bond. These four electron groups repel each other to form a tetrahedral arrangement around the fluorine atom. The result is a linear molecule.

Worked example 3.2.1

PREDICTING THE SHAPE OF MOLECULES

Predict the shape of a molecule of phosphine (PH_3).	
Thinking	Working
Draw the Lewis structure for the molecule.	$\begin{array}{c} \cdot\cdot \\ \text{H} \times \text{P} \times \text{H} \\ \cdot\cdot \\ \times \\ \text{H} \end{array}$
Count the number of electron groups around the central atom.	There are four electron groups (three single bonds and one non-bonding pair).
Determine how the electron groups will be arranged to get maximum separation.	Because there are four electron groups, they will be arranged in a tetrahedral arrangement.
Deduce the shape of the molecule by considering the arrangement of just the atoms.	The phosphorus and hydrogen atoms are arranged in a pyramidal shape.

Worked example: Try yourself 3.2.1

PREDICTING THE SHAPE OF MOLECULES

Predict the shape of a molecule of hydrogen sulfide (H_2S).

Molecules with fewer than four electron groups

Molecules where the central atom forms double or triple covalent bonds tend to have fewer than four electron groups. VSEPR theory treats double and triple bonds in the same way that it treats single bonds and non-bonding pairs of electrons as single electron groups.

i When using VSEPR theory to determine the shape of molecules, double and triple bonds each count as one electron group.

For example, if a central atom has two single bonds and one double bond, then the three electron groups will repel each other to get maximum separation. This results in a molecular shape known as **trigonal planar** because the atoms form a triangle in one plane. An example of this structure is the methanal (CH_2O) molecule shown in Figure 3.2.7.

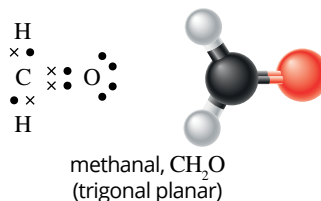


FIGURE 3.2.7 Methanal has a central carbon atom that forms a double bond with an oxygen atom and single bonds with two hydrogen atoms. The three electron groups repel each other to form a trigonal planar arrangement.

If the central atom has two double bonds, then the two electron groups repel each other. This results in a linear molecule like carbon dioxide (CO_2), shown in Figure 3.2.8.

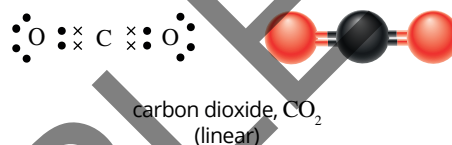


FIGURE 3.2.8 In a carbon dioxide molecule, the carbon atom forms double bonds with two oxygen atoms. The two electron groups repel each other. This results in a linear molecule.

Finally, if the central atom has a single bond and a triple bond, as in hydrogen cyanide (HCN), then the molecule also has two electron groups, and is linear (Figure 3.2.9).

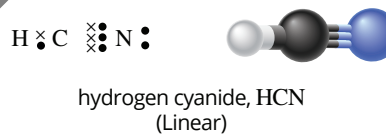
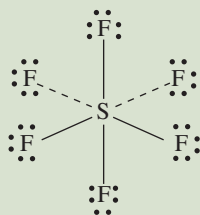


FIGURE 3.2.9 The hydrogen cyanide molecule is linear. In this case, the central carbon atom forms a triple bond with the nitrogen atom and a single bond with the hydrogen atom.

CHEMFILE

The molecular shape of sulfur hexafluoride

Sulfur hexafluoride (SF_6) is made up of a central atom of sulfur with six valence electrons. The sulfur atom forms single bonds to six fluorine atoms. These six electron groups repel each other to form an octahedral shape (see figure below). Sulfur hexafluoride is a gas at room temperature and is denser than air. It is mainly used as an insulating gas in high voltage equipment. As a greenhouse gas, it is 23 900 times worse than carbon dioxide so its use is highly regulated.



Bond angles in SF_6

STRUCTURAL FORMULAS

In the previous section, you were introduced to Lewis structures as a way of representing how valence shell electrons of atoms in a molecule are arranged. A limitation of a Lewis structure is that it is not always drawn in a way that shows the shape of the molecule. After using VSEPR to determine a molecule's shape, it can be represented using a **structural formula**. In a structural formula, each bonding pair of electrons is shown as a line. Non-bonding electrons are not shown. For example, Figure 3.2.10a shows the Lewis structure of nitrogen trifluoride (NF_3) and Figure 3.2.10b is its structural formula, showing its pyramidal shape. You will see more examples of how structural formulas are used to represent carbon based molecular compounds in Chapter XX.

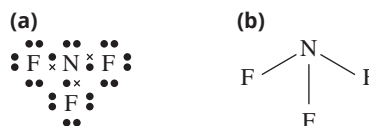


FIGURE 3.2.10 (a) Lewis structure and (b) structural formula of nitrogen trifluoride (NF_3)

PA2
TPO

3.2 Review



SUMMARY

- The shapes of simple molecules can be predicted by the valence shell electron pair repulsion (VSEPR) theory.
- The VSEPR theory is based on the principle that electron groups around an atom repel each other. As a consequence, these electron groups are arranged as far away from each other as possible.
- Electron groups can be covalent bonds or non-bonding pairs of electrons.
- Non-bonding pairs influence a molecule's shape but are not considered a part of the shape.
- Structural formulas are used to represent the shape and bonds within molecules.

TABLE 3.2.1 Summary of shapes of molecules

Number of electron groups	No non-bonding pairs	1 non-bonding pair	2 non-bonding pairs	3 non-bonding pairs
4	<p>tetrahedral</p>	<p>pyramidal</p>	<p>bent</p>	<p>linear</p>
3	<p>trigonal planar</p>	<p>angular or bent</p>	<p>linear</p>	
2	<p>linear</p>	<p>linear</p>		

KEY QUESTIONS

Knowledge and understanding

- Explain VSEPR theory and how it is used to determine the shape of molecules.
- How many electron groups are around the fluorine atom in a hydrogen fluoride molecule?

Analysis

- Draw the Lewis structure for each of the following molecules.
 - H_2S
 - HI
 - CCl_4
 - PH_3
 - CS_2
 - SiH_4

- Identify the shape of each of the molecules in Question 3.
- Draw the structural formula of each of the molecules in Question 3.

3.3 Polarity in molecules



FIGURE 3.3.1 A stream of water bending near a statically charged balloon

The covalent molecules examined so far in this chapter are neutral. They do not have an overall charge because the number of protons equals the number of electrons in the molecules. However, a substance such as water can behave as though it is charged. When a statically charged balloon is held near a stream of water, it bends towards the balloon (Figure 3.3.1). This behaviour is due to the uneven distribution of electrons within the water molecules causing them to be partially charged. The following section examines how the shape of a molecule and the electronegativity of its atoms can cause these uneven electron distributions.

ELECTRONEGATIVITY AND POLAR BONDS

Electronegativity is the key factor that determines the electron distribution in diatomic molecules. Electronegativity is the ability of an atom to attract electrons towards itself when forming a chemical bond. Electronegativity increases from left to right across the periods of the periodic table and decreases down the groups of the table, as shown in Figure 3.3.2. (Note that the electronegativity scale is a relative scale, so there are no units.) You will remember seeing these patterns in Chapter 2.

Period	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1													2.2 H					He
2	1.0 Li	1.6 Be											2.0 B	2.6 C	3.0 N	3.4 O	4.0 F	Ne
3	0.9 Na	1.3 Mg											1.6 Al	1.9 Si	2.2 P	2.6 S	3.2 Cl	Ar
4	0.8 K	1.0 Ca	1.4 Sc	1.5 Ti	1.6 V	1.7 Cr	1.6 Mn	1.8 Fe	1.9 Co	1.9 Ni	1.9 Cu	1.7 Zn	1.8 Ga	2.0 Ge	2.0 As	2.55 Se	3.0 Br	Kr
5	0.8 Rb	1.0 Sr	1.2 Y	1.3 Zr	1.6 Nb	2.2 Mo	2.0 Tc	2.2 Ru	2.3 Rh	2.2 Pd	2.0 Ag	1.7 Cd	1.8 In	2.0 Sn	2.0 Sb	2.1 Te	2.7 I	Xe
6	0.8 Cs	0.9 Ba																

FIGURE 3.3.2 Table of electronegativity values. This periodic table shows the electronegativities of the atoms of each element. The electronegativities generally increase from left to right across the periods and decrease down the groups.

Non-polar bonds

When two atoms form a covalent bond, you can regard the atoms as competing for the electrons being shared between them. If the two atoms in a covalent bond are the same (i.e. have identical electronegativities), then the electrons are shared equally between the two atoms. This is the case for diatomic molecules such as chlorine (Cl_2), oxygen (O_2), hydrogen (H_2), and nitrogen (N_2).

Bonds with an equal distribution of bonding electrons are said to be **non-polar** because there is no charge on either end of the bond.

Electron density is the measure of the probability of an electron being present at a particular location within an atom. In molecules, areas of electron density are commonly found around the atom and its bonds.

Figure 3.3.3 shows the electron distribution in the non-polar fluorine (F_2) molecule. The molecule has a high electron density between the two fluorine atoms, forming the covalent bond. The bonding electrons are distributed evenly between the two atoms, making the bond and the molecule non-polar.

Polar bonds

If the covalent bond is between atoms of two different elements, then the electrons will stay closer to the most electronegative atom as it has a stronger pull on the electrons in the bond. An example is the hydrogen fluoride (HF) molecule, shown in Figure 3.3.4. Bonds with an imbalanced electron distribution are said to be **polar**.

A fluorine atom is more electronegative than a hydrogen atom. Therefore, in a hydrogen fluoride molecule the electrons tend to stay closer to the fluorine atom. The fluorine atom is described as having a partial negative charge, which is represented with the Greek letter delta (lowercase) as δ^- . The hydrogen atom is described as having a partial positive charge, δ^+ . The separation into positive and negative charges is known as a **dipole** as they have two oppositely charged poles at each end of the molecule.

Hydrogen fluoride has a permanent dipole due to the different electronegativities of the two atoms. All diatomic (two-atom) molecules that are made up of different elements are polar to some extent. The level of **polarity** will depend on the difference between the electronegativities of the two atoms. The greater the difference between the electronegativities, the greater the polarity of the molecule.

It is not just the covalent bonds in diatomic molecules that can be polar. The polarity of any covalent bond can be compared by examining the difference in the electronegativities of the atoms involved in the bond.

Worked example 3.3.1

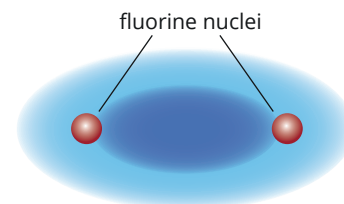
COMPARING THE POLARITY OF COVALENT BONDS

Compare the polarity of the bond in hydrogen fluoride (HF) and carbon monoxide (CO).	
Thinking	Working
Use the table of electronegativity values in Figure 3.3.2 to find the electronegativities of the atoms in each bond.	HF: hydrogen 2.2; fluorine 4.0 CO: carbon 2.6; oxygen 3.4
For each bond, subtract the lowest electronegativity value from the highest value.	HF: $4.0 - 2.2 = 1.8$ CO: $3.4 - 2.6 = 0.8$
Determine which bond has the biggest difference in electronegativity to determine the more polar bond.	The bond in HF is more polar than in CO.

Worked example: Try yourself 3.3.1

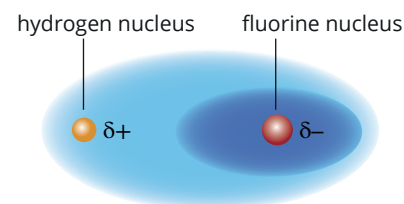
COMPARING THE POLARITY OF COVALENT BONDS

Compare the polarity of the bond in nitrogen monoxide (NO) and hydrogen chloride (HCl).



F_2 contains a non-polar bond.

FIGURE 3.3.3 Fluorine molecules have a symmetric distribution of electrons and are therefore non-polar.



HF contains a polar bond; fluorine is more electronegative than hydrogen.

FIGURE 3.3.4 The electron distribution in hydrogen fluoride is asymmetric because of the different electronegativities of the hydrogen and fluorine atoms. Hydrogen fluoride is an example of a polar molecule.

The range of bond types

The type and polarity of a chemical bond can be predicted by considering the electronegativity difference between the atoms involved in bond formation. There is a range (continuum) of bond types, ranging from non-polar covalent to polar covalent to ionic (a bond formed when an electron is transferred from one atom to another). The type of bond depends upon the extent to which electrons are shared. This, in turn, depends upon the electronegativity difference between the atoms involved in the bond.

When the electronegativity difference between two atoms is zero, the bonding electrons are shared equally, and the bond formed between the two atoms is covalent and non-polar. For example, in a fluorine (F_2) molecule both atoms have the same electronegativity and as a result, the covalent bond between the two fluorine atoms is non-polar. If two different elements have the same electronegativity, the covalent bond between them will also be non-polar. For example, the electronegativity of both carbon and sulfur is 2.6. The covalent bonds between atoms of carbon and sulfur in carbon disulfide (CS_2) are non-polar.

As you have learnt in this section, any difference in electronegativity between two bonded atoms will result in an unequal sharing of electrons and the bond will be polar. For example, in a hydrogen fluoride (HF) molecule, fluorine is more electronegative than hydrogen. As a result, HF has a dipole, and the bond in HF is described as polar covalent.

The polar nature of a bond between two atoms increases as the electronegativity difference between these atoms increases. The bonding in HF is more polar than in HCl because the fluorine atom is more electronegative than the chlorine atom. Electrons will be transferred between two atoms if the electronegativity difference between them is great enough. As you will discover in Chapter 7, electron transfer between metallic and non-metallic atoms results in the formation of ionic bonds. A fluorine atom is much more electronegative than a sodium atom. When fluorine and sodium react, the sodium atom's valence electron is transferred to the outer shell of the fluorine atom. This results in the formation of Na^+ and F^- ions. The bonding between the ions is described as ionic. The range of bond types is illustrated in Figure 3.3.5.

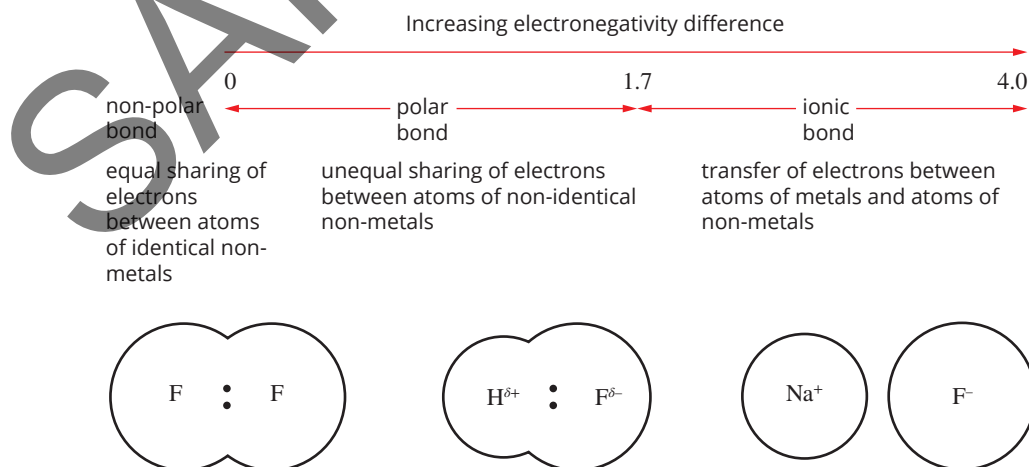


FIGURE 3.3.5 The range of bond types. There is a transition of bond type from non-polar, through to polar then ionic as the difference in electronegativity increases.

An electronegativity difference of 1.7 is often used as the approximate cut-off point between polar covalent bonding and ionic bonding (Table 3.3.1). In fact, there is no sharp distinction between polar covalent and ionic bonding at this level of electronegativity difference. Compounds such as aluminium chloride (AlCl_3) that have an electronegativity difference between their atoms of around 1.7 should be considered as having both polar covalent and ionic bonding characteristics.

TABLE 3.3.1 Electronegativity difference and bond type

Electronegativity difference	Distribution of bonding electrons	Type of bond	Example
zero	electrons shared equally	non-polar covalent	H_2 , Cl_2 , CS_2
less than 1.7	electrons attracted to the more electronegative atom	polar covalent	NH_3 , H_2O , HCl
greater than 1.7	electrons transferred to the more electronegative atom	ionic	NaCl , CaF_2

POLARITY OF POLYATOMIC MOLECULES

Determining the polarity of molecules with more than two atoms is a little more complicated. This is because the polarity of polyatomic molecules depends on the shape of the molecule as well as the polarity of its covalent bonds. A molecule can possess polar bonds yet still be non-polar.

- Molecules that contain only non-polar bonds are non-polar molecules.
- **Symmetrical molecules** (molecules that contain polar bonds that are evenly distributed) are non-polar, as the bond dipoles cancel each other out.
- **Asymmetrical molecules** that contain polar bonds are polar molecules, as a net dipole is created in the molecule.

Non-polar molecules

Even molecules with polar covalent bonds can be non-polar if the arrangement of these bonds within the molecule is symmetrical.

In methane, the carbon atom is slightly more electronegative than the hydrogen atoms. Therefore, the carbon atom has a partial negative charge, leaving hydrogen with a partial positive charge (Figure 3.3.6a). However, the methane molecule has a tetrahedral shape and is therefore symmetrical. The symmetry of the molecule means that the individual dipoles of the covalent bonds (represented by arrows) cancel each other perfectly (Figure 3.3.6b). The result is a molecule with no overall dipole. It is non-polar.

The methane molecule shown in Figure 3.3.6 is an example of a non-polar molecule with polar covalent bonds.

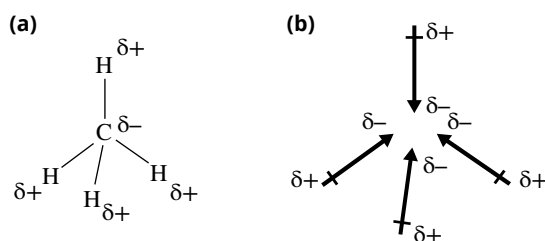
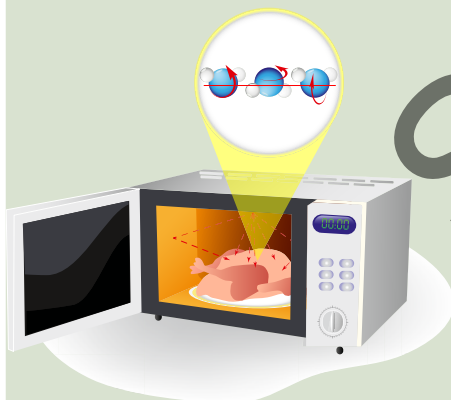


FIGURE 3.3.6 (a) Structure of a methane molecule showing the partial charges on the atoms. (b) The individual bond dipoles are distributed symmetrically around the molecule.

CHEMFILE

How a microwave oven works

Microwave ovens use the polarity of molecules (especially water molecules) to heat food. The microwave oven irradiates the food with microwaves. The microwaves produce an electric field that interacts with polar molecules. The electric field causes the molecules to rotate up and down billions of times per second. This gives the molecules extra kinetic energy. As the kinetic energy of the molecules increases, the temperature increases. Therefore, the molecules heat and cook the food.



Food heats up in a microwave because polar molecules, such as water molecules, rotate billions of times per second in response to microwave radiation.

PA2
TPO

Polar molecules

In asymmetrical molecules, the individual dipoles of the covalent bonds do not cancel each other. This results in a net dipole, making the overall molecule polar.

The chloromethane molecule shown in Figure 3.3.7 is an example of an asymmetric molecule. The chlorine atom is more electronegative than the carbon atom. Therefore, the chlorine atom attracts electrons from the carbon atom while the carbon atom attracts electrons from the hydrogen atoms (Figure 3.3.7a). The individual dipoles of the covalent bonds are shown in Figure 3.3.7b. These add to give the molecule a net dipole (Figure 3.3.7c).

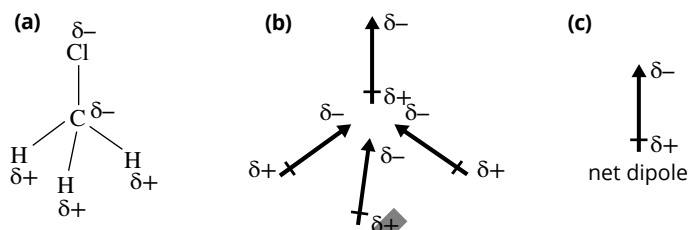


FIGURE 3.3.7 (a) Structure of a chloromethane molecule showing the partial charges on the atoms. (b) The individual dipoles are added together. (c) The result is a net dipole.

Table 3.3.2 shows some more examples of how symmetry determines the polarity of covalent molecules.

TABLE 3.3.2 Examples of polar and non-polar covalent molecules

Molecule	Structure	Symmetrical/asymmetrical	Polar/non-polar
methanal		asymmetrical	polar
carbon dioxide		symmetrical	non-polar
tetrafluoromethane		symmetrical	non-polar
water		asymmetrical	polar
ammonia		asymmetrical	polar

3.3 Review



SUMMARY

- As the difference in electronegativities of two atoms increases, a covalent bond increases in polarity.
- Diatomic molecules containing the same type of atom are non-polar.
- In general, symmetrical molecules are non-polar and asymmetrical molecules with polar bonds are polar.
- The polarity of polyatomic molecules depends on the electronegativity of the atoms in the molecule and the asymmetry of the molecule.

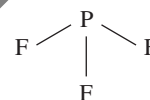
KEY QUESTIONS

Knowledge and understanding

- 1 Define each of the following.
 - a non-polar bond
 - b polar bond
- 2 Covalent bonds can form between the following pairs of elements in a variety of compounds. Use the electronegativity values given in Figure 3.3.2 to identify the atom in each pair that would have the largest share of bonding electrons.
 - a S and O
 - b C and H
 - c C and N
 - d N and H
 - e F and O
 - f P and F
- 3 The greater the differences in electronegativity between two atoms, the more polar the bond formed between them.
 - a Which of the examples in Question 2 would be the most polar bond?
 - b Which of the examples in Question 2 would be the least polar bond?

Analysis

- 4 Use the electronegativity values in Figure 3.3.2 to order the following diatomic molecules from least to most polar: HCl, N₂, HBr, NO.
- 5 Label the following structural formula a phosphorus trifluoride molecule to show the partial charges that would occur on each atom.



- 6 Determine whether each of the following molecules is polar or non-polar.
 - a CF₄
 - b CHF₃
 - c CH₂F₂
 - d CH₃F
 - e CH₄
- 7 For each of the following pairs of molecules:
 - i draw the structure of each molecule
 - ii determine which is a polar molecule
 - iii on the polar molecule, indicate the polarities of the bonds and the direction of the net dipole.
 - a CHF₃ or CF₄
 - b CO₂ or SO₂
 - c NH₃ or CH₄

3.4 Intermolecular forces

i Covalent bonds between atoms within a molecule (intramolecular bonds) are much stronger than the intermolecular forces between molecules.

When liquid water is heated (Figure 3.4.1), the water molecules gain kinetic energy. Some molecules gain enough energy to break free from the others and escape from the surface of the liquid. The water vapour formed still contains molecules of water, so the covalent bonds between atoms (the intramolecular bonds) have not been broken. Instead, it is the **intermolecular forces** between water molecules that have been disrupted. This indicates that the covalent bonds between atoms are much stronger than the intermolecular forces between molecules.

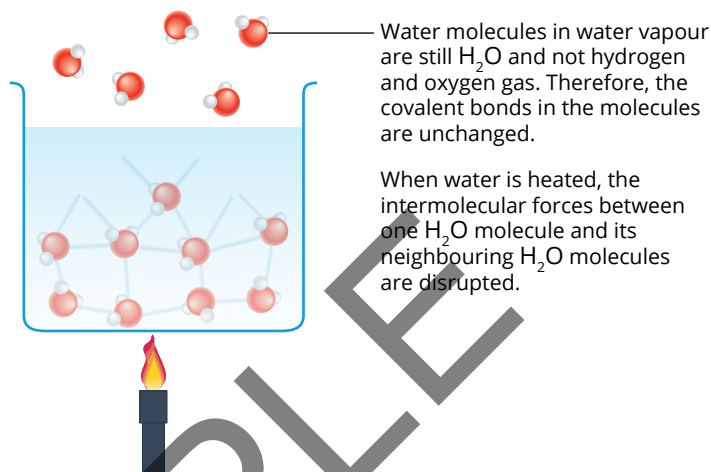


FIGURE 3.4.1 Changes occur to the forces between water molecules when it starts to boil.

Many factors determine the strength of intermolecular forces, including the size, shape and polarity of molecules. These factors not only determine the strength of the intermolecular forces in a substance, they also determine the types of intermolecular forces.

There are three main types of intermolecular forces:

- dispersion forces
- dipole–dipole attraction
- hydrogen bonding.

In this section, you will examine the nature of these three types of intermolecular forces and their role in determining the physical properties of covalent molecular substances.

DISPERSION FORCES

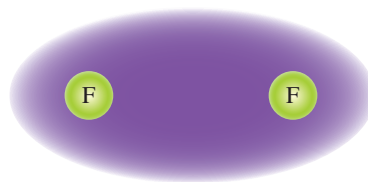
Dispersion forces are forces that exist between all molecules, whether they are polar or non-polar. Dispersion forces are caused by **temporary dipoles** in the molecules that are the result of random movement of the electrons surrounding the molecule. These temporary dipoles are also known as **instantaneous dipoles**.

Dispersion forces are always present between molecules, as electrons are constantly in motion within atoms (Figure 3.4.2). As they are caused by temporary dipoles, dispersion forces are the weakest of the three types of intermolecular forces.

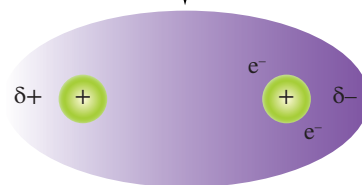
Strength of dispersion forces

The strength of dispersion forces increases as the relative molecular mass of the molecule increases. Larger molecules have more electrons. It is easier to produce temporary dipoles in molecules with large numbers of electrons. Since larger molecules have stronger dispersion forces, they have higher melting and boiling points.

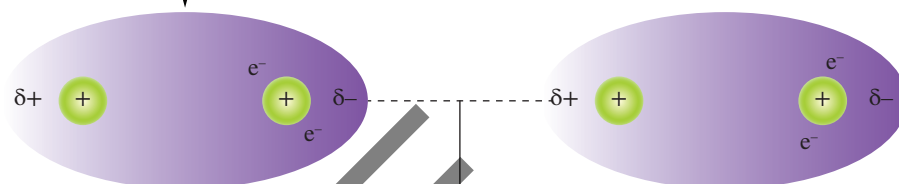
In a molecule, the electrons are constantly moving. In the case of a non-polar molecule, such as fluorine, the electrons spend an equal amount of time around each atom.



Occasionally, the electrons gather more closely together at one end of the molecule, causing one end of the molecule to become negative and the other end to become positive. This is known as a temporary dipole.



These temporary dipoles can then induce (create) dipoles in the neighbouring molecules.



The neighbouring molecules then induce dipoles in their neighbours and so on. The temporary dipoles attract each other to create the intermolecular forces known as dispersion forces.

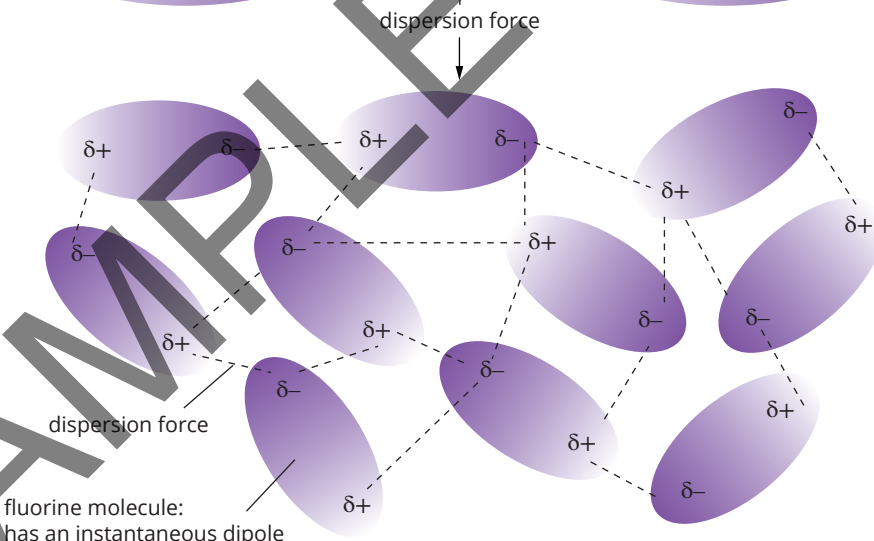


FIGURE 3.4.2 How dispersion forces form within non-polar substances. These diagrams show the forces forming between fluorine molecules.

Table 3.4.1 shows the boiling points of the halogens (group 17), which all form non-polar, diatomic molecules. The only forces between their molecules are dispersion forces. You can see that as molecular mass increases and the dispersion forces become stronger, the boiling points of the substances increase.

TABLE 3.4.1 The effect of dispersion forces on the boiling points of the halogens

Molecule	Molecular mass	Number of electrons	Boiling point (°C)
fluorine (F ₂)	38.0	18	-188
chlorine (Cl ₂)	71.0	34	-35
bromine (Br ₂)	159.8	70	59
iodine (I ₂)	253.8	106	184

The shape of a molecule also influences the strength of the dispersion forces. Molecules that form long chains will tend to have stronger dispersion forces than more compact molecules with similar molecular masses.

CHEMFILE

Use of beeswax by Indigenous Australians

Indigenous Australians have traditionally used the properties of beeswax to make useful objects. One example is when beeswax is used to seal woven bags. These conical bags are used for gathering food and in men's ceremonies. Conical bags coated in beeswax are suited to collecting liquids, such as native honey.



Beeswax is used to seal this conical bag.

Beeswax is a soft substance, and it melts at about 65°C. It is made up of a mixture of long-chain molecules containing many carbon and hydrogen atoms. The typical formula of a molecule of beeswax is $C_{46}H_{92}O_2$. Beeswax will soften when warmed in your hand, making it easy to mould into a desired shape. Dispersion forces are the main type of bonding between wax molecules. As the wax is warmed, the dispersion forces are weakened, enabling the long-chain molecules to slide past one another. As the wax cools, new dispersion forces are formed between adjacent molecules, locking the piece of wax into a new shape.

For example, butane and 2-methylpropane (Figure 3.4.3) both contain four carbon atoms and 10 hydrogen atoms. The boiling point of butane is -0.5°C , while the boiling point of 2-methylpropane is -11°C . The higher boiling point of butane is because of the different shapes of the two molecules; butane is a long molecule while 2-methylpropane is branched. Being longer and un-branched means butane has more contact area to interact with its neighbouring molecules to form stronger dispersion forces.

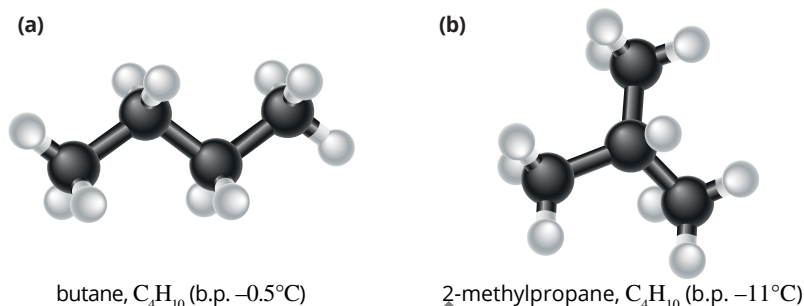


FIGURE 3.4.3 Butane and 2-methylpropane have different boiling points because their molecules are different shapes.

DIPOLE-DIPOLE ATTRACTION

In addition to dispersion forces, **dipole-dipole attraction** occurs between polar molecules. These forces result from the attraction between the positive and negative ends of the polar molecules, as shown in Figure 3.4.4. As dipole-dipole attraction is due to **permanent dipoles** within molecules, dipole-dipole attraction is stronger than the dispersion forces found between molecules.

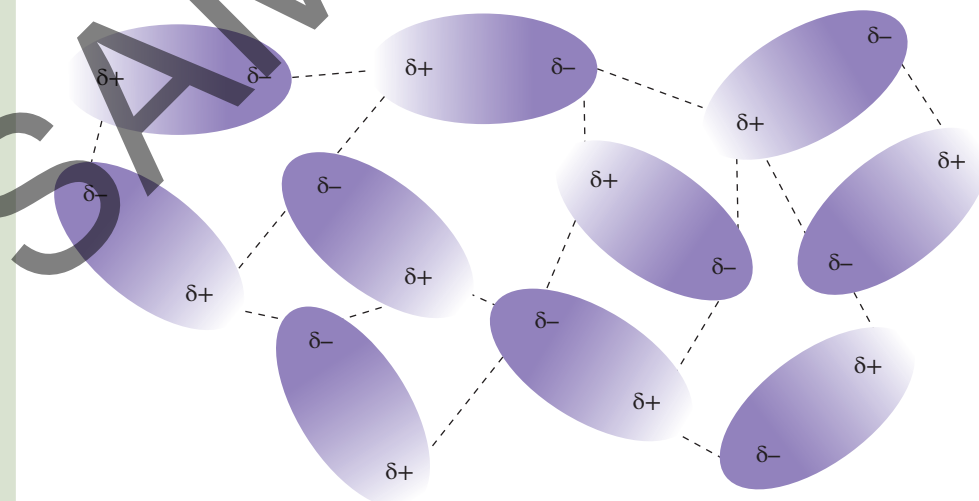


FIGURE 3.4.4 The positive and negative ends of polar molecules attract each other.

The more polar a molecule is, the stronger the dipole-dipole attraction. The molecular dipole will be stronger when there is a large difference in the electronegativities of the atoms and a large asymmetry in the shape of the molecule. Molecules that are more polar have stronger dipole-dipole attraction between them.

The melting and boiling points of a substance are directly related to the strength of the dipole–dipole attraction between molecules. The stronger the dipole–dipole attraction, the higher the melting and boiling points. This is because it takes more energy (i.e. higher temperatures) to break the stronger dipole–dipole attraction when the substance changes from a solid to a liquid or a liquid to a gas.

For example, compare methanal (CH_2O) and ethane (CH_3CH_3), shown in Figure 3.4.5. Methanal molecules are asymmetrical and polar. This results in dipole–dipole attraction between molecules and methanal has a relatively high boiling point of -19°C . On the other hand, ethane molecules are symmetrical and non-polar. There are only weaker dispersion forces between molecules so ethane has a much lower boiling point of -88.5°C .

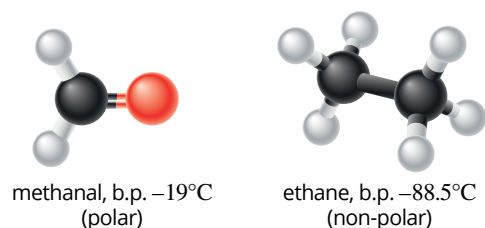


FIGURE 3.4.5 Dipole–dipole attraction exists between molecules of methanal, giving it a much higher boiling point than ethane.

HYDROGEN BONDING

Hydrogen bonding is a particularly strong form of dipole–dipole attraction. Hydrogen bonding only occurs between highly polar molecules in which one of the molecules has a hydrogen atom covalently bonded to a nitrogen, oxygen or fluorine atom.

Nitrogen, oxygen and fluorine atoms are small and highly electronegative. When bonded with a hydrogen atom, they strongly attract the electron pair in the covalent bond and a large dipole forms. Remember that hydrogen atoms only have one electron and it is pulled towards the highly electronegative atom in the bond. The hydrogen nucleus (a proton) is therefore left exposed and is attracted to a non-bonding pair of electrons on the nitrogen, oxygen or fluorine atom of a neighbouring molecule. The small size of the hydrogen atom allows the neighbouring molecule to closely approach and the resulting attractive force is relatively strong.

This intermolecular force is known as a **hydrogen bond**. It is approximately ten times stronger than a dipole–dipole attraction but about one-tenth the strength of an ionic or a covalent bond. Figure 3.4.6 shows examples of hydrogen bonding among molecules where at least one of the molecules contains a hydrogen atom covalently bonded to either an N, O or F atom.

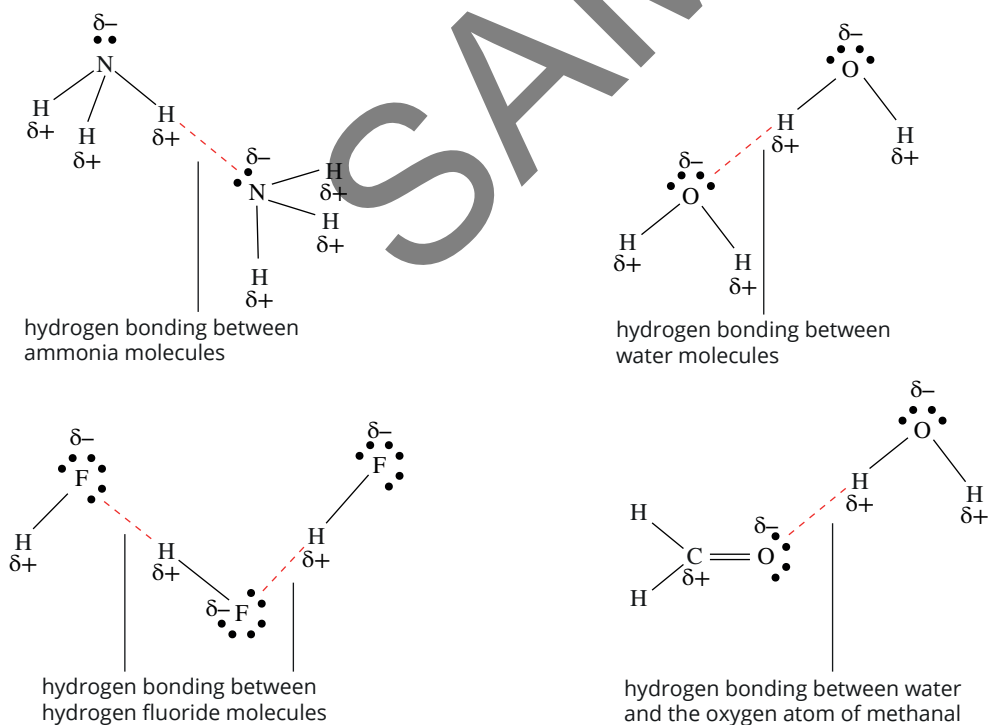


FIGURE 3.4.6 Examples of polar hydrogen bonding between molecules

The presence of hydrogen bonds results in higher melting and boiling points. Figure 3.4.7 demonstrates the effect of hydrogen bonding on boiling point by comparing methanol to ethane and methanal. Recall that ethane only has weak dispersion forces between non-polar molecules. Methanal contains polar molecules that attract each other through dipole–dipole attraction but not hydrogen bonds. Methanol, however, contains molecules where a hydrogen atom is attached to an oxygen atom. This part of the methanol molecule is highly polar and can form a hydrogen bond with neighbouring methanol molecules. As a result, the boiling point of methanol (64.7°C) is significantly higher than the boiling points of methanal (–19°C) and ethane (–88.5°C).

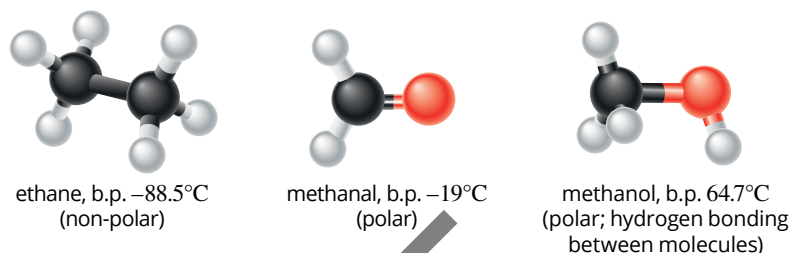


FIGURE 3.4.7 Hydrogen bonding exists between molecules of methanol, giving it a much higher boiling point than methanal and ethane.

- i** For hydrogen bonding to occur, the molecules must have:
- 1 a hydrogen atom covalently bonded to a nitrogen, oxygen or fluorine atom
 - 2 a non-bonding pair of electrons on the nitrogen, oxygen or fluorine atoms on neighbouring molecules.

There are two key requirements for hydrogen bonding:

- 1 a hydrogen atom covalently bonded to a nitrogen, oxygen or fluorine atom
- 2 a non-bonding pair of electrons on the nitrogen, oxygen or fluorine atoms of neighbouring molecules.

You may wonder why other highly electronegative atoms do not form hydrogen bonds. For example, chlorine atoms have a high electronegativity but they are not involved in hydrogen bonding. This is because they are larger atoms and the electron density is more spread out and less concentrated. This results in weaker dipole–dipole attraction with the hydrogen atoms on neighbouring molecules.

MOLECULAR SIZE AND INTERMOLECULAR FORCES

It is important to remember that dispersion forces occur between all molecules; those that are polar as well as those that are non-polar. In substances with large molecular masses, the dispersion forces between molecules can even be stronger than dipole–dipole attraction and hydrogen bonding.

Table 3.4.2 shows the boiling points of four hydrogen halides: hydrogen fluoride (HF), hydrogen chloride (HCl), hydrogen bromide (HBr) and hydrogen iodide (HI). Of the last three hydrogen halides shown, hydrogen chloride is the most polar of these molecules and therefore has the strongest dipole–dipole attraction. However, hydrogen iodide has the highest boiling point. This is because it has the largest molecular mass and can form stronger dispersion forces, which outweigh the effects of the dipole–dipole attraction seen in hydrogen chloride.

The boiling point of hydrogen fluoride is 19.5°C, which is much higher than any of these other compounds. This is because the hydrogen bonding between hydrogen fluoride molecules is much stronger than both the dispersion forces and the dipole–dipole attraction between the other molecules listed in Table 3.4.2.

TABLE 3.4.2 Comparison of the boiling points of the first four hydrogen halides

Hydrogen halide	Molecular mass	Number of electrons	Boiling point (°C)
hydrogen fluoride (HF)	20.0	10	19.5
hydrogen chloride (HCl)	36.5	18	–85.1
hydrogen bromide (HBr)	80.9	36	–66.8
hydrogen iodide (HI)	127.9	54	–35.4

3.4 Review



SUMMARY

- Covalent bonds (intramolecular bonds) are much stronger than intermolecular forces.
- The melting and boiling points of covalent molecular substances increase as the strength of the intermolecular forces increase.
- There are three main types of intermolecular forces: dispersion forces, dipole–dipole attraction and hydrogen bonding.
- Dispersion forces exist between all molecules and are the result of attraction between temporary dipoles that form in molecules.
- Dispersion forces are stronger between larger molecules because it is easier to create temporary dipoles in molecules with a larger number of electrons.
- Dispersion forces are stronger between linear molecules than between highly branched molecules.
- Dipole–dipole attraction is only present between polar molecules and are the result of the attraction between the partial positive and negative ends of the molecules.
- The greater the polarity of a molecule, the stronger the dipole–dipole attraction.
- Hydrogen bonds are the strongest of the three main types of intermolecular forces.
- Hydrogen bonding occurs between highly polar molecules in which one of the molecules has a hydrogen atom covalently bonded to a nitrogen, oxygen or fluorine atom. The other molecule has a non-bonding pair of electrons on a nitrogen, oxygen or fluorine atom.

KEY QUESTIONS

Knowledge and understanding

- 1 Identify the types of intermolecular forces that exist between:
 - a polar molecules
 - b non-polar molecules
- 2 Identify which of the following substances would contain dipole–dipole forces between their molecules: fluorine (F_2), hydrogen iodide (HI), methane (CH_4), tetrafluoromethane (CF_4), fluoromethane (CH_3F).
- 5 Consider the following substances. Identify the strongest type of intermolecular force found between their molecules.
 - a PH_3
 - b $CHCl_3$
 - c CH_3Cl
 - d F_2O
 - e CO_2
 - f HBr
 - g H_2S
 - h HF
 - i CH_3OH
 - j H_2

Analysis

- 3 In ice, each water molecule is surrounded, at equal distances, by four other water molecules. In each case, there is an attraction between the partial positive hydrogen atom on one water molecule and a non-bonding pair associated with the oxygen atom of another water molecule.
 - a Draw a diagram to show the arrangement of four water molecules around another water molecule.
 - b Identify the strongest type of intermolecular force present in ice.
- 6 For each of the following pairs of substances, predict which has the higher boiling point and explain in terms of the intermolecular forces found in each substance.
 - a CHF_3 or CF_4
 - b O_2 or CO_2
 - c NH_3 or CH_4
- 7 When sugar is gently heated, it turns into a clear liquid. If the liquid is heated strongly, it turns black and a gas is produced. Explain what is happening to the bonds in sugar when it is heated. Use the terms ‘intramolecular bonds’ and ‘intermolecular forces’ in your answer.

3.5 Covalent lattices

In the previous sections, you were introduced to covalent bonding in the context of substances made up of molecules. Alternatively, covalent bonding also occurs between non-metal atoms in a way that results in a continuous three-dimensional **covalent lattice** structure. This section will focus on two key examples of substances with a covalent lattice structure: diamond and graphite.

ALLOTROPES

Some elements can exist with their atoms in several different structural arrangements called **allotropes**. In different allotropes, the atoms are bonded to each other in different, specific ways. This gives them significantly different properties from other allotropes of the same element.

Oxygen forms allotropes. Oxygen gas consists of diatomic molecules with the formula O_2 . Each oxygen atom in this arrangement is bound to one other oxygen atom. Ozone is another molecule containing only oxygen. Ozone molecules have the formula O_3 and consist of a central oxygen atom bound to two other oxygen atoms. Figure 3.5.1 shows the structure of these two molecules. As both contain only oxygen atoms, they are allotropes of oxygen. Diamond and graphite, the focus of this section, are both different allotropes of carbon.

ALLOTROPES OF CARBON

Diamonds (Figure 3.5.2) might be a ‘girl’s best friend’ but it is unlikely that graphite (Figure 3.5.3) will ever be held in the same esteem. Both of these minerals are made of the same single element—carbon.

i Allotropes are different forms of the same element.

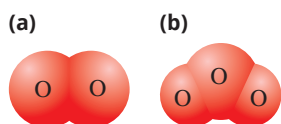


FIGURE 3.5.1 (a) O_2 oxygen molecule (b) O_3 ozone molecule



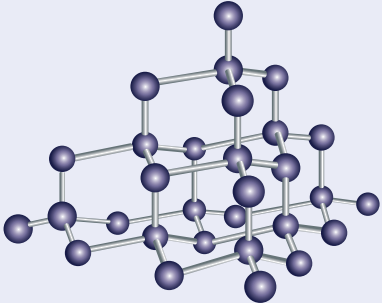
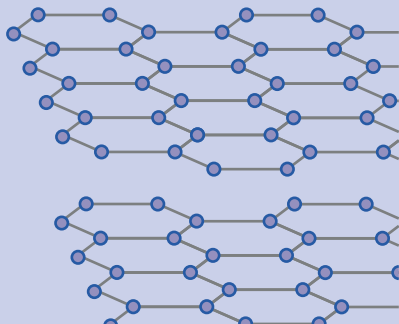
FIGURE 3.5.2 Diamond is the hardest naturally occurring substance.



FIGURE 3.5.3 Natural graphite is soft and black.

Table 3.5.1 summarises some information about the structure, properties and uses of the three most common allotropes of carbon: diamond, graphite and amorphous carbon.

TABLE 3.5.1 Comparison of properties of some of the allotropes of carbon

Allotrope	Structure	Properties	Uses
diamond	 <p>Covalent network lattice, each carbon surrounded by four other carbon atoms in a tetrahedral arrangement</p>	<ul style="list-style-type: none"> • Very hard • Sublimes • Non-conductive • Brittle 	<ul style="list-style-type: none"> • Jewellery • Cutting tools • Drills
graphite	 <p>Covalent layer lattice, each carbon bonded to three other carbons, one delocalised electron per carbon atom</p>	<ul style="list-style-type: none"> • Conductive • Slippery • Soft • Greasy material 	<ul style="list-style-type: none"> • Lubricant • Pencils • Electrodes • Reinforcing fibres
amorphous carbon	Irregular structure of carbon atoms. Many varieties exist with many different, non-continuous packing arrangements	<ul style="list-style-type: none"> • Conductive • Non-crystalline • Cheap 	<ul style="list-style-type: none"> • Printing ink • Carbon black filler • Activated charcoal • Photocopying

Diamond

Diamond is the hardest naturally occurring substance known.

Diamond does not contain small, discrete (individual) molecules. Instead, the carbon atoms bond to each other to form a continuous three-dimensional structure called a **covalent network lattice**. There are no weak intermolecular forces present, only strong covalent bonds. This is what gives diamond its strength.

In general, substances that have a network lattice structure have very high melting points or decomposition temperatures. They are also very hard because the atoms are held firmly in fixed positions in the lattice.

As you saw in previously in Section 3.2, when an atom has four electron pairs in its outer shell, the electron pairs position themselves as far away from each other as possible in a tetrahedral shape. In the covalent network lattice for diamond shown in Figure 3.5.4, you can also see that individual atoms within diamond form single covalent bonds to four other carbon atoms in a tetrahedral arrangement.

The properties of diamond are directly related to its structure.

- Single covalent bonds between carbon atoms are strong bonds. The entire structure of a diamond consists of a continuous network of these bonds, making diamond very hard and rigid.

i Diamond is made up of carbon atoms that bond with four neighbouring carbon atoms forming a covalent network lattice. This structure makes diamond extremely hard.

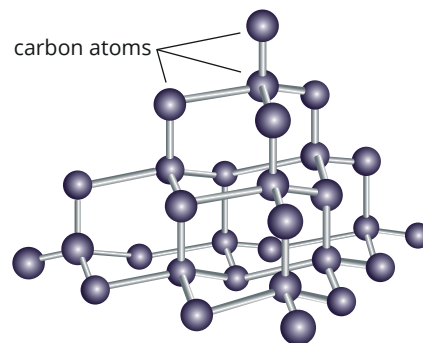


FIGURE 3.5.4 The structure of diamond showing each carbon atom with four single covalent bonds to neighbouring atoms



FIGURE 3.5.5 Diamond-tipped drills used to drill through rock in the oil mining industry

- Since there are only strong covalent bonds between carbon atoms, this makes diamond's **sublimation** point (the process by which a substance goes directly from the solid phase to the gaseous phase, without passing through a liquid phase) very high (around 3500°C).
- The rigidity means that diamonds are brittle and break rather than bend.
- Diamond does not conduct electricity because it does not contain any charged particles that are free to move.
- Because the atoms in diamonds are held together very strongly, the heat conductivity is extremely high. It is five times greater than that of copper, leading to some specialty electronic uses where diamond is used to transfer heat away from important electrical components.

The crystalline appearance of diamonds and their high refractive index make them sparkle and has made them extremely popular as jewellery, but the hardness of diamond also lends itself to industrial uses. Many industrial cutting and drilling tools for working with tough materials are diamond tipped. The drill tips in Figure 3.5.5 are used to drill through rock in the oil mining industry. They contain small pieces of diamond that improve the hardness and durability of the tool.

CHEMFILE

Impact diamonds

'We are speaking about trillions of carats,' trumpeted the 2012 headline from the British Daily Mail. It was in reference to a 100 km wide meteorite crater, the Popigai Crater, in Russia that could supply world markets with diamonds for 3000 years. The now closed Mirny mine, shown in Figure 3.5.6, is also in Russia. This open-cut mine is over 500 metres deep and has yielded diamonds worth more than \$20 billion since 1951.

It is thought that the impact of a large meteorite created enough heat and pressure in the Popigai Crater to make diamonds. Russian scientists are reported to have known of this deposit since 1971, but kept details hidden until supplies from other sources began to run out. Diamonds formed from a meteorite strike, like those in Figure 3.5.7, are referred to as 'impact diamonds'.



FIGURE 3.5.6 The Mirny diamond mine is over 500 metres deep.



FIGURE 3.5.7 High-quality 'impact diamonds' can be almost the size of a 20-cent coin.

Mined versus synthetic diamonds

You might have seen or heard advertisements trying to convince you of the idea that mined diamonds, which might be referred to as ‘real’ or ‘natural’ diamonds are much better than synthetic diamonds which are grown under specific laboratory conditions.

Mined diamonds are produced naturally in a process that takes billions of years. Around 120–150 km deep underground, under high temperature (around 1100°C) and pressure conditions, carbon is crystallised to form diamonds. Then, through volcanic activity, the diamonds are brought closer to the Earth’s surface. The diamonds are extracted in large open cut mines such as the Argyle mine in Western Australia (which closed in November 2020) (Figure 3.5.8).



FIGURE 3.5.8 An aerial photo of the Argyle diamond mine in Western Australia

Synthetic diamonds are grown in laboratories under controlled conditions that match the high temperature and pressure conditions found deep underground. This allows the diamonds to be grown in weeks instead of the billions of years for mined diamonds. Synthetic diamonds are chemically identical to mined diamonds – they are both made of carbon and have the same

covalent network lattice structure. As the conditions for growing synthetic diamonds is highly controlled, they are very pure which gives them excellent clarity (one of the key indicators of a diamond’s value). There are also very few flaws (as these are due to the inclusion of atoms of other elements in the lattice structure). One key difference between the two types of diamond is price. Synthetic diamonds are about a quarter the price of mined diamonds.

Due to the almost identical chemical composition and crystal structure of mined and synthetic diamonds, experts cannot tell the two apart by just looking at them (Figure 3.5.9). More complex analytical techniques are needed to differentiate the two types of diamonds.



FIGURE 3.5.9 Mined and synthetic diamonds look identical.

Analysis

- 1 Outline the similarities and differences in the chemical structure and composition of mined and synthetic diamonds.
- 2 Using online resources, outline some of the environmental and social issues linked to the production of mined diamonds.
- 3 Evaluate the statement ‘natural diamonds are real and synthetic diamonds are fake’.

i In graphite, each carbon atom is covalently bonded to three other carbon atoms. The layered network structure contains delocalised electrons. Bonds within the layers are strong but bonds between layers are weak dispersion forces.

CHEMFILE

Black-lead pencils

In 1564, a very pure deposit of graphite was discovered in England. The graphite was so stable that it could be cut into thin, square sticks that could be used for writing. String was wrapped around the graphite to make the first pencils. Later the string was replaced with wood.

The pencils were so effective that during the Napoleonic Wars, the English were considered to have a technological advantage, because their pencil-written communications were far more effective than the French equivalents. Napoleon commissioned a French inventor, Nicholas-Jacques Conte, to develop an alternative to pure graphite. The mixtures of clay and powdered graphite that he designed are the basis for the 'lead' in modern pencils.



An early pencil that consisted of a strip of graphite placed between pieces of wood

Graphite

Graphite is a very different form of carbon. As you can see in Figure 3.5.10, the carbon atoms in graphite are in layers. There are strong covalent bonds between the carbon atoms in each layer. However, there are weak dispersion forces between the layers. As a consequence, it is hard in one direction but quite slippery and soft in another direction. The structure of graphite is referred to as a **covalent layer lattice**.

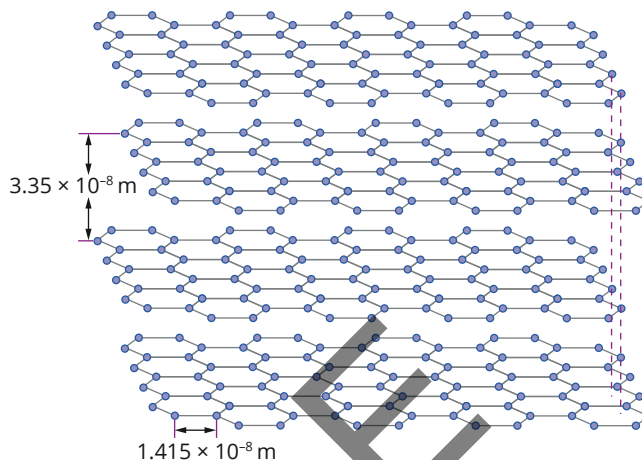


FIGURE 3.5.10 Graphite has a covalent layer lattice structure. The carbon atoms within each layer are covalently bonded to each other. Weak dispersion forces exist between the layers.

The covalent layer lattice structure of graphite also explains some of its other properties.

- The strong covalent bonds between the atoms in each layer explain graphite's resistance to heat. Graphite sublimates at a temperature of about 3600°C .
- Each carbon atom is bonded to three other carbon atoms. The fourth valence electron from each atom is able to move within the layer. The electrical conductivity of graphite is due to these delocalised electrons.

The conductivity of graphite makes it suitable for applications such as battery electrodes where conductivity is required but a metal is not suitable.

Graphite can also be used as a lubricant. The weak dispersion forces between layers allow these layers to slide over each other and to reduce the friction between moving parts, such as in locks or machinery.

Graphite is also used as an additive to improve the properties of rubber products and it can be woven into a fibre. This helps to reinforce plastics. Figure 3.5.11 shows spun graphite fibre, which can be used to make strong composite materials such as those used in tennis racquets, fishing rods and racing car shells.

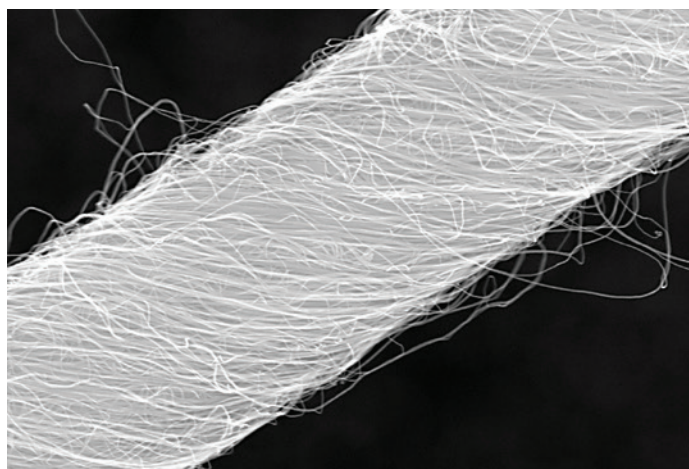


FIGURE 3.5.11 Graphite fibre can be used to reinforce plastics.

Amorphous forms of carbon

Charcoal (Figure 3.5.12) and carbon black (Figure 3.5.13) are examples of **amorphous** carbon that has no consistent structure. It contains irregularly packed, tiny crystals of graphite and other non-uniform arrangements. Lumps of charcoal are produced for use as a fuel, while carbon black is used to make printer toner ink.

Amorphous carbon can be formed from the **combustion** of wood and other plant matter when there is a limited supply of air. There are several other types of amorphous carbon, including soot, which can be seen in Figure 3.5.14 being emitted from an industrial chimney. The distinctions between the different forms of amorphous carbon are blurred.



FIGURE 3.5.14 Soot is emitted from an industrial chimney.

Each form of amorphous carbon has its uses and some have been used by society for centuries. Since the Middle Ages it has been common to produce charcoal in ovens. Figure 3.5.15 shows a number of beehive-shaped ovens that were used to produce charcoal from timber. These ovens were built between 1876 and 1879.



FIGURE 3.5.15 These ovens in Nevada, USA, were built between 1876 to 1879 to make charcoal.

Uses of carbon black

Carbon black is a refined type of amorphous carbon in which the particle size is more uniform. Most carbon black is used to reinforce rubber products such as tyres and hoses, causing their black appearance. The surface interaction between the fine carbon particles and the rubber molecules increases the strength and toughness of the product.

Many printer and photocopier toners contain carbon black particles mixed with a binder polymer and other additives. More than 9 million tonnes of carbon black is used annually worldwide.



FIGURE 3.5.12 Lumps of charcoal are produced for use as a fuel.

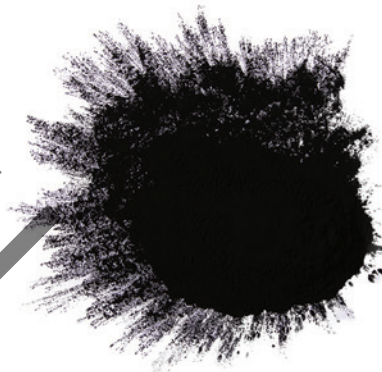


FIGURE 3.5.13 Carbon black is used in printer toner ink.

3.5 Review



SUMMARY

- Allotropes are different forms of the same element.
- Carbon can be found in the Earth's crust in the form of diamond, graphite or charcoal. The structures and properties of these allotropes are very different.
- In diamond, each carbon atom is covalently bonded to another four carbon atoms in a tetrahedral shape, forming a covalent network lattice structure. Diamond sublimes at a high temperature, is extremely hard, is a good conductor of heat and has a sparkling, crystalline appearance. Due to its properties, diamonds have diverse applications such as jewellery and industrial cutting and drilling tools.
- In graphite, each carbon atom is covalently bonded to three other carbon atoms. The layered network structure contains delocalised electrons. Bonds within the layers are strong but bonds between layers are weak dispersion forces. Graphite is slippery, conducts electricity and sublimes at a high temperature. Due to its properties, graphite has diverse applications such as an electrical conductor, a lubricant and as a component of strong composite materials.
- Amorphous carbon products, such as carbon black, soot and charcoal, are formed from the combustion of plant and animal matter in a limited supply of air. Amorphous carbon has no consistent structure.

KEY QUESTIONS

Knowledge and understanding

- 1 How many covalent bonds are formed by each carbon atom in diamond and graphite?
- 2 **a** What is meant by the word sublime?
b Explain why diamond and graphite only sublime at temperatures over 3500°C.
- 3 List three uses for amorphous carbon.

Analysis

- 4 Explain the following properties of diamond in terms of its bonding and structure.
 - a** Hardness or softness
 - b** Ability or inability to conduct electricity
 - c** Ability or inability to conduct heat
- 5 Explain the following properties of graphite in terms of its bonding and structure.
 - a** Hardness or softness
 - b** Ability or inability to conduct electricity

Chapter review



03

KEY TERMS

allotrope	graphite	single covalent bond
amorphous	hydrogen bond	structural formula
asymmetrical molecule	instantaneous dipole	symmetrical molecule
combustion	intermolecular force	temporary dipole
covalent bond	intramolecular bond	tetrahedral
covalent lattice	Lewis structure	trigonal planar
covalent layer lattice	molecular formula	triple covalent bond
covalent network lattice	molecule	valence shell electron
diamond	non-bonding electron	pair repulsion
diatomic molecule	non-polar	(VSEPR) theory
dipole	octet rule	
dipole-dipole attraction	permanent dipole	
dispersion forces	polar	
double covalent bond	polarity	
electron density	polyatomic molecule	
electron group	pyramidal	
electronegativity	sublimation	

REVIEW QUESTIONS

Knowledge and understanding

- Select the statement that best describes the way hydrogen atoms bond to each other.
 - One hydrogen atom donates an electron to another hydrogen atom to form a molecule.
 - Hydrogen atoms form a lattice with delocalised electrons.
 - Hydrogen atoms share electrons to obtain a complete outer shell of eight electrons.
 - Two hydrogen atoms share an electron each to form a hydrogen molecule.
- The formula of a molecule is XY_4 . Select the alternative that could match this formula.
 - OH_4
 - CH_4
 - HBr_4
 - CO_4
- Oxygen forms a compound with fluorine with the molecular formula OF_2 . Identify the correct shape of the molecule.
 - bent
 - linear
 - pyramidal
 - tetrahedral
- The following substances all contain carbon atoms. Which one will have the highest boiling point (or sublimation point)?
 - carbon dioxide
 - methane
 - graphite
 - methanol
- Solid ammonia (NH_3) has a melting point of $-73^\circ C$. Explain what happens to the bonds in ammonia when it melts. Use the terms 'intramolecular bonds' and 'intermolecular forces' in your answer.
- Explain why neon atoms do not form covalent bonds.
- All of the following molecules have four electron groups around the central atom. Classify the molecular shapes as bent, pyramidal or tetrahedral.
 -
 -
 -
 -
 -

CHAPTER REVIEW CONTINUED

- 8 Match the molecular formula to the correct molecular shape.

Molecular formula	Molecular shape
Nitrogen tribromide (NBr_3)	Tetrahedral
Water (H_2O)	Linear
Difluoromethane (CH_2F_2)	Bent
Hydrogen cyanide (HCN)	Pyramidal

- 9 Use the electronegativities from Figure 3.3.2 to order the following covalent bonds from least to most polar. Si–O, N–O, F–F, H–Br, O–Cl

- 10 Use the electronegativities from Figure 3.3.2 to determine which of the following molecules contains the most polar bond.

- CO_2
- H_2O
- H_2
- H_2S
- NH_3

- 11 Water is a polar molecule. Explain how this fact shows that water is not a linear molecule.

- 12 Hydrogen chloride (HCl) exists as a gas at room temperature. What can you conclude about the strength of the intermolecular forces in pure hydrogen chloride?

- 13 At room temperature, CCl_4 is a liquid whereas CH_4 is a gas.

- Which substance has the stronger intermolecular forces?
- Explain the difference in the strengths of the intermolecular forces.

- 14 Explain the difference between a permanent molecular dipole and a temporary molecular dipole. Your explanation should describe how the dipoles are formed and the type of intermolecular bonding that results.

- 15 ‘Carbon forms several allotropes.’ Explain the meaning of this statement.

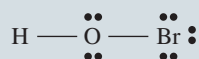
- 16 Why does diamond have such a high sublimation point?

- 17 Explain why graphite sublimes at a high temperature, conducts electricity and can be used as a lubricant.

- 18 Describe the geometry of the bonds around carbon atoms in diamond and graphite.

Application and analysis

- 19 Examine the following Lewis structure and use the VSEPR theory to predict the shape of the molecule.

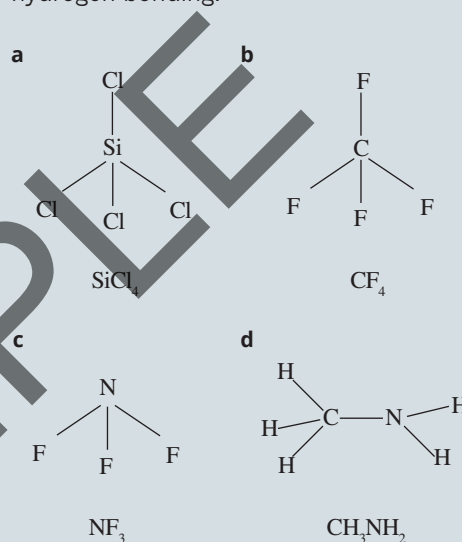


- 20 Are the following molecules polar or non-polar? Draw structural formulas to help you decide.

- CS_2
- Cl_2O
- SiH_4
- CH_3Cl
- CH_3CH_3
- CCl_4

- 21 For each of the following structures, state whether:

- the molecule is polar or non-polar
- the strongest intermolecular forces of attraction between molecules of each type would be dispersion forces, dipole–dipole attraction or hydrogen bonding.



- 22 Consider solid samples of the following compounds. In which cases are there only dispersion forces between molecules? (Hint: First draw the structural formula for each molecule, then determine whether each one is polar or non-polar.)

- Tetrachloromethane (CCl_4)
- Methanal (CH_2O)
- Carbon dioxide (CO_2)
- Hydrogen sulfide (H_2S)

- 23 Draw Lewis structures for each of the following molecules and identify the number of bonding and non-bonding electrons in each molecule.

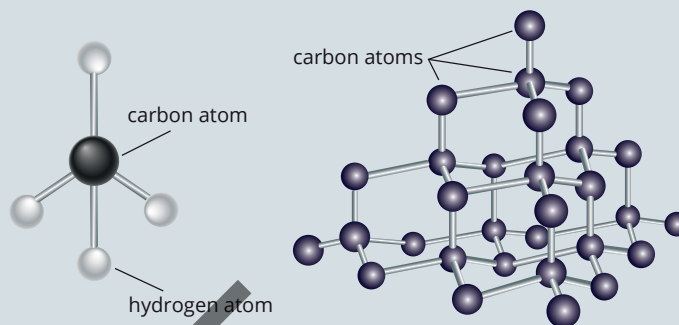
- HBr
- CCl_2F_2
- C_2H_6
- PF_3

- 24** Identify whether the following statements about carbon dioxide (CO_2) are true or false.
- Carbon dioxide is a molecular compound.
 - A molecule of carbon dioxide contains three atoms.
 - The bonds between the carbon and oxygen atoms in carbon dioxide are intramolecular bonds.
 - There are two single covalent bonds in a molecule of carbon dioxide.
 - There are four non-bonding pairs of electrons in a molecule of carbon dioxide.
- 25** Differentiate between the non-metallic elements argon (Ar) and chlorine (Cl) in terms of their electronic configurations and the types of bonds their atoms form with other atoms.
- 26** The melting points of four halogens are given in the table below. Describe and explain the trend in melting points of these elements.

Halogen	Melting point ($^{\circ}\text{C}$)
fluorine (F_2)	-220
chlorine (Cl_2)	-101
bromine (Br_2)	-7
iodine (I_2)	114

- 27** Consider the two compounds OF_2 and CF_4 . OF_2 has a boiling point of -145°C and CF_4 has a boiling point of -128°C . Between molecules of which compound would the intermolecular forces of attraction be greater? Explain your answer in terms of the polarity of each of the molecules and the relative strength of the intermolecular forces in each substance.
- 28** The mass of a hydrogen fluoride molecule is similar to the mass of a neon atom. However, the boiling points of these substances are very different. The boiling point of hydrogen fluoride is 19.5°C whereas that of neon is -246°C . Explain the difference in this property of the two substances.

- 29** The structures of methane and diamond are shown in the image below. Each carbon atom in methane (CH_4) has a tetrahedral arrangement of atoms around it. A carbon atom in diamond also has a tetrahedral arrangement. However, the two substances have very different properties.



- Describe all of the types of bonding that would be present in each substance.
 - Use the types of bonding present in each substance to explain the different properties you would expect each to have.
- 30** The table below lists some key properties of diamond and graphite.

Material	Hardness (Moh scale)	Electrical conductivity, S m^{-1}	Thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$
diamond	10	10^{-13}	2000
graphite	<1	3×10^5	200

- Explain the difference in hardness and electrical conductivity of diamond and graphite, referring to the structure and bonding of each substance.
- When discussing the conductivity of diamond and graphite, why it is important to be specific as to what type of conductivity you are referring to?
- One method used by jewellers to test the quality of diamonds is to heat them to 1000°C and time the rate of cooling. How will a high-quality diamond compare to a low quality one in this test?

