

3 Chemical Bonding and Structure

SINGAPORE JUNIOR CHEMISTRY OLYMPIAD

Salt shatters, copper bends, water boils at 100 °C and diamond barely melts at all. Each property comes from the particles in a substance and the forces that hold them together. This chapter explains those forces, the shapes of molecules, and how structure decides properties.

Learning objectives

By the end of this chapter, you can:

Foundation O LEVEL

- use the Periodic Table to find valence electrons, and predict how an atom reaches an octet
- describe ionic, covalent and metallic bonding
- explain the charges on ions, and write the formulae of ionic compounds
- explain what makes one ionic or metallic bond stronger than another
- draw dot-and-cross diagrams for ionic and covalent substances
- relate the properties of giant ionic, giant covalent, metallic and simple molecular substances, and of alloys, to their structure

→

Core A LEVEL

- describe σ and π bonds and dative bonds
- predict shapes and bond angles with VSEPR theory
- deduce bond polarity and molecular polarity from electronegativity and shape
- compare bond strength using bond energy and bond length
- explain intermolecular forces and hydrogen bonding, and rank boiling points

Prerequisites

Chapter 1 (particles, elements, compounds, solutions, melting and boiling) and Chapter 2 (protons, electrons and ions, electron shells and orbitals, valence electrons, the Periodic Table, and the mole as a counting unit). Fill in the blanks as the lesson goes.

3.1 The Periodic Table and the octet

The Periodic Table (Chapter 2) lists the elements in order of proton number. Its rows are **periods** and its columns are **groups**. An element's position gives its electron arrangement without working it out (Figure 3.1):

- The **period** number is the number of occupied electron shells.
- For Groups 1 and 2, the **group** number is the number of valence electrons. For Groups 13 to 18, take away 10: Group 13 has 3 valence electrons and Group 17 has 7. Group 18 has a full outer shell of 8, and helium

has 2.

Chlorine is in Period 3 and Group 17, so it has three shells with 7 electrons in the outer one: 2.8.7. Magnesium is in Period 3 and Group 2: 2.8.2.

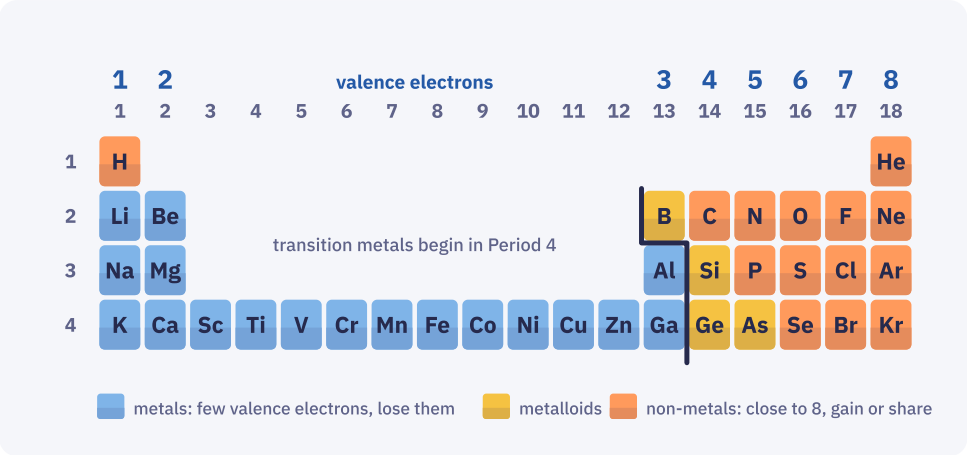


Figure 3.1 The first four periods. Above each column are its group number and, in bold, its number of valence electrons. The thick staircase separates metals from non-metals.

THE ATOM'S GOAL Every atom is driven to reach a _____ of eight electrons, an **octet**, the arrangement of the noble gases (helium has two, a **duplet**). This is the atom's goal in life. Nearly every bond in this chapter is a way of reaching it: atoms _____, _____ or _____ electrons until each has an octet.

A zigzag line, the **staircase**, runs down from boron. Elements to its left are **metals** and elements to its right are **non-metals**. Hydrogen, at the top left, is a non-metal. Elements along the staircase, such as silicon and germanium, are **metalloids**, with some properties of each.

Which way an atom reaches its octet depends on how many valence electrons it starts with.

- **Metals** have few valence electrons, usually 1 to 3. Losing those few is far easier than gaining five or more, so metal atoms give electrons away and form positive ions.
- **Non-metals** have 4 to 7 valence electrons, already close to 8. Gaining a few more is far easier than losing many, so non-metal atoms pull electrons towards themselves.

How strongly an atom pulls electrons towards itself in a bond is its **electronegativity**. A useful first picture: non-metals are _____ because they are already close to an octet, while metals are less electronegative because their few valence electrons are easily lost. Fluorine is the most electronegative element of all. Chapter 8 explains the real reasons for these trends.

Check your understanding

1. Use the Periodic Table to give the number of shells and of valence electrons in (a) magnesium and (b) sulfur.
2. Does a calcium atom reach an octet more easily by losing or by gaining electrons? Explain.

3.2 Why atoms bond

The noble gases (Group 18) hardly react, because their valence shells are already full, and they exist as single atoms: they are **monoatomic**. Every other atom bonds to reach the same octet (Section 3.1): metals by losing electrons, non-metals by gaining or sharing them.

> Every chemical bond is an _____ attraction between positive and negative charges.

bond	forms between	attraction between
ionic	a metal and a non-metal	oppositely charged ions
covalent	non-metals	a shared pair of electrons and the nuclei of both atoms
metallic	metal atoms	positive metal ions and a sea of _____ electrons

These bonds are strong. Molecules are also attracted to one another by much weaker **intermolecular forces** (3.9). Which bonds and forces a substance has decides its structure, and its structure decides its properties (3.10).

3.3 Ionic bonding

A metal atom loses its valence electrons to become a positive ion, a **cation**. A non-metal atom gains electrons to become a negative ion, an **anion**. Each ion then has a noble gas configuration. Sodium (2.8.1) loses one electron to give Na^+ (2.8): $Na \rightarrow Na^+ + e^-$. Chlorine (2.8.7) gains one to give Cl^- (2.8.8): $Cl + e^- \rightarrow Cl^-$.

3.3.1 Charges and formulae

An atom forms the ion that reaches an octet by moving the _____ (Section 3.1). A Group 1 atom has one valence electron. Losing it leaves the full shell underneath, while gaining seven would be far harder, so it forms a 1+ ion. In the same way a Group 2 atom loses two electrons (2+) and aluminium in Group 13 loses three (3+). On the other side, a Group 17 atom gains one electron (1–), Group 16 gains two (2–) and Group 15 gains three (3–). A Group 14 atom would have to lose or gain four, so carbon and silicon share electrons instead (Section 3.5). The charge on a simple ion therefore follows from its group.

group	1	2	13	15	16	17
charge on the ion	+1	+2	+3	−3	−2	_____
example	Na^+	Mg^{2+}	Al^{3+}	N^{3-}	O^{2-}	Cl^-

A **polyatomic ion** is a group of covalently bonded atoms that carries an overall charge. Its charge does not follow from a group, so it must be learnt.

LEARN THESE IONS

polyatomic ions	formula	other ions to learn	formula
ammonium	NH_4^+	hydrogen	H^+
hydroxide	OH^-	silver	Ag^+
nitrate	NO_3^-	zinc	Zn^{2+}
hydrogencarbonate	HCO_3^-	copper(II)	Cu^{2+}
carbonate	CO_3^{2-}	iron(II)	Fe^{2+}
sulfate	SO_4^{2-}	iron(III)	Fe^{3+}
phosphate	PO_4^{3-}		

A simple anion takes the ending *-ide*: chloride, oxide, nitride. Transition metals such as iron and copper can form more than one ion, so the charge is shown in brackets in the name: iron(II) is Fe^{2+} and iron(III) is Fe^{3+}.

An ionic compound has no overall charge, so its formula combines the ions so that the charges _____. Brackets go round a polyatomic ion when more than one is needed.

WORKED EXAMPLE Write the formulae of (a) magnesium chloride, (b) aluminium oxide and (c) calcium nitrate.

(a) Mg^{2+} and Cl^-: two Cl^- balance one Mg^{2+}, so $MgCl_2$. *+2 + 2(−1) = 0*

(b) Al^{3+} and O^{2-}: two Al^{3+} (+6) and three O^{2-} (−6), so Al_2O_3. *The lowest whole numbers that balance.*

(c) Ca^{2+} and NO_3^-: $Ca(NO_3)_2$. *Brackets keep the nitrate ion together.*

3.3.2 Dot-and-cross diagrams and the ionic lattice

A dot-and-cross diagram shows the valence electrons only, the electrons of one element as dots and of the other as crosses. Each ion goes in _____ brackets with its charge outside. The number of each ion is written in front: calcium fluoride is shown as one $[Ca]^{2+}$ with $2[F]^-$.

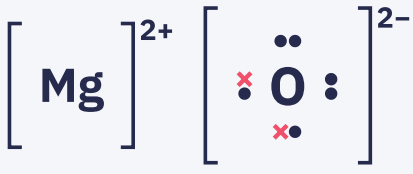


Figure 3.2 Magnesium oxide. Magnesium gives its two valence electrons (crosses) to oxygen.

An **ionic bond** is the strong electrostatic attraction between oppositely charged ions. In the solid, the ions are held in a regular arrangement called a **giant ionic lattice**.

Each ion attracts every oppositely charged ion around it, in all directions. In sodium chloride each Na^+ is surrounded by 6 Cl^- and each Cl^- by 6 Na^+ (Figure 3.3 shows one layer). This number is the **coordination number**.

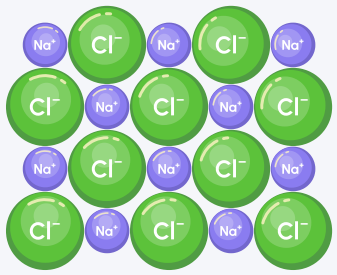


Figure 3.3 One layer of the sodium chloride lattice. One more Cl^- sits above each Na^+ and one below.

3.3.3 Properties of ionic compounds

- **High melting and boiling points**: a large amount of energy is needed to overcome the strong attraction between the ions.
- **Conduct electricity only when molten or dissolved**: the ions must be _____ to carry charge. In the solid they are held in fixed positions (Figure 3.4).
- **Hard but brittle**: a force can push one layer along by one ion, so that ions of the same charge meet and repel, and the lattice shatters (Figure 3.5).
- **Often soluble in water**, but insoluble in solvents such as hexane and oil.

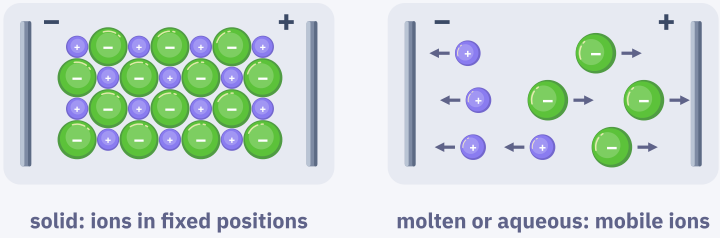


Figure 3.4 Ions can carry charge only when they are free to move.

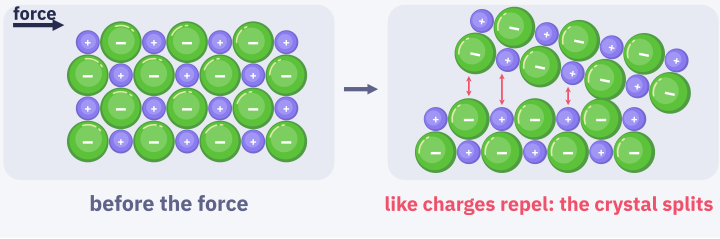


Figure 3.5 Why an ionic crystal is brittle.

How strong the attraction is, and so how high the melting point, depends on the charges and sizes of the ions (Section 3.8).

3.3.4 Ionic bonds with covalent character CORE · A LEVEL

A small, highly charged cation pulls the electron cloud of a nearby anion towards itself. It **polarises** the anion. Electron density is drawn between the two nuclei, so the electrons are partly shared and the bond gains covalent character (Figure 3.6).

- The **polarising power** of a cation rises with its _____, its charge divided by its radius. Al^{3+} polarises far more than Na^+.
- A larger anion is more easily polarised: I^- more than Cl^-, Cl^- more than F^-.

- So aluminium chloride behaves as a covalent compound, while sodium chloride and aluminium fluoride are ionic.

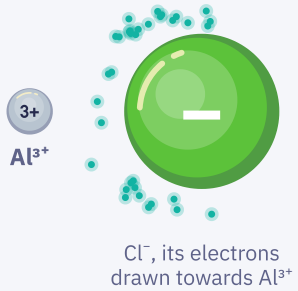


Figure 3.6 Al^{3+} polarises Cl^-: the outer electrons of Cl^- are found more often towards Al^{3+}.

Check your understanding

1. Write the formulae of potassium oxide, iron(III) chloride and ammonium sulfate.
2. Why does solid sodium chloride not conduct electricity, while molten sodium chloride does?

3.4 Metallic bonding

A **metallic bond** is the strong electrostatic attraction between a lattice of positive metal ions and a sea of _____ valence electrons.

Each metal atom gives its valence electrons to the sea. The electrons are not tied to any one ion, and they move throughout the lattice (Figure 3.7).

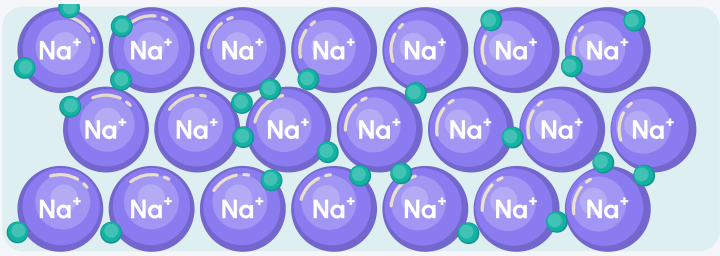


Figure 3.7 Sodium: Na^+ ions in a sea of delocalised electrons.

- **Conduct electricity and heat** in the solid and liquid: the delocalised electrons are mobile and carry charge and energy through the metal.
- **Malleable and ductile**: layers of ions can slide over one another, and the sea of electrons still holds them together, so the metal bends instead of breaking.
- **Usually high melting points**: a lot of energy is needed to overcome the strong metallic bonds. How strong they are varies from metal to metal (Section 3.8).

3.4.1 Alloys

An **alloy** is a mixture of a metal with one or more other elements, such as brass (copper and zinc) and steel (iron and carbon). The atoms of the added element are a different size, so they disrupt the regular layers. The layers can no longer slide easily, which makes alloys _____ but less malleable than the pure metal (Figure 3.8). Like other mixtures, alloys usually melt over a range of temperatures.

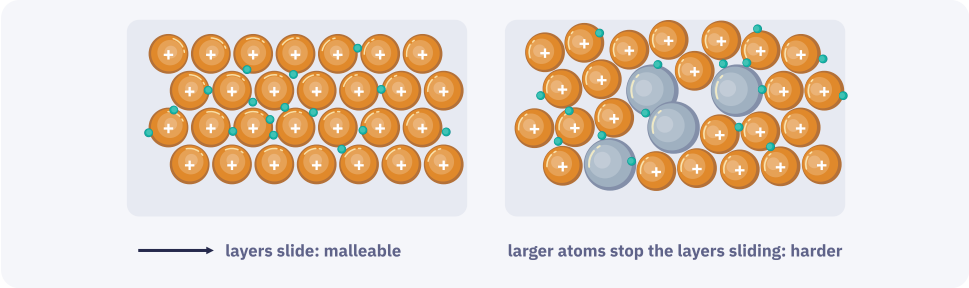


Figure 3.8 A pure metal and an alloy. Atom sizes are drawn for illustration.

Check your understanding

1. Why can metals conduct electricity in the solid state but ionic compounds cannot?
2. Why is bronze (copper and tin) harder than pure copper?

3.5 Covalent bonding

DEFINITION A **covalent bond** is the strong electrostatic attraction between a _____ of electrons and the nuclei of the two bonded atoms.

Two non-metal atoms each provide one electron to a shared pair, so both reach an octet (hydrogen reaches 2). The number of bonds an atom forms, its **valency**, is the number of electrons it still needs, 8 minus its valence electrons: C forms 4, N 3, O 2 and Cl 1. Hydrogen forms 1. Two shared pairs make a double bond and three make a triple bond. Pairs of valence electrons not used in bonding are **lone pairs**. In a structural formula each line is one shared pair: H–Cl, O=O, N≡N.

3.5.1 Drawing dot-and-cross diagrams

1. Choose the central atom: the one that forms the most bonds, or the least electronegative (3.7). Hydrogen is never central.
2. For an ion, add one electron per negative charge to the more electronegative atoms, or remove one per positive charge. Put the ion in square brackets with its charge outside.
3. Give every atom an octet using single, double or triple bonds. A Period 2 atom can hold at most 8 valence electrons.



Cl_2
one shared pair



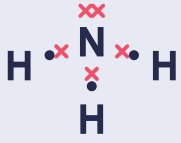
O_2
a double bond



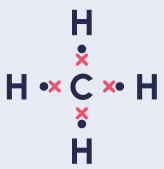
N_2
a triple bond



H_2O
two lone pairs on O



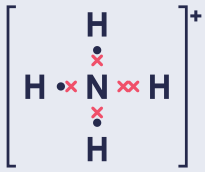
NH_3
one lone pair on N



CH_4
four shared pairs



CO_2
two double bonds



NH_4^+
a dative pair from N (xx)

Figure 3.9 Dot-and-cross diagrams. Crosses are the central atom's electrons, dots are the other atoms' electrons.

3.5.2 Exceptions to the octet rule CORE · A LEVEL

- **Fewer than 8** around the central atom: $BeCl_2$ (4), BF_3 and $AlCl_3$ (6). These are **electron-deficient**.
- **More than 8**: PCl_5 (10), SF_6 (12). Atoms of Period 3 and below have empty 3d orbitals close in energy to their valence orbitals, so they can _____ the octet. A Period 2 atom cannot, so NCl_5 does not exist.
- **An odd number of electrons**: NO and NO_2. A particle with an unpaired electron is a **radical**, and is very reactive.

3.5.3 σ and π bonds CORE · A LEVEL

A covalent bond forms when two half-filled orbitals, one from each atom, overlap and their electrons pair up (Figure 3.10).

DEFINITION A **σ bond** forms from the _____ overlap of orbitals along the line between the nuclei. A **π bond** forms from the _____ overlap of p orbitals, above and below that line.

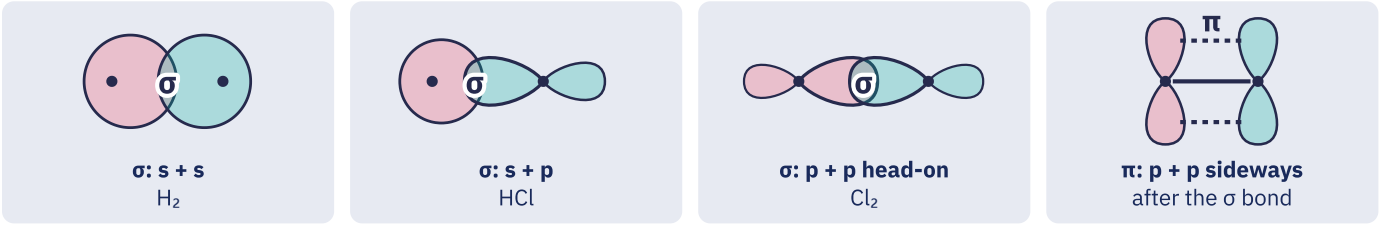


Figure 3.10 Orbital overlap in H_2, HCl and Cl_2 (σ), and the sideways overlap of a π bond.

- A single bond is one σ bond. A double bond is one σ and one π. A triple bond is one σ and _____ π.
- Sideways overlap is less effective, so a π bond is weaker than a σ bond. A π bond forms only after a σ bond has brought the atoms close.

3.5.4 Dative bonds CORE · A LEVEL

DEFINITION A **dative bond** (co-ordinate bond) is a covalent bond in which both shared electrons come from the same atom: one atom donates a _____ into an empty orbital of the other.

In the ammonium ion, N donates its lone pair to H^+. H_3O^+ forms the same way from H_2O and H^+, and in $H_3N{\rightarrow}BF_3$ the lone pair goes into the empty orbital of the electron-deficient B. In Al_2Cl_6, a Cl atom of each $AlCl_3$ donates a lone pair to the Al of the other, so each Al reaches an octet. A dative bond is drawn as an arrow from donor to acceptor. Once formed, it is identical to any other covalent bond (Figure 3.11).

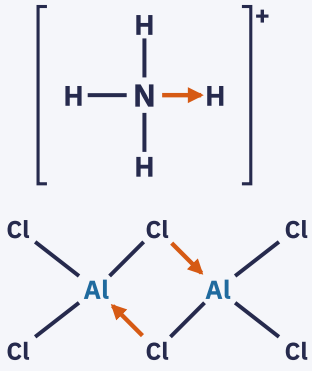


Figure 3.11 Dative bonds (arrows) in NH_4^+ and Al_2Cl_6.

Check your understanding

1. How many shared pairs and lone pairs are in a molecule of ammonia, NH_3?
2. How many σ and π bonds are in ethene, $H_2C{=}CH_2$?
3. Why can sulfur form SF_6 when oxygen cannot form OF_6?

3.6 Shapes of molecules

CORE · A LEVEL

Valence shell electron pair repulsion (VSEPR) theory predicts shapes from the electron pairs around the central atom.

1. Electron pairs repel, so they arrange themselves as _____ as possible.
2. A double or triple bond counts as one region, like a single bond.
3. Lone pairs repel more strongly than bond pairs, because a lone pair is held closer to the nucleus: lone pair–lone pair > lone pair–bond pair > bond pair–bond pair.
4. The shape is named from the positions of the _____ only, though the lone pairs still take up space.

2 electron pairs	**linear** 180° CO_2 (2 bp, 0 lp)			
3 electron pairs	**trigonal planar** 120° BF_3 (3 bp, 0 lp)	**bent** <120° SO_2 (2 bp, 1 lp)		
4 electron pairs	**tetrahedral** 109.5° CH_4 (4 bp, 0 lp)	**trigonal pyramidal** 107° NH_3 (3 bp, 1 lp)	**bent** 104.5° H_2O (2 bp, 2 lp)	
5 electron pairs lone pairs in the middle	**trigonal bipyramidal** 120°, 90° PCl_5 (5 bp, 0 lp)	**see-saw** <120°, <90° SF_4 (4 bp, 1 lp)	**T-shaped** <90° ClF_3 (3 bp, 2 lp)	**linear** 180° XeF_2 (2 bp, 3 lp)
6 electron pairs lone pairs opposite	**octahedral** 90° SF_6 (6 bp, 0 lp)	**square pyramidal** <90° BrF_5 (5 bp, 1 lp)	**square planar** 90° XeF_4 (4 bp, 2 lp)	

Figure 3.12 Shapes and bond angles (bp: bond pairs, lp: lone pairs). A wedge points towards you and a hatched bond away from you. Lone pairs are shaded.

Each lone pair squeezes the bond angles: CH_4 109.5°, NH_3 107°, H_2O 104.5°. With 5 pairs the lone pairs go in the middle (equatorial) positions, and with 6 pairs they sit opposite each other.

To count the pairs on an ion, take the central atom's valence electrons, add one for each singly bonded atom, take away a positive charge or add a negative charge, and halve the total. PCl_4^+ has (5 + 4 − 1)/2 = 4 pairs, all bond pairs: tetrahedral. ICl_4^- has (7 + 4 + 1)/2 = 6 pairs, 4 bond pairs and 2 lone pairs: square planar.

An oxygen atom usually joins the central atom by a double bond, as in CO_2 and SO_2. In an oxoanion, the charge says how many O^- have a single bond instead. ClO_3^- has one O^- and two =O, which leaves Cl one lone pair: 3 bond pairs and 1 lone pair, trigonal pyramidal.

WORKED EXAMPLE Predict the shape of and bond angle in ammonia, NH_3.

1. N has 5 valence electrons. Three pair with the three H atoms, leaving one lone pair. *Count the pairs on the central atom.*

2. There are 3 bond pairs and 1 lone pair around N. *4 pairs in total.*

3. To minimise repulsion, the 4 pairs point to the corners of a tetrahedron. *As far apart as possible.*

4. NH_3 is _____ with a bond angle of 107°. *The lone pair squeezes 109.5° down.*

GOING FURTHER The electronegativity of the atoms changes the angle a little. NF_3 (102°) has a smaller angle than NH_3 (107°): the bonding pairs are pulled out towards F, so there is less crowding round N. H_2O (104.5°) has a larger angle than H_2S (92°) because O pulls the bonding pairs closer to itself.

Check your understanding

1. State the shapes and bond angles of BF_3, H_2O and SF_6.

2. CO_2 has two double bonds. Why is it linear?

3. XeF_4 has 4 bond pairs and 2 lone pairs. Name its shape.

3.7 Electronegativity and polarity

CORE · A LEVEL

DEFINITION **Electronegativity** is the ability of an atom to attract the shared pair of electrons in a covalent bond towards itself.

- It _____ across a period and _____ down a group, so the most electronegative elements are at the top right, apart from the noble gases. Chapter 8 explains why.
- Fluorine is the most electronegative element, then oxygen, then nitrogen and chlorine.

3.7.1 Polar bonds and polar molecules

When two different atoms share electrons, the more electronegative atom pulls the pair closer. It gains a partial negative charge, δ−, and the other atom a partial positive charge, δ+. The bond has a **dipole** and is **polar** (Figure 3.13). Bonds between identical atoms, such as H–H and Cl–Cl, are non-polar.

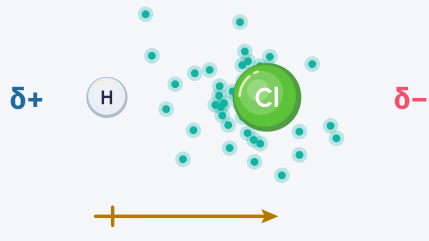


Figure 3.13 The polar H–Cl bond. The dipole arrow points to the negative end.

A molecule with polar bonds may still be non-polar overall: if its shape is symmetrical, the bond dipoles _____. To decide, find the polar bonds, work out the shape, then see whether the dipoles cancel (Figure 3.14).

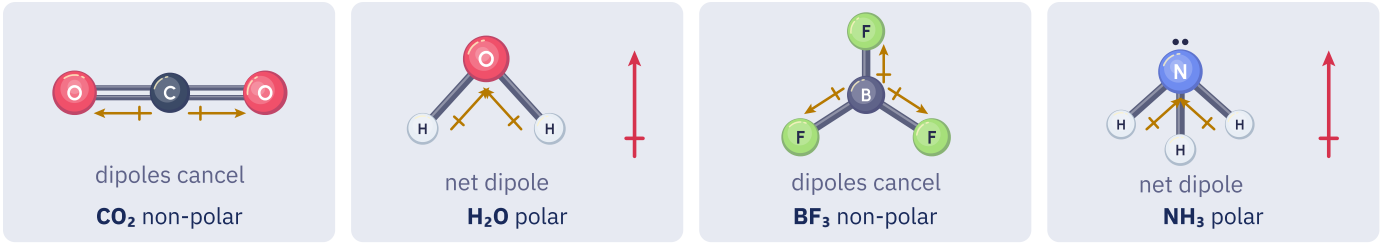


Figure 3.14 CO_2 and BF_3 are non-polar because their dipoles cancel. H_2O and NH_3 are polar.

Check your understanding

1. Which bond is more polar, C–Cl or C–F? Explain.
2. CCl_4 has four polar bonds. Why is the molecule non-polar?

3.8 What makes a bond strong

Sections 3.3 to 3.5 describe the properties shared by all ionic, all metallic and all covalent substances. This section explains why one bond of a type is stronger than another. Every bond is an electrostatic attraction, so the same two ideas run through all three: the attraction is stronger when the _____ and when they are _____.

3.8.1 Ionic bonds

Not every ionic attraction is equally strong. It is stronger when the ions carry _____ and when they are _____, so their centres are closer. Down a group, ions have more shells and get larger. Across a period, positive ions with the same number of electrons get smaller as the nuclear charge rises: $Na^+ > Mg^{2+} > Al^{3+}$.

WORKED EXAMPLE Explain why magnesium oxide (melting point 2852 °C) melts at a higher temperature than sodium oxide (1132 °C).

1. Both have a giant ionic lattice.	*The same kind of attraction must be overcome.*
2. Mg^{2+} has a higher charge and a smaller radius than Na^+.	*The factors that set the strength.*
3. The attraction between Mg^{2+} and O^{2-} is stronger, so more energy is needed to overcome it.	*Higher melting point.*

3.8.2 Metallic bonds

The metallic bond is stronger when each atom gives _____ to the sea and when the metal ions are _____, with a higher charge. Sodium, magnesium and aluminium give 1, 2 and 3 electrons each, so their melting points rise: Na (98 °C) < Mg (650 °C) < Al (660 °C). Down Group 1 the ions get larger, so the bond gets weaker and the melting point falls from lithium to caesium.

3.8.3 Covalent bonds CORE · A LEVEL

DEFINITION The **bond energy** is the energy needed to break one mole of a covalent bond between atoms in the _____ state. The **bond length** is the distance between the nuclei of the two bonded atoms.

Breaking a bond always takes in energy, so bond energies are positive: $Cl_2(g) \rightarrow 2Cl(g)$ needs +244 kJ mol^{-1}. A stronger bond has a larger bond energy and is usually shorter.

what changes	bonds compared (bond energy / kJ mol^{-1})	why
size of the atoms	Cl–Cl 244 > Br–Br 193 > I–I 151	larger, more diffuse orbitals overlap less effectively
number of shared pairs	C–C 350 < C=C 610 < C≡C 840, lengths 0.154, 0.134, 0.120 nm	more shared electrons between the nuclei. C=C is less than twice C–C because the π bond is weaker than the σ bond
polarity	N–H 390 < O–H 460 < F–H 562	the extra attraction between δ+ and δ− adds to the bond

Check your understanding

1. Which has the higher melting point, sodium fluoride or caesium chloride? Explain.
2. Explain why magnesium has a higher melting point than sodium.
3. Why is the I–I bond weaker than the Cl–Cl bond?

3.9 Intermolecular forces

In a **simple molecular** substance, strong covalent bonds hold the atoms together inside each molecule, but only weak **intermolecular forces** hold the molecules to one another. Melting and boiling overcome the intermolecular forces only, not the covalent bonds, so simple molecular substances have _____ melting and boiling points. Many are **volatile**: they evaporate easily. They do not conduct electricity, because their molecules carry no overall charge. Hydrogen chloride is different in water: it forms H^+ and Cl^- ions, which are mobile, so the solution conducts.

3.9.1 Instantaneous dipole–induced dipole forces CORE · A LEVEL

The electrons in a molecule are always moving. At any instant the electron cloud may sit more on one side, giving a temporary dipole. This **instantaneous dipole** distorts the electron cloud of a neighbouring molecule, _____ a dipole in it, and the two attract (Figure 3.15). These **id–id** forces act between all molecules, and they are the only intermolecular forces between non-polar molecules.

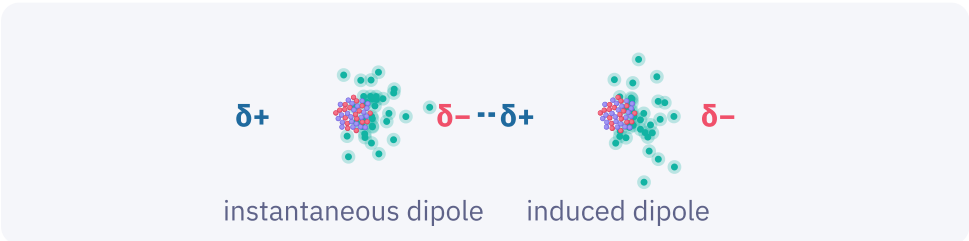


Figure 3.15 An instantaneous dipole induces a dipole in its neighbour.

- **More electrons** give a larger, more easily distorted electron cloud and stronger id–id forces: F_2 boils at −188 °C, Cl_2 at −34 °C and Br_2 at 59 °C.

- **More surface contact** gives stronger id–id forces. Long chain-shaped molecules touch along their length, compact ball-shaped ones only at a point: pentane (a chain of five carbon atoms) boils at 36 °C, its compact isomer 2,2-dimethylpropane at 10 °C.

3.9.2 Permanent dipole–permanent dipole forces CORE · A LEVEL

Polar molecules have permanent dipoles. The δ+ end of one molecule attracts the δ− end of the next. These **pd–pd** forces act in addition to id–id forces. Between molecules with a similar number of electrons, the polar one boils higher: propene (non-polar, M_r 42) boils at −48 °C but ethanal (polar, M_r 44) at 20 °C. When the numbers of electrons differ greatly, id–id forces can win: CH_3Br (M_r 94.9, 4 °C) boils higher than the more polar CH_3Cl (M_r 50.5, −24 °C).

3.9.3 Hydrogen bonding CORE · A LEVEL

DEFINITION A **hydrogen bond** is the attraction between a hydrogen atom bonded to _____ in one molecule and a _____ on F, O or N in another molecule.

F, O and N are so electronegative that the H bonded to them carries a large δ+, almost a bare proton, and their lone pairs are small and concentrated. A hydrogen bond is the strongest kind of intermolecular force, though still far weaker than a covalent bond. To draw one, show the lone pair, the δ+ and δ− charges and the bond itself (Figure 3.16).

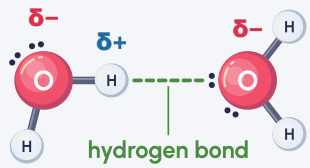


Figure 3.16 A hydrogen bond between two water molecules.

- The number of hydrogen bonds a molecule can form is the smaller of its number of H atoms on F, O or N and its number of lone pairs on F, O or N. Water forms 2 per molecule, HF and NH_3 only 1.
- So water (100 °C) boils higher than HF (20 °C), which boils higher than NH_3 (−33 °C), because the H–F bond is more polar than N–H.
- H_2O, HF and NH_3 boil far higher than the other hydrides in their groups, which have no hydrogen bonding (Figure 3.17).
- In ice, each water molecule forms hydrogen bonds to 4 others in an open structure, so ice is _____ than water and floats.
- Ethanol, ammonia and HF mix with water because they form hydrogen bonds with water molecules.

GOING FURTHER Ethanoic acid dissolved in benzene has an apparent M_r of 120, not 60, because its molecules pair up as hydrogen-bonded dimers. A molecule can also hydrogen bond within itself. 2-nitrophenol boils at 216 °C and its isomer 4-nitrophenol at 279 °C: the groups of 2-nitrophenol are close enough to form an intramolecular hydrogen bond, which leaves fewer sites for hydrogen bonds between molecules.

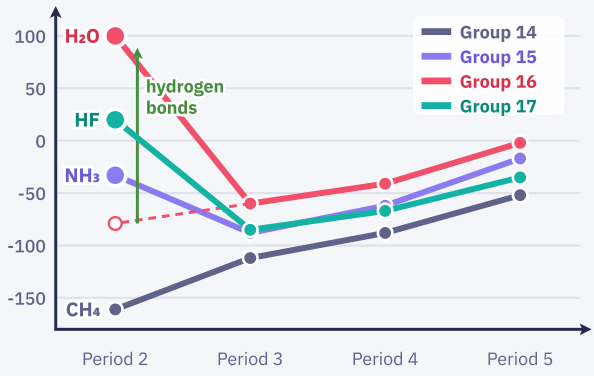


Figure 3.17 Boiling points of the hydrides of Groups 14 to 17 in °C.

3.9.4 Solubility

"Like dissolves like." A substance dissolves when the attractions it forms with the solvent make up for the attractions broken. Polar and hydrogen-bonded substances, and many ionic compounds, dissolve in water. Non-polar substances, such as oils and iodine, dissolve in non-polar solvents such as hexane, and not in water. That is why hexane and water are immiscible.

WORKED EXAMPLE Explain why water (M_r 18) boils at 100 °C while hydrogen sulfide, H_2S (M_r 34), boils at −60 °C.

1. Both have simple molecular structures.	*Boiling overcomes the intermolecular forces.*
2. H_2O has hydrogen bonds between molecules: H is bonded to O, and O has lone pairs.	*S is not electronegative enough.*
3. More energy is needed to overcome the hydrogen bonds in water than the weaker id–id and pd–pd forces in H_2S.	*Even though H_2S has more electrons.*

Check your understanding

1. Which forces are overcome when iodine sublimes, and why does it happen at a low temperature?
2. Which of these can form hydrogen bonds between their own molecules: CH_4, CH_3OH, HCl, NH_3?
3. Put Cl_2, Br_2 and I_2 in order of increasing boiling point and explain.

3.10 Giant covalent structures and properties

In a **giant covalent** (giant molecular) structure, every atom is joined to its neighbours by covalent bonds that extend throughout the solid. Melting means breaking many strong covalent bonds, so these substances have very high melting points and are insoluble in all solvents. Examples are diamond, graphite and silicon dioxide (Figure 3.18). Diamond and graphite are **allotropes** of carbon: different forms of the same element, with different arrangements of atoms.

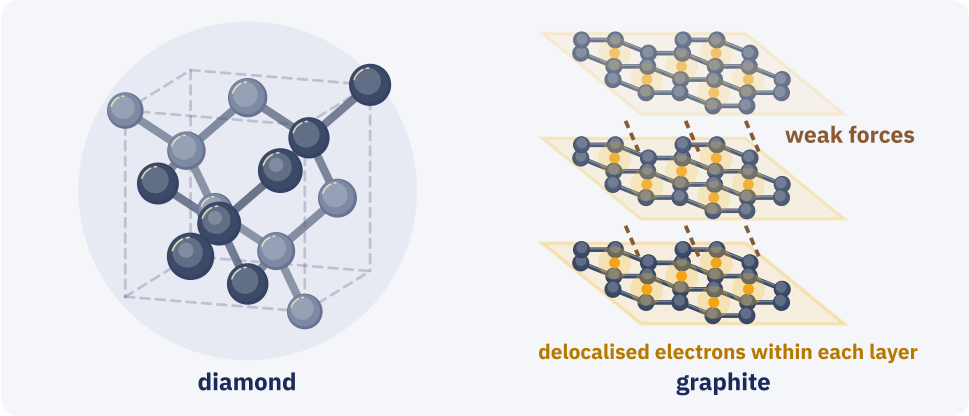


Figure 3.18 The structures of diamond and graphite.

	diamond	graphite
bonding	each C bonded to _____ others in a tetrahedral arrangement	each C bonded to _____ others in flat layers of hexagons. The fourth valence electron is delocalised within each layer
hardness	very hard: atoms are held rigidly. Used in cutting tools	soft and slippery: weak forces between the layers let them slide. Used as a lubricant and in pencils
electrical conductivity	none: all valence electrons are in bonds	conducts along the layers: the delocalised electrons move

Silicon dioxide, SiO_2, has a structure like diamond, with each Si bonded to 4 O and each O to 2 Si. It melts at 1710 °C, while carbon dioxide, a simple molecular substance, is a gas at room temperature.

3.10.1 Structure and properties

structure	examples	melting and boiling points	electrical conductivity	solubility in water
giant ionic	NaCl, MgO	high	only molten or dissolved	often soluble
giant metallic	Na, Cu, alloys	usually high	good, solid and liquid	insoluble (some react)
giant covalent	diamond, graphite, SiO_2	_____	none (graphite conducts)	insoluble
simple molecular	H_2O, CO_2, I_2	low	none	depends on polarity

WORKED EXAMPLE Substance Z melts at 801 °C. It does not conduct electricity as a solid, but conducts when molten. Suggest its structure.

1. The high melting point rules out a simple molecular structure. *Strong bonds must be broken.*
2. It conducts only when molten, so it has ions that become mobile on melting. *A metal or graphite conducts as a solid.*
3. Z has a _____ structure. *Sodium chloride fits these data.*

Check your understanding

1. Why does graphite conduct electricity while diamond does not?

2. Explain why silicon dioxide has a far higher melting point than carbon dioxide.

3. A substance melts at −23 °C and does not conduct in any state. What is its structure?

Answers to Check your understanding

3.1

1. (a) Period 3, Group 2: three shells and 2 valence electrons (2.8.2). (b) Period 3, Group 16: three shells and 6 valence electrons (2.8.6).
2. By losing. Calcium is in Group 2, so it has 2 valence electrons. Losing two is far easier than gaining six, so it forms Ca^{2+}.

3.3

1. K_2O, $FeCl_3$ and $(NH_4)_2SO_4$.
2. In the solid the ions are held in fixed positions and cannot move. When molten they are free to move and carry charge.

3.4

1. A metal has delocalised electrons that move through the solid. In a solid ionic compound the ions are fixed and there are no free electrons.
2. The tin atoms are a different size from the copper atoms, so they disrupt the layers, which can no longer slide over each other easily.

3.5

1. Three shared pairs (three N–H bonds) and one lone pair on N.
2. Five σ bonds (four C–H and one in C=C) and one π bond.
3. Sulfur is in Period 3 and has empty 3d orbitals, so it can expand its octet to 12 electrons. Oxygen is in Period 2 and can hold at most 8.

3.6

1. BF_3 trigonal planar, 120°. H_2O bent, 104.5°. SF_6 octahedral, 90°.
2. Each double bond counts as one region, so there are two regions round C, which point in opposite directions: 180°.
3. Square planar, with the two lone pairs opposite each other.

3.7

1. C–F. Fluorine is more electronegative than chlorine, so the difference in electronegativity from carbon is greater.
2. It is tetrahedral and symmetrical, so the four bond dipoles cancel and there is no overall dipole.

3.8

1. Sodium fluoride. The ions have the same charges, but Na^+ and F^- are smaller than Cs^+ and Cl^-, so the attraction between them is stronger and needs more energy to overcome.

2. Each magnesium atom gives two electrons to the sea and forms a smaller ion with a 2+ charge, so the metallic bond is stronger than in sodium, which gives one.
3. Iodine atoms are larger, so their orbitals are more diffuse and overlap less effectively.

3.9

1. The weak instantaneous dipole–induced dipole forces between I_2 molecules, not the covalent bonds inside them. Little energy is needed to overcome them.
2. CH_3OH and NH_3. Each has H bonded to O or N and a lone pair on that atom. CH_4 and HCl have no H on F, O or N.
3. $Cl_2 < Br_2 < I_2$. The number of electrons increases, so the instantaneous dipole–induced dipole forces get stronger and need more energy to overcome.

3.10

1. In graphite each C uses only 3 electrons in bonds, and the fourth is delocalised and mobile within its layer. In diamond all 4 are in bonds.
2. Silicon dioxide is giant covalent, so melting breaks many strong covalent bonds. Carbon dioxide is simple molecular, so only weak forces between molecules are overcome.
3. Simple molecular.