Chemistry Units 1 & 2

Chapter 2 — Covalent substances

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Theory

Many of the most familiar substances around us — the water we drink, the oxygen and nitrogen in the air, the methane in natural gas — are not made of ions or of metal lattices, but of small, discrete groups of atoms called **molecules**. The atoms within a molecule are held together by **covalent bonds**. This subtopic is about what a covalent bond is, and about the three standard ways chemists draw and write covalent molecules so that others can see exactly how the atoms are joined.

Covalent bonding: a shared pair of electrons. A **covalent bond** is a bond formed when two atoms **share a pair of electrons**. Covalent bonding occurs between **non-metal atoms**. A non-metal atom has a strong attraction for electrons, so instead of one atom transferring electrons to another (as happens when a metal and a non-metal form an ionic compound), two non-metal atoms bring their outer-shell electrons together and *share* them. The shared pair is attracted to the nuclei of *both* atoms at once, and it is this common attraction that holds the two atoms together. A single shared pair of electrons is one covalent bond.

Why atoms share: the octet rule. Atoms bond because doing so lowers their energy and makes them more stable. The noble gases (group 18) are exceptionally unreactive because their outer electron shells are already full — most of them have **eight** electrons in the outer shell. Other atoms tend to react in ways that give them the same stable arrangement. This tendency is summarised by the **octet rule**: *atoms share (or transfer) electrons so as to obtain a full outer shell of eight electrons*, matching the nearest noble gas. By sharing a pair of electrons, each atom in a covalent bond gets to *count* both shared electrons as part of its own outer shell, helping it towards a complete octet.

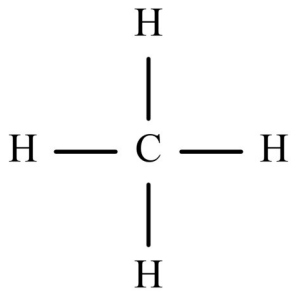
The important exception is **hydrogen**. Hydrogen's outer shell (the first shell) is full with just **two** electrons, the arrangement of helium. A hydrogen atom therefore aims for a **duet** (two electrons), not an octet, and it forms exactly **one** covalent bond. Within this course the octet rule (with hydrogen's duet) accounts for every molecule you will be asked to draw; a small number of molecules elsewhere in chemistry have atoms with fewer or more than eight outer electrons, but none of those occur in the set below.

Bonding pairs and lone pairs. The outer-shell electrons of an atom are grouped into pairs. In a molecule these pairs are of two kinds. A **bonding pair** (or *shared pair*) is a pair of electrons shared between two atoms — it *is* a covalent bond. A **lone pair** (or *non-bonding pair*) is a pair of outer-shell electrons that belongs to a single atom and is **not** involved in bonding. Both kinds count towards an atom's octet, but only bonding pairs hold atoms together. Keeping track of both is the key to drawing any covalent molecule correctly.

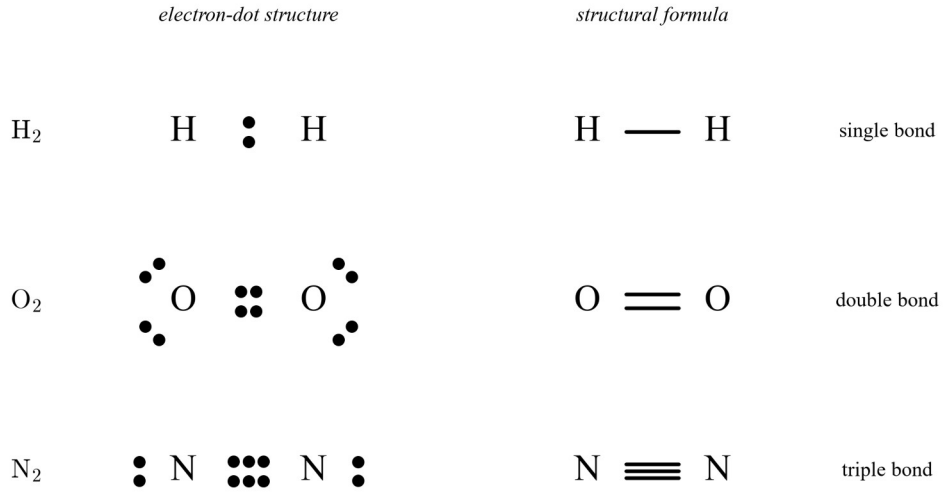
Three ways to represent a covalent molecule. The study design requires three related representations, each showing more detail than the last.

- The **molecular formula** states only *how many atoms of each element* are present in one molecule — for example H_2O (two hydrogen atoms and one oxygen atom) or CH_4 (one carbon and four hydrogen atoms). It says nothing about how the atoms are joined.
- The **structural formula** shows *which atoms are bonded to which*, drawing every covalent bond as a short line: a single line for a single bond, a double line for a double bond and a triple line for a triple bond. Lone pairs are usually not shown. Water's structural formula is H–O–H; methane's is a central carbon joined by four lines to four hydrogen atoms.
- The **electron-dot structure** (also called a **Lewis structure**) shows *all* of the outer-shell electrons: each bonding pair is drawn either as a line or as a pair of dots between the atoms, and every lone pair is drawn as a pair of dots on the atom it belongs to. This is the most complete of the three representations because it shows the lone pairs as well as the bonds.

Methane, CH_4, is the simplest molecule for comparing the three. Its central carbon atom (4 valence electrons) shares one pair with each of four hydrogen atoms, forming four single bonds and no lone pairs; carbon thereby reaches an octet and each hydrogen a duet. Because methane has no lone pairs at all, there is nothing for a structural formula to leave out, so its structural formula and its electron-dot structure look the same — the drawing below serves as both.



Single, double and triple bonds. Two atoms need not share only one pair. If they share **one** pair the bond is a **single bond**; **two** shared pairs make a **double bond**; **three** shared pairs make a **triple bond**. The number of shared pairs in a bond is called its **bond order**. A double bond is stronger and shorter than a single bond, and a triple bond stronger and shorter still. The three diatomic molecules below show each case: hydrogen H_2 has a single bond (H–H), oxygen O_2 a double bond (O=O), and nitrogen N_2 a triple bond (N≡N). The figure shows each first as an electron-dot structure and then as a structural formula, so that you can see how one shared pair corresponds to one line.



Notice, in the electron-dot column, that the hydrogen atoms carry no lone pairs (each has only its single bonded pair, a duet), while each oxygen atom carries two lone pairs and each nitrogen atom one lone pair, so that every non-hydrogen atom is surrounded by eight electrons. The structural formulas in the right-hand column show the same bonds but leave those lone pairs out — which is precisely what separates the two representations.

A method for drawing electron-dot (Lewis) structures. For the small molecules in this course the following steps work reliably.

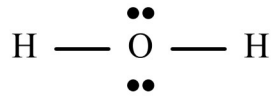
1. **Count the total number of valence (outer-shell) electrons** by adding the valence electrons of every atom. For a main-group element the periodic table gives this straight away: in groups 1 and 2 the number of valence electrons *is* the group number, and in groups 13–18 it is the group number **minus 10**. So hydrogen (group 1) contributes 1, carbon (group 14) 4, nitrogen (group 15) 5, oxygen (group 16) 6, and a halogen such as chlorine (group 17) 7.
2. **Arrange the atoms**, putting the atom that forms the most bonds in the centre and hydrogen atoms on the outside (hydrogen forms only one bond, so it is never central).
3. **Join the atoms with one single bond each**, using one shared pair (two electrons) per bond.
4. **Add the remaining electrons as lone pairs**, first completing the octets of the outer atoms.

5. **If a central atom still lacks an octet**, move one or more lone pairs from a neighbouring atom into the bond, making a **double** or **triple** bond, until every atom has its full shell.
6. **Check** that the number of electrons drawn equals the total from step 1, and that every atom has an octet (a duet for hydrogen).

A useful consistency check follows directly from this bookkeeping. Because every electron ends up either in a bonding pair or in a lone pair,

$$\text{total valence electrons} = 2 \times (\text{number of bonding pairs}) + 2 \times (\text{number of lone pairs}).$$

Water illustrates the method: its 8 valence electrons ($6 + 1 + 1$) form two O–H bonding pairs (4 electrons), leaving 4 electrons as two lone pairs on the oxygen atom.



Extension (not assessed in Units 1 & 2). In a normal covalent bond each atom contributes one electron to the shared pair. In a **coordinate** (or **dative**) covalent bond, *both* shared electrons come from the same atom — for example when a lone pair on a nitrogen or oxygen atom is donated to form an extra bond. None of the molecules named in this subtopic contains a coordinate bond, and you will not be asked to draw one here; it is mentioned only so the term is not unfamiliar later.

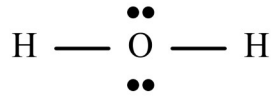
The molecules you must be able to represent are the eleven named in the study design: hydrogen H_2, oxygen O_2, chlorine Cl_2, nitrogen N_2, hydrogen chloride HCl, carbon dioxide CO_2, water H_2O, ammonia NH_3, methane CH_4, ethane C_2H_6 and ethene C_2H_4. Every one obeys the octet rule (with the hydrogen duet), and the method above draws all of them.

Worked examples

Worked Example 1 — Draw the electron-dot (Lewis) structure of water, H_2O, and state the number of bonding pairs and the number of lone pairs in the molecule.

Working	Comment
Valence electrons $= 6 + (2 \times 1) = 8$	Oxygen is in group 16, so it has $16 - 10 = 6$ valence electrons; each hydrogen is in group 1 (1 each).
Oxygen is central; the two H atoms go on the outside	Hydrogen forms only one bond, so it can never be the central atom.
Draw two O–H single bonds: $2 \times 2 = 4$ electrons used	One shared (bonding) pair joins oxygen to each hydrogen.
Remaining electrons $= 8 - 4 = 4 \Rightarrow$ 2 lone pairs, placed on oxygen	The outer H atoms already have their duet; the leftover electrons complete oxygen's shell.
Check: O has 2 bonds + 2 lone pairs $= 8$ electrons; each H has 2	Every atom satisfies the octet rule (hydrogen the duet).

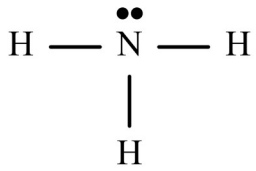
The completed structure (see figure) has **2 bonding pairs** and **2 lone pairs**. Its structural formula is H–O–H.



Worked Example 2 — Draw the electron-dot structure of ammonia, NH_3, and state the number of bonding pairs and lone pairs. Explain how the structure satisfies the octet rule for nitrogen.

Working	Comment
Valence electrons $= 5 + (3 \times 1) = 8$	Nitrogen is in group 15, so it has $15 - 10 = 5$ valence electrons; each of the three hydrogens contributes 1.
Nitrogen is central; the three H atoms go on the outside	Nitrogen forms three bonds here, hydrogen only one each.
Draw three N–H single bonds: $3 \times 2 = 6$ electrons used	Three bonding (shared) pairs, one to each hydrogen.
Remaining electrons $= 8 - 6 = 2 \Rightarrow$ 1 lone pair on nitrogen	Two electrons are left over; they stay on nitrogen as a non-bonding pair.
Check: N has 3 bonds $+ 1$ lone pair $= 8$ electrons	Nitrogen is surrounded by 8 electrons — a complete octet.

The molecule has **3 bonding pairs** and **1 lone pair** (see figure). Nitrogen reaches an octet by sharing three pairs (which count towards its shell) plus keeping one lone pair, giving $3 \times 2 + 2 = 8$ electrons around the nitrogen atom.

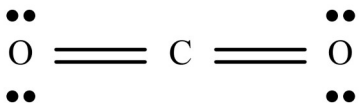


Worked Example 3 — Determine the electron-dot structure of carbon dioxide, CO_2. State the type of each carbon–oxygen bond, write the structural formula, and give the total number of bonding pairs and lone pairs.

Carbon dioxide has $4 + (2 \times 6) = 16$ valence electrons. Placing carbon in the centre with an oxygen on each side and joining them with single bonds uses $2 \times 2 = 4$ electrons; completing the octets of the two oxygen atoms would then use the remaining 12 electrons as lone pairs, but this leaves carbon with only 4 electrons (two bonds) — short of an octet. To fix this, one lone pair from *each* oxygen is moved into the bond, so that each carbon–oxygen bond becomes a **double bond**. Now carbon shares four pairs ($4 \times 2 = 8$ electrons, an octet), and each oxygen has one double bond (4 electrons) plus two lone pairs (4 electrons), also reaching 8. The structural formula is O=C=O.

Counting up: two double bonds give 4 bonding pairs in total, and the two oxygen atoms carry $2 + 2 = 4$ lone pairs. Check: $2 \times 4 + 2 \times 4 = 16$ electrons, matching the valence total.

$\therefore$ carbon dioxide contains two carbon–oxygen **double** bonds, with **4 bonding pairs** and **4 lone pairs** in all.



Worked Example 4 — Deduce the electron-dot structure of nitrogen, N_2, and hence state the bond type, the number of bonding pairs and the number of lone pairs.

Nitrogen gas is diatomic with $5 + 5 = 10$ valence electrons. A single N–N bond uses 2 electrons and leaves 8; sharing those as lone pairs (two on each nitrogen) would give each nitrogen only $2 + 4 = 6$ electrons — not an octet. Moving one lone pair from *each* nitrogen into the bond adds two more shared pairs, making a **triple bond**. Each nitrogen now has one triple bond (6 electrons) and one lone pair (2 electrons), a full octet, and the structural formula is N≡N. The three shared pairs account for 6 electrons and the two lone pairs for 4, totalling the 10 valence electrons.

∴ nitrogen has a **triple bond**, giving **3 bonding pairs** and **2 lone pairs** (one lone pair on each nitrogen atom).

Practice questions

Question 1 — Consider the molecule hydrogen chloride, HCl (hydrogen is in group 1, chlorine in group 17).

a. State the total number of valence electrons in the molecule.
b. State the number of bonding (shared) pairs of electrons.
c. State the number of lone pairs on the chlorine atom, and write the structural formula.

Question 2 — Consider methane, CH_4 (carbon is in group 14).

a. State the number of bonding pairs of electrons in the molecule.
b. State the number of lone pairs in the molecule.
c. Explain, in terms of the octet rule, why the carbon atom forms four bonds.

Question 3 — Oxygen gas, O_2, is a diatomic molecule (oxygen is in group 16).

a. State the total number of valence electrons in the molecule.
b. Deduce the type of bond (single, double or triple) between the two oxygen atoms so that each has an octet, and justify your answer.
c. State the number of lone pairs on each oxygen atom.

Question 4 — Ethane has the structure in which two carbon atoms are joined to each other and each carbon is also joined to three hydrogen atoms.

a. Write the molecular formula of ethane.
b. State the number of carbon–hydrogen bonds and the number of carbon–carbon bonds.
c. State whether the bonds are single, double or triple, and give the total number of bonding pairs.

Question 5 — Chlorine gas, Cl_2, is a diatomic molecule (chlorine is in group 17).

a. State the total number of valence electrons in the molecule.
b. State the number of bonding pairs of electrons.
c. State the total number of lone pairs in the molecule, and show that your answers to parts a–c satisfy $\text{total valence electrons} = 2 \times (\text{bonding pairs}) + 2 \times (\text{lone pairs})$.

Question 6 — This question is about the nature of covalent bonding.

a. State what is meant by a *covalent bond*.
b. State the *octet rule*.
c. Explain why hydrogen is an exception to the octet rule, and state how many electrons a hydrogen atom aims to have in its outer shell.

Question 7 — Draw the electron-dot structure of hydrogen, H_2. State the number of bonding pairs and lone pairs, and explain why a single shared pair is enough to satisfy both hydrogen atoms.

Question 8 — Ethene has the molecular formula C_2H_4, with the two carbon atoms joined to each other and each carbon also bonded to two hydrogen atoms.

a. Draw the structural formula of ethene.

b. Identify the type of the carbon–carbon bond.
c. State the total number of bonding pairs and lone pairs in the molecule.

Question 9 — For each of the following molecules, state whether the bond between the two central heavy atoms (or, for CO_2, the carbon–oxygen bonds) is single, double or triple: H_2, O_2, N_2 and CO_2.

Question 10 — Both nitrogen, N_2, and carbon dioxide, CO_2, contain multiple bonds. Explain, using the octet rule, why nitrogen forms a triple bond whereas each carbon–oxygen bond in carbon dioxide is a double bond.

Question 11 — A student is asked to convert molecular formulas into structural formulas.

a. Draw the structural formula of methane, CH_4, and state the number of covalent bonds it contains.
b. Draw the structural formula of water, H_2O, and state the number of covalent bonds it contains.

Question 12 — A molecule is drawn as a central nitrogen atom joined by single lines to three hydrogen atoms, with one pair of dots on the nitrogen.

a. Write the molecular formula of this molecule.
b. State the number of lone pairs and the number of bonding pairs.
c. Name the molecule.

Question 13 — Explain, in terms of valence electrons and the octet rule, why two chlorine atoms form a single covalent bond in Cl_2 rather than a double bond.

Question 14 — Distinguish between a *bonding pair* and a *lone pair* of electrons. Use the ammonia molecule, NH_3, as an example, stating how many of each it contains.

Question 15 — Explain why non-metal atoms share electrons to form covalent bonds. Refer in your answer to outer-shell electrons, the octet rule and the idea of stability.

Question 16 — Copy and complete the table below for the four molecules shown, giving in each case the number of bonding pairs, the number of lone pairs, and the highest bond order present (single, double or triple).

Molecule	Bonding pairs	Lone pairs	Highest bond order
H_2O			
CO_2			
N_2			
CH_4			

Question 17 — Using ethene, C_2H_4, as your example, explain what information is provided by (a) its molecular formula, (b) its structural formula, and (c) its electron-dot (Lewis) structure. State one thing that the electron-dot structure shows which the structural formula usually does not.

Question 18 — Carbon dioxide, CO_2, and methane, CH_4, are both covalent molecules of carbon.

a. Draw the electron-dot structure of each molecule.
b. State the number of bonding pairs and lone pairs in each.
c. Explain why the carbon atom forms four single bonds in methane but is drawn with two double bonds in carbon dioxide, referring to the octet rule for carbon and for its bonding partners.

Answers

1 a 8; b 1; c 3 lone pairs on Cl; structural formula H–Cl. **2** a 4; b 0; c carbon (4 valence electrons) shares one pair with each of four H atoms, giving carbon 8 electrons (an octet). **3** a 12; b a double bond, so each oxygen gains a share of the extra electrons it needs for an octet; c 2 lone pairs on each oxygen. **4** a C_2H_6; b 6 C–H bonds and 1 C–C bond; c all single bonds; 7 bonding pairs in total. **5** a 14; b 1; c 6 lone pairs (3 on each Cl); check $2 \times 1 + 2 \times 6 = 14$, matching part a. **6** a a shared pair of electrons between two (non-metal) atoms; b atoms share or transfer electrons to gain a full outer shell of eight electrons (a noble-gas arrangement); c hydrogen's first shell is full with only two electrons (a duet, like helium), so it aims for 2, not 8, and forms one bond. **7** 1 bonding pair, 0 lone pairs; each H needs only a duet (2 electrons), and the single shared pair gives both H atoms their two electrons. **8** a $H_2C=CH_2$ (each carbon bonded to two H atoms and, by a double bond, to the other carbon); b a double bond; c 6 bonding pairs and 0 lone pairs. **9** H_2 single; O_2 double; N_2 triple; CO_2 each carbon–oxygen bond is double. **10** each nitrogen needs 3 more electrons for an octet, so the two N atoms share 3 pairs (a triple bond); each oxygen in CO_2 needs only 2 more, so each C=O bond is a double bond, and carbon's four shared pairs (two per double bond) complete its octet. **11** a four single C–H bonds; 4 bonds; b H–O–H, two single O–H bonds; 2 bonds. **12** a NH_3; b 1 lone pair, 3 bonding pairs; c ammonia. **13** each Cl has 7 valence electrons and needs just one more to reach 8, so sharing one pair gives both an octet; a double bond would place more than eight electrons around each chlorine. **14** a bonding pair is shared between two atoms (it is a covalent bond); a lone pair belongs to one atom and is not shared; ammonia has 3 bonding pairs and 1 lone pair. **15** non-metal atoms attract electrons strongly; by sharing outer-shell electrons each atom gains a full outer shell (octet, or duet for H), the stable low-energy arrangement of a noble gas. **16** H_2O: 2, 2, single; CO_2: 4, 4, double; N_2: 3, 2, triple; CH_4: 4, 0, single. **17** a molecular formula: the number and type of atoms (2 C, 4 H); b structural formula: which atoms are bonded together and the bond types (a C=C double bond and four C–H single bonds); c electron-dot structure: all outer-shell electrons, as bonding pairs and lone pairs; it shows lone pairs (here none), which a structural formula usually omits. **18** a two structures: O=C=O (with two lone pairs on each O) and CH_4 (four single C–H bonds); b CO_2: 4 bonding pairs, 4 lone pairs; CH_4: 4 bonding pairs, 0 lone pairs; c carbon needs 4 electrons for an octet, so it forms four bonds in both; each H needs only a duet (one bond), giving four single bonds in methane, whereas each O needs two more electrons, so carbon shares two pairs with each oxygen — two double bonds — still four bonds from carbon.

Fully-worked solutions

Question 1 a. Hydrogen contributes 1 valence electron and chlorine (group 17, so $17 - 10 = 7$ valence electrons) contributes 7, so the total is $1 + 7 = 8$. b. Hydrogen forms one bond, so there is a single H–Cl bond — that is **1 bonding pair** (2 electrons). c. Of the 8 electrons, 2 are in the bonding pair, leaving $8 - 2 = 6$ electrons as **3 lone pairs**, all on the chlorine atom. Hydrogen has its duet; chlorine has $2 + 6 = 8$ (an octet). The structural formula is H–Cl.

Question 2 a. Carbon (group 14, so $14 - 10 = 4$ valence electrons) shares one pair with each of four hydrogen atoms, giving **4 bonding pairs**. b. All 8 valence electrons ($4 + 4 \times 1$) are used in the four bonds, so there are **0 lone pairs**. c. A carbon atom has 4 outer-shell electrons and needs 4 more to reach an octet of 8. By forming four covalent bonds it shares in four extra electrons; counting the four shared pairs gives carbon $4 \times 2 = 8$ electrons around it, a complete octet, while each hydrogen gains its duet.

Question 3 a. Each oxygen atom (group 16, so $16 - 10 = 6$) contributes 6 valence electrons, so $6 + 6 = 12$ in total. b. A single O–O bond would leave each oxygen with only $2 + 4 = 6$ electrons (one bond plus two lone pairs) — not an octet. Sharing a second pair makes a **double bond**, after which each oxygen has $4 + 4 = 8$ electrons. So the bond is double. c. After the double bond (4 electrons) the remaining $12 - 4 = 8$ electrons form four lone pairs, shared equally: **2 lone pairs on each oxygen atom**.

Question 4 a. Two carbon atoms and $2 \times 3 = 6$ hydrogen atoms give the molecular formula C_2H_6. b. Each carbon is bonded to three hydrogen atoms ($2 \times 3 = 6$ C–H bonds) and the two carbons are bonded to each other (1 C–C bond). c. All are single bonds. There are $6 + 1 = 7$ bonds, hence **7 bonding pairs**. (Check: valence electrons $= 2 \times 4 + 6 \times 1 = 14 = 2 \times 7$, with no lone pairs — consistent.)

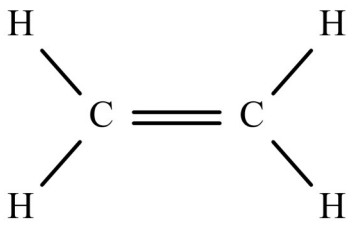
Question 5 a. Each chlorine atom (group 17, so $17 - 10 = 7$) has 7 valence electrons, so $7 + 7 = 14$ in total. b. The two chlorine atoms are joined by a single bond — **1 bonding pair**. c. After the bonding pair (2 electrons) there are

$14 - 2 = 12$ electrons left, forming **6 lone pairs** (3 on each chlorine). Checking the bookkeeping: $2 \times (\text{bonding pairs}) + 2 \times (\text{lone pairs}) = 2 \times 1 + 2 \times 6 = 2 + 12 = 14$, which matches the 14 valence electrons found in part a — so every valence electron is accounted for, either in the shared pair or in a lone pair. (Each chlorine is surrounded by $2 + 6 = 8$ electrons, an octet.)

Question 6 a. A covalent bond is a shared pair of electrons between two atoms (both non-metals); the shared pair is attracted to the nuclei of both atoms and so holds them together. b. The octet rule states that atoms tend to share or transfer electrons so as to obtain a full outer shell of eight electrons, the stable arrangement of the nearest noble gas. c. Hydrogen's outer shell is the first shell, which is full with only **two** electrons (the arrangement of helium). Hydrogen therefore aims for a duet of 2 electrons rather than an octet of 8, and forms just one covalent bond.

Question 7 Two hydrogen atoms contribute $1 + 1 = 2$ valence electrons, which form a single shared pair between them: **1 bonding pair and 0 lone pairs** (structural formula H–H). Each hydrogen atom's outer shell (the first shell) is complete with only two electrons — a duet — so the one shared pair, counted by both atoms, gives each hydrogen its full shell. No further electrons are needed, so there are no lone pairs.

Question 8 a. Ethene is drawn with the two carbon atoms joined by a double bond, each carbon also bonded to two hydrogen atoms: $H_2C = CH_2$ (see figure). b. The carbon–carbon bond is a **double bond**. c. There are four C–H single bonds (4 bonding pairs) plus the C=C double bond (2 bonding pairs), giving **6 bonding pairs**. No atom has any left-over electrons, so there are **0 lone pairs**. (Check: valence electrons $= 2 \times 4 + 4 \times 1 = 12 = 2 \times 6$.)



Question 9 - H_2: each hydrogen needs only a duet, so one shared pair — a **single** bond. - O_2: two shared pairs are needed for each oxygen to reach an octet — a **double** bond. - N_2: three shared pairs are needed for each nitrogen to reach an octet — a **triple** bond. - CO_2: each carbon–oxygen bond is a **double** bond (O=C=O).

Question 10 A nitrogen atom has 5 valence electrons and so needs 3 more to reach an octet of 8. Two nitrogen atoms therefore share **three** pairs of electrons — a triple bond — so that each nitrogen counts $3 \times 2 = 6$ shared electrons plus its own lone pair (2), giving 8. An oxygen atom has 6 valence electrons and needs only 2 more, so each oxygen shares **two** pairs with the central carbon — a double bond. In carbon dioxide the carbon (4 valence electrons, needing 4 more) forms one double bond to each oxygen; its four shared pairs total 8 electrons, an octet, while each oxygen also reaches 8. The different number of electrons each atom needs is what makes N_2 triple-bonded but the C–O bonds double.

Question 11 a. Methane's structural formula is a central carbon joined by four single lines to four hydrogen atoms; it contains **4 covalent bonds** (four C–H single bonds). b. Water's structural formula is H–O–H; it contains **2 covalent bonds** (two O–H single bonds). (The two lone pairs on oxygen are not usually drawn in a structural formula.)

Question 12 a. A nitrogen atom bonded to three hydrogen atoms has the molecular formula NH_3. b. The single pair of dots on nitrogen is **1 lone pair**; the three N–H lines are **3 bonding pairs**. c. The molecule is **ammonia**. (Nitrogen has $3 \times 2 + 2 = 8$ electrons around it — an octet.)

Question 13 Each chlorine atom has 7 valence electrons and is one electron short of a full octet of 8. When the two atoms share a single pair, each chlorine gains a share of one extra electron, bringing its count to 8 — a complete octet. A double bond would require each chlorine to share two pairs, placing $2 \times 2 = 4$ bonded electrons plus its lone pairs around the atom and exceeding eight; there is no need for this, so Cl_2 has just a single bond, with three lone pairs left on each chlorine.

Question 14 A **bonding pair** is a pair of electrons shared between two atoms; it constitutes a covalent bond and is attracted to both nuclei. A **lone pair** (non-bonding pair) is a pair of outer-shell electrons that belongs to a single atom and is not shared with any other atom. Both count towards an atom's octet, but only bonding pairs join atoms together. Ammonia, NH_3, contains **3 bonding pairs** (the three N–H bonds) and **1 lone pair** (on the nitrogen atom).

Question 15 Non-metal atoms have almost-full outer shells and a strong attraction for electrons, so they do not readily give electrons away. Instead, two non-metal atoms **share** outer-shell electrons: the shared pair is counted by *both* atoms, moving each towards a full outer shell of eight electrons (an octet), or two electrons (a duet) in the case of hydrogen. A full outer shell is the same stable, low-energy arrangement possessed by the noble gases. Atoms bond because the shared arrangement is more stable (lower in energy) than the separate atoms, so covalent bonding is favoured whenever it lets both atoms complete their outer shells.

Question 16

Molecule	Bonding pairs	Lone pairs	Highest bond order
H_2O	2	2	single
CO_2	4	4	double
N_2	3	2	triple
CH_4	4	0	single

Working: water has two O–H single bonds and two lone pairs on oxygen; carbon dioxide has two C=O double bonds (4 bonding pairs) and two lone pairs on each oxygen (4 in all); nitrogen has one triple bond (3 bonding pairs) and one lone pair on each atom (2 in all); methane has four C–H single bonds and no lone pairs. Each row satisfies $\text{VE} = 2(\text{bonding pairs}) + 2(\text{lone pairs})$: $8, 16, 10, 8$ respectively.

Question 17 a. The **molecular formula** C_2H_4 tells us only the number and kind of atoms present: two carbon atoms and four hydrogen atoms per molecule. b. The **structural formula** $H_2C=CH_2$ tells us which atoms are joined to which and the type of each bond: the two carbons are joined by a **double** bond, and each carbon carries two single C–H bonds. c. The **electron-dot (Lewis) structure** shows every outer-shell electron — each bonding pair and each lone pair. For ethene it confirms six bonding pairs and (in this case) no lone pairs. The one extra thing an electron-dot structure shows, which a structural formula usually omits, is the **lone (non-bonding) pairs** of electrons.

Question 18 a. **Carbon dioxide**: O=C=O, a double bond from carbon to each oxygen, with two lone pairs on each oxygen. **Methane**: a central carbon joined by four single bonds to four hydrogen atoms, with no lone pairs (see the methane figure in the Theory). b. Carbon dioxide has **4 bonding pairs** (two per double bond) and **4 lone pairs** (two on each oxygen). Methane has **4 bonding pairs** and **0 lone pairs**. c. A carbon atom has 4 valence electrons and needs to share in 4 more, so it forms **four bonds** in both molecules. In methane each bonding partner is hydrogen, which needs only a single shared pair to complete its duet; four hydrogen atoms therefore give four **single** bonds. In carbon dioxide each bonding partner is oxygen, which needs to share **two** pairs to complete its octet; carbon therefore forms a **double** bond to each oxygen. Either way carbon ends up sharing four pairs — eight electrons — and reaches its octet.

Chapter 2 Covalent substances — 2B Molecular shapes and polarity

Theory

A Lewis (electron dot) structure (subtopic 2A) shows how many bonding and lone (non-bonding) pairs of electrons surround each atom in a molecule, but it is drawn flat on the page. A real molecule is three-dimensional, and its **shape** — together with the **polarity** of its bonds — decides whether the molecule as a whole is polar or non-polar. This subtopic predicts both, working directly from the Lewis structure.

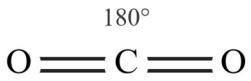
Valence shell electron pair repulsion (VSEPR). Every pair of electrons in the outer (valence) shell of the central atom is a region of negative charge, so the pairs repel one another. VSEPR theory states that these regions arrange themselves **as far apart as possible**, which minimises the repulsion between them; this arrangement fixes the shape of the molecule. To apply it, count the **regions of electron density** around the central atom:

- each **bonding region** — a single, double or triple bond to another atom — counts as **one** region (a double or triple bond is a single region of charge, because its pairs all point the same way);
- each **lone pair** on the central atom counts as one region.

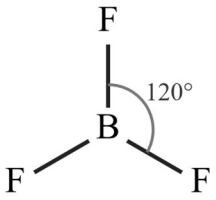
The total number of regions sets the basic geometry; the number of those regions that are **lone pairs** then decides the final shape, because a lone pair pushes the surrounding bonds closer together.

Molecular shapes. The study design names **four** shapes — **linear, bent, pyramidal** and **tetrahedral** — and asks you to predict them by VSEPR, *excluding bond angles*. A fifth arrangement, **trigonal planar**, is met in a few Units 1 & 2 molecules and is included below as **extension** (beyond the required four). The approximate bond angles in the last column are given for interest only and are **not required by the study design**.

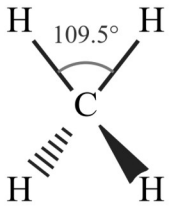
Linear (CO_2)



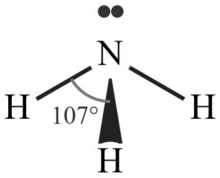
Trigonal planar (BF_3)



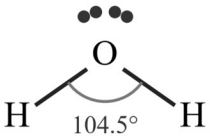
Tetrahedral (CH_4)



Trigonal pyramidal (NH_3)



Bent (H_2O)



Bonding regions	Lone pairs	Shape	Approx. angle *(not required)*	Example
2	0	linear	180°	CO_2
3	0	trigonal planar *(extension)*	120°	BF_3
4	0	tetrahedral	109.5°	CH_4

Bonding regions	Lone pairs	Shape	Approx. angle *(not required)*	Example
3	1	trigonal pyramidal	107°	NH_3
2	2	bent (V-shaped)	104.5°	H_2O

For example, each carbon atom in ethene, C_2H_4, has three regions of electron density — two C–H bonds and one C=C double bond — so the molecule is **planar** (three regions give a trigonal planar arrangement, an *extension* case beyond the four required shapes). Counting a multiple bond as one region is also what makes the central carbon of CO_2 (two C=O bonds, no lone pairs) come out as two regions, and therefore **linear**.

Lone pairs and the shape. A lone pair is held by only one nucleus, so it spreads out more than a bonding pair and repels its neighbours more strongly. Replacing a bonding pair with a lone pair therefore *squeezes* the remaining bonds closer together — which is why methane (four bonding pairs) is a full **tetrahedral**, ammonia (one lone pair) is **pyramidal** and water (two lone pairs) is **bent**, even though all three central atoms are surrounded by four regions of electron density. (The exact bond-angle values that go with this — about 109.5° in methane, 107° in ammonia and 104.5° in water — are **not required by the study design** and are quoted here only as enrichment; what is examinable is the **shape name** and the fact that a lone pair repels more strongly and so distorts the shape.)

Note the two **bent** cases. Water is bent because its oxygen has two bonding pairs **and two lone pairs** (four regions). A molecule such as SO_2, whose central atom has two bonding regions and **one** lone pair (three regions), is also bent, but with an angle closer to 120°. In both, the lone pair(s) leave the two bonds on the same side of the central atom, giving the characteristic V-shape.

Bond polarity. Whether a covalent bond is polar depends on **electronegativity** — the ability of an atom to attract the shared bonding electrons (a periodic trend from 1C). Electronegativity increases across a period and decreases down a group, so fluorine is the most electronegative element and metals are the least. When two bonded atoms have **different** electronegativities, the more electronegative atom draws the bonding electrons towards itself and gains a small partial negative charge, written $\delta-$; the other atom is left slightly electron-poor, $\delta+$. The bond then has a permanent separation of charge — a **bond dipole** — and is a **polar bond**. When the two atoms are identical, the electrons are shared evenly and the bond is **non-polar**.

The larger the electronegativity difference (ΔEN), the more polar the bond. As a rough guide, a difference below about 0.4 gives an essentially non-polar bond — this is why the C–H bonds in hydrocarbons are treated as non-polar — while larger differences give clearly polar bonds. The values below (Pauling scale) are used throughout this subtopic.

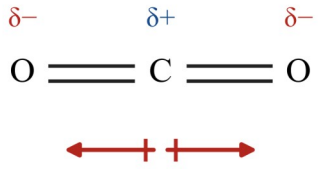
Element	H	B	C	N	O	F	S	Cl	Br
Electronegativity	2.20	2.04	2.55	3.04	3.44	3.98	2.58	3.16	2.96

Molecular polarity. A molecule that contains polar bonds is **not necessarily** a polar molecule. Each bond dipole has a direction — it points towards the $\delta-$ atom — and the polarity of the whole molecule is the **vector sum** of its bond dipoles. Two outcomes are possible:

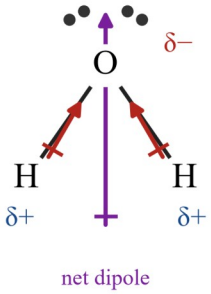
- If the polar bonds are arranged **symmetrically** around the central atom — the peripheral atoms all the same and no lone pair on the central atom — the bond dipoles are equal in size and point in balanced, opposing directions, so they **cancel**. The molecule has no net dipole and is **non-polar**. This is the case for the three symmetric shapes: linear (CO_2), trigonal planar (BF_3) and tetrahedral (CCl_4).
- If the arrangement is **not symmetric** — because the central atom carries a lone pair (bent or pyramidal), or because the peripheral atoms are not all the same — the bond dipoles do **not** cancel. There is a net dipole, and the molecule is **polar** (H_2O, NH_3, $CHCl_3$).

The classic contrast is carbon dioxide versus water. Both contain two polar bonds. In linear CO_2 the two C=O dipoles point in exactly opposite directions and cancel, so the molecule is non-polar. In bent H_2O the two O–H dipoles both point towards the oxygen but are set at an angle to each other, so they add to give a net dipole directed towards the oxygen — water is polar.

Bond dipoles equal and opposite cancel → non-polar molecule



Bond dipoles do not cancel net dipole → polar molecule



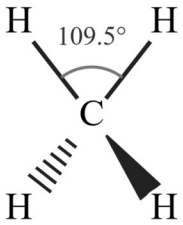
A molecule whose bonds are **all** non-polar (for example CH_4, any hydrocarbon, or CS_2) is non-polar whatever its shape, simply because there are no bond dipoles to add together.

The reasoning chain. For any small molecule the prediction runs in one direction: Lewis structure → count the bonding pairs and lone pairs on the central atom → VSEPR shape → decide whether each bond is polar (electronegativity difference) → decide whether the bond dipoles cancel by symmetry → polar or non-polar molecule. Every worked example below follows this chain.

Worked examples

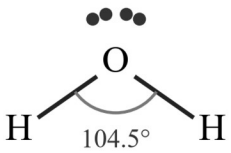
Worked Example 1 — Methane, CH_4, has a central carbon atom bonded to four hydrogen atoms, with no lone pairs on carbon. Predict the shape of the molecule and state whether CH_4 is polar. (Electronegativities: C 2.55, H 2.20.)

Working	Comment
Central atom C: 4 bonding pairs, 0 lone pairs → **4 regions** of electron density	Each single bond is one region; there are no lone pairs to add.
4 regions, all bonding → **tetrahedral**	Four regions point to the corners of a tetrahedron.
(Enrichment, not required: the H–C–H bond angle is about 109.5°.)	The four identical bonding pairs are spread as far apart as possible.
$\Delta EN(C–H) = 2.55 - 2.20 = 0.35$ → **non-polar bond**	The difference is below 0.4, so C–H is treated as non-polar.
∴ CH_4 is a **non-polar molecule**	There are no bond dipoles to add up (and the tetrahedral shape is symmetric in any case).



Worked Example 2 — Water, H_2O, has a central oxygen atom bonded to two hydrogen atoms; the oxygen also carries two lone pairs. Predict the shape, explain in terms of the lone pairs why water's shape differs from methane's even though both have four regions of electron density, and determine whether water is polar. (Electronegativities: O 3.44, H 2.20.)

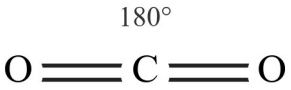
Working	Comment
Central atom O: 2 bonding pairs + 2 lone pairs → **4 regions**	Lone pairs are counted as regions of electron density.
4 regions, 2 of them lone pairs → **bent (V-shaped)**	The two bonding pairs are left on the same side.
Reason: two lone pairs repel more strongly than bonding pairs, pushing the two O–H bonds closer together	This is why water is **bent** rather than tetrahedral like methane — lone-pair repulsion distorts the shape.
(Enrichment, not required: the H–O–H bond angle is about 104.5°, a little less than methane's.)	Quoted here only for interest.
$\Delta EN(O–H) = 3.44 - 2.20 = 1.24$ → **polar bond**; O is δ−, H is δ+	Oxygen is far more electronegative than hydrogen.
Bent shape → the two O–H dipoles do **not** cancel → net dipole	The molecule is not symmetric.
∴ H_2O is a **polar molecule**	



Worked Example 3 — Explain, using VSEPR and bond polarity, why carbon dioxide, CO_2, is a non-polar molecule even though it contains polar bonds. (Electronegativities: C 2.55, O 3.44.)

The central carbon is joined to the two oxygen atoms by double bonds and has no lone pairs. A double bond is a single region of electron density, so carbon has **2 regions**; these point in opposite directions, giving a **linear** molecule, O=C=O.

Each C=O bond has $\Delta EN = 3.44 - 2.55 = 0.89$, so it is **polar**, with each oxygen δ− and the carbon δ+. However, because the molecule is linear and symmetric, the two bond dipoles are equal in magnitude and point in exactly opposite directions along the same line, so they cancel and leave no net dipole.

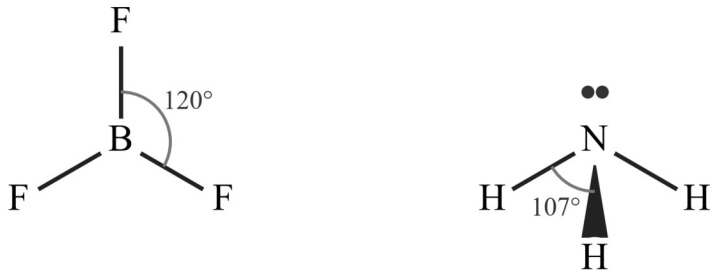


∴ although CO_2 contains two polar bonds, its symmetric linear shape makes it a **non-polar molecule**.

Worked Example 4 — Boron trifluoride, BF_3, and ammonia, NH_3, both have a central atom bonded to three other atoms. Predict and compare their shapes and their polarities. (Electronegativities: B 2.04, F 3.98, N 3.04, H 2.20.)

Boron trifluoride. Boron has 3 bonding pairs and 0 lone pairs → 3 regions → **trigonal planar** (an *extension* shape beyond the four required by the study design). Each B–F bond has $\Delta EN = 3.98 - 2.04 = 1.94$, so it is strongly polar (each fluorine δ−). The three equal dipoles point outwards symmetrically and cancel, so BF_3 is **non-polar**.

Ammonia. Nitrogen has 3 bonding pairs **and 1 lone pair** → 4 regions → **trigonal pyramidal**. Each N–H bond has $\Delta EN = 3.04 - 2.20 = 0.84$, so it is polar (nitrogen δ−). The lone pair makes the arrangement unsymmetrical, so the three N–H dipoles do not cancel; they add to a net dipole directed through the nitrogen, and NH_3 is **polar**.



∴ although both molecules have three bonds to the central atom, the lone pair on nitrogen changes the shape from planar to pyramidal and makes ammonia polar, whereas boron trifluoride — with no lone pair and a symmetric shape — is non-polar.

Practice questions

Question 1 — Carbon tetrachloride, CCl_4, has a central carbon atom bonded to four chlorine atoms, with no lone pairs on carbon. (Electronegativities: C 2.55, Cl 3.16.)

a. State the number of bonding pairs and lone pairs around the carbon atom.
b. Name the shape of the molecule.
c. State whether the C–Cl bonds are polar, and whether the CCl_4 molecule is polar. Explain.

Question 2 — Sulfur dioxide, SO_2, has a central sulfur atom with two bonding regions (to the two oxygen atoms) and one lone pair. (Electronegativities: S 2.58, O 3.44.)

a. State the total number of regions of electron density around the sulfur atom.
b. Name the shape of the molecule.

c. Explain whether SO_2 is a polar molecule.

Question 3 — Use the electronegativity values H 2.20, C 2.55, O 3.44, F 3.98 and Cl 3.16.

a. Calculate the electronegativity difference for each of the bonds H–F, C–H, O–H and Cl–Cl.
b. Classify each bond as polar or non-polar.
c. For each polar bond, state which atom carries the δ− charge, and identify the most polar bond.

Question 4 — Carbon dioxide, CO_2, and water, H_2O, both contain two polar bonds.

a. Name the shape of CO_2 and the shape of H_2O.
b. State whether the C=O bond and the O–H bond are polar.
c. Explain why CO_2 is a non-polar molecule while H_2O is polar.

Question 5 *(Extension — trigonal planar is beyond the four shapes required by the study design.)* — Boron trichloride, BCl_3, has a central boron atom bonded to three chlorine atoms, with no lone pairs on boron. (Electronegativities: B 2.04, Cl 3.16.)

a. Predict the shape of the molecule.
b. State whether the B–Cl bonds are polar.
c. Explain whether BCl_3 is a polar molecule.

Question 6 — Chloromethane, CH_3Cl, can be thought of as methane with one hydrogen atom replaced by a chlorine atom. (Electronegativities: C 2.55, H 2.20, Cl 3.16.)

a. Name the shape around the carbon atom.
b. Classify the C–H and C–Cl bonds as polar or non-polar.
c. Explain, in terms of symmetry, why CH_3Cl is polar whereas CH_4 is non-polar.

Question 7 — Phosphorus trichloride, PCl_3, has a central phosphorus atom bonded to three chlorine atoms, with one lone pair on phosphorus. Predict its shape and state, with a reason, whether the molecule is polar. (Electronegativities: P 2.19, Cl 3.16.)

Question 8 — Using the electronegativity values N 3.04, H 2.20, C 2.55, O 3.44 and Br 2.96, classify each of the bonds N–H, C–C, C=O and Br–Br as polar or non-polar, and for each polar bond state which atom is δ−.

Question 9 — Carbon disulfide, CS_2, has a central carbon joined to two sulfur atoms by double bonds, with no lone pairs on carbon. Predict its shape and state, with a reason, whether it is polar. (Electronegativities: C 2.55, S 2.58.)

Question 10 — Oxygen difluoride, OF_2, has a central oxygen atom bonded to two fluorine atoms, with two lone pairs on oxygen. Predict its shape and explain whether it is polar. (Electronegativities: O 3.44, F 3.98.)

Question 11 — Tetrafluoromethane, CF_4, and trifluoromethane (fluoroform), CHF_3, are both tetrahedral. Explain why one of them is non-polar and the other is polar. (Electronegativities: C 2.55, F 3.98, H 2.20.)

Question 12 — Explain, using VSEPR, why ammonia is **trigonal pyramidal** whereas methane is **tetrahedral**, even though the central atom in each is surrounded by four regions of electron density. In your answer, describe how the lone pair on nitrogen affects the arrangement of the three N–H bonds.

Question 13 — Hydrogen cyanide, HCN, is a linear molecule (H–C≡N); its central carbon has two regions of electron density and no lone pairs. Explain why HCN is a polar molecule. (Electronegativities: H 2.20, C 2.55, N 3.04.)

Question 14 — Methanal (formaldehyde), CH_2O, has a central carbon atom bonded to two hydrogen atoms and, by a double bond, to one oxygen atom, with no lone pairs on carbon. The three bonds lie in a plane around the carbon. Explain whether the molecule is polar. (Electronegativities: C 2.55, H 2.20, O 3.44.)

Question 15 — Carbon dioxide, CO_2, and sulfur dioxide, SO_2, are both triatomic molecules in which two oxygen atoms are bonded to a central atom. Explain, in terms of shape, why CO_2 is non-polar but SO_2 is polar.

Question 16 — Nitrogen trifluoride, NF_3, has a central nitrogen atom bonded to three fluorine atoms, with one lone pair on nitrogen. Predict its shape and explain whether it is polar. (Electronegativities: N 3.04, F 3.98.)

Question 17 — Beryllium chloride, $BeCl_2$, in the gas phase has a central beryllium atom bonded to two chlorine atoms, with no lone pairs on beryllium. Predict its shape, and explain whether the molecule is polar. (Electronegativities: Be 1.57, Cl 3.16.)

Question 18 — A molecule with the general formula XY_4 is found to have four polar X–Y bonds, yet the molecule as a whole is non-polar. A different molecule, ZY_3, also has polar bonds but is found to be polar.

a. What does the non-polarity of XY_4 tell you about its shape and the arrangement of its bonds?

b. Suggest why ZY_3 is polar, referring to the electron pairs around atom Z.

c. Name one real molecule that behaves like XY_4 and one that behaves like ZY_3.

Answers

1 a 4 bonding pairs, 0 lone pairs; b tetrahedral; c C–Cl polar (ΔEN 0.61), but the four dipoles cancel by symmetry → CCl_4 non-polar. **2** a 3 regions; b bent; c S–O bonds polar and the bent shape means they do not cancel → polar. **3** a H–F 1.78, C–H 0.35, O–H 1.24, Cl–Cl 0; b H–F polar, C–H non-polar, O–H polar, Cl–Cl non-polar; c F is δ− in H–F, O is δ− in O–H; most polar bond = H–F. **4** a CO_2 linear, H_2O bent; b both polar; c linear CO_2 is symmetric so its dipoles cancel (non-polar); bent H_2O is not symmetric so its dipoles add to a net dipole (polar). **5** a trigonal planar *(extension)*; b polar (ΔEN 1.12); c the three dipoles cancel by symmetry → BCl_3 non-polar. **6** a tetrahedral; b C–H non-polar, C–Cl polar; c the single C–Cl dipole is not balanced by an opposing identical dipole, so CH_3Cl has a net dipole (polar); in CH_4 the four identical bonds cancel (non-polar). **7** trigonal pyramidal; P–Cl polar (ΔEN 0.97) and the lone pair makes the shape unsymmetrical → polar. **8** N–H polar (N δ−), C–C non-polar, C=O polar (O δ−), Br–Br non-polar. **9** linear; C=S essentially non-polar (ΔEN 0.03) → CS_2 non-polar. **10** bent; O–F polar (ΔEN 0.54) and bent → polar. **11** CF_4 has four identical polar bonds arranged symmetrically (tetrahedral) so its dipoles cancel → non-polar; in CHF_3 one C–F is replaced by a (non-polar) C–H, breaking the symmetry, so the dipoles do not cancel → polar. **12** ammonia has a lone pair (4 regions, one a lone pair) → **trigonal pyramidal**, whereas methane has four bonding pairs → **tetrahedral**; the lone pair repels the bonding pairs more strongly, pushing the three N–H bonds closer together. **13** the two ends of the linear molecule are different — C≡N is polar (N δ−) while C–H is essentially non-polar — so the bond dipoles do not cancel; there is a net dipole towards the nitrogen → polar. **14** planar around the carbon; the C=O bond is polar and the molecule is not symmetric (oxygen differs from the two hydrogens), so the dipoles do not cancel → polar. **15** CO_2: carbon has no lone pair → 2 regions → linear → the two polar dipoles cancel → non-polar. SO_2: sulfur has a lone pair → 3 regions → bent → the two dipoles do not cancel → polar. **16** trigonal pyramidal; N–F polar (ΔEN 0.94) and the lone pair makes the shape unsymmetrical → polar. **17** linear; Be–Cl polar (ΔEN 1.59) but the two dipoles cancel by symmetry → non-polar. **18** a it must be symmetric — a tetrahedral arrangement of four identical bonds whose dipoles cancel; b atom Z carries a lone pair, so ZY_3 is trigonal pyramidal (not planar) and the dipoles do not cancel; c e.g. XY_4 like CCl_4 (or CF_4), ZY_3 like NH_3 (or PCl_3).

Fully-worked solutions

Question 1 a. Carbon forms four single bonds to chlorine and has no lone pairs, so there are **4 bonding pairs and 0 lone pairs** (4 regions of electron density). b. Four regions, all bonding, point to the corners of a tetrahedron: the shape is **tetrahedral**. c. $\Delta EN(C–Cl) = 3.16 - 2.55 = 0.61$, which is above 0.4, so each **C–Cl bond is polar** (Cl is δ−). However, the four identical dipoles point symmetrically to the corners of the tetrahedron and cancel exactly, leaving no net dipole. ∴ CCl_4 is a **non-polar molecule**.

Question 2 a. Sulfur has two bonding regions (to the oxygens) plus one lone pair, giving **3 regions** of electron density. b. Three regions, one of them a lone pair, gives a **bent** molecule. The lone pair leaves the two S–O bonds on the same side of the sulfur, giving the characteristic V-shape. c. $\Delta EN(S–O) = 3.44 - 2.58 = 0.86$, so each S–O bond is polar (O is δ−). The molecule is bent, not linear, so the two bond dipoles do not point in opposite directions and do not cancel; there is a net dipole. ∴ SO_2 is **polar**.

Question 3 a. H–F: $3.98 - 2.20 = 1.78$; C–H: $2.55 - 2.20 = 0.35$; O–H: $3.44 - 2.20 = 1.24$; Cl–Cl: $3.16 - 3.16 = 0$. b. Using the 0.4 guide: **H–F polar**, **C–H non-polar**, **O–H polar**, **Cl–Cl non-polar**. c. In H–F the fluorine is δ−; in O–H the oxygen is δ−. The **largest difference (1.78) is H–F**, so it is the most polar bond.

Question 4 a. CO_2 is **linear** (carbon has two regions, no lone pairs); H_2O is **bent** (oxygen has four regions, two of them lone pairs). b. Both bonds are polar: $\Delta EN(C=O) = 0.89$ and $\Delta EN(O–H) = 1.24$, each above 0.4. c. In linear CO_2 the two C=O dipoles are equal and point in exactly opposite directions, so they cancel and the molecule has no net dipole — it is non-polar. In bent H_2O the two O–H dipoles point towards the oxygen but are set at an angle to each other, so they add rather than cancel, giving a net dipole towards the oxygen — the molecule is polar. The difference is entirely due to shape.

Question 5 a. Boron has 3 bonding pairs and 0 lone pairs → 3 regions → **trigonal planar** *(extension — beyond the four required shapes)*. b. $\Delta EN(B–Cl) = 3.16 - 2.04 = 1.12$, above 0.4, so the **B–Cl bonds are polar** (Cl is δ−). c. The

three equal dipoles point outwards at 120° to one another in a symmetric, planar arrangement, so they cancel. ∴ BCl_3 is a **non-polar molecule**.

Question 6 a. The carbon has four bonding pairs and no lone pairs, so the shape around carbon is **tetrahedral**. b. $\Delta EN(C–H) = 0.35$ → **non-polar**; $\Delta EN(C–Cl) = 0.61$ → **polar**. c. In CH_4 all four C–H bonds are identical and arranged symmetrically, so any small dipoles cancel and the molecule is non-polar. In CH_3Cl one bond (C–Cl) is polar and different from the other three; its dipole is not balanced by an equal, opposite dipole, so the molecule has a **net dipole** and is **polar**. Replacing one atom has broken the symmetry.

Question 7 Phosphorus has 3 bonding pairs and 1 lone pair → 4 regions → **trigonal pyramidal**. $\Delta EN(P–Cl) = 3.16 - 2.19 = 0.97$, so the P–Cl bonds are polar (Cl is δ−). Because of the lone pair the shape is not symmetric, so the three dipoles do not cancel; there is a net dipole. ∴ PCl_3 is **polar**.

Question 8 $\Delta EN(N–H) = 3.04 - 2.20 = 0.84$ → **polar**, N is δ−. $\Delta EN(C–C) = 0$ → **non-polar**. $\Delta EN(C=O) = 3.44 - 2.55 = 0.89$ → **polar**, O is δ−. $\Delta EN(Br–Br) = 0$ → **non-polar**.

Question 9 The carbon has two double bonds and no lone pairs, so it has **2 regions → linear** (S=C=S). $\Delta EN(C=S) = 2.58 - 2.55 = 0.03$, well below 0.4, so the C=S bonds are essentially **non-polar**. With no bond dipoles to add, CS_2 is a **non-polar molecule** (and its linear shape would make it non-polar in any case).

Question 10 Oxygen has 2 bonding pairs and 2 lone pairs → 4 regions → **bent**. $\Delta EN(O–F) = 3.98 - 3.44 = 0.54$, above 0.4, so each O–F bond is polar (F is δ−). Because the molecule is bent, the two dipoles do not cancel; there is a net dipole. ∴ OF_2 is **polar**.

Question 11 Both molecules are tetrahedral. In CF_4 the four bonds are identical polar C–F bonds (ΔEN 1.43) arranged symmetrically, so their dipoles cancel exactly and the molecule is **non-polar**. In CHF_3 one of the four positions is a (non-polar) C–H bond instead of a C–F bond, so the four dipoles are no longer identical and do not cancel; the molecule has a **net dipole** and is **polar**. Symmetry, not the bond polarity itself, decides the difference.

Question 12 Both nitrogen (in NH_3) and carbon (in CH_4) are surrounded by four regions of electron density, so both are based on the tetrahedral arrangement. In methane all four regions are **bonding pairs**, so all four point to the corners of a tetrahedron and the molecule is **tetrahedral**. In ammonia one of the four regions is a **lone pair**, which is held by only the nitrogen nucleus and so spreads out and repels the bonding pairs more strongly than another bonding pair would. Only the three N–H **bonds** define the visible shape, so ammonia is **trigonal pyramidal**, and the extra lone-pair repulsion pushes the three N–H bonds slightly closer together than in methane. (The exact bond-angle values are not required by the study design.)

Question 13 Although HCN is linear, its two ends are **not the same**. The C≡N bond is polar — $\Delta EN = 3.04 - 2.55 = 0.49$, so nitrogen is δ− — while the C–H bond is essentially non-polar (ΔEN 0.35). Because the two bond dipoles are unequal and are not arranged to oppose one another symmetrically, they do not cancel. The result is a **net dipole** directed towards the nitrogen end, so HCN is a **polar molecule**.

Question 14 The carbon has three regions of electron density — two C–H single bonds and one C=O double bond (counted as one region) — and no lone pairs, so the three bonds lie in a **plane** around the carbon (a trigonal planar arrangement, an *extension* case beyond the four required shapes). The C=O bond is polar (ΔEN 0.89, O is δ−) while the two C–H bonds are essentially non-polar. Because the oxygen differs from the two hydrogens, the arrangement is not symmetric and the bond dipoles do not cancel; there is a net dipole towards the oxygen. ∴ CH_2O is **polar**.

Question 15 In CO_2 the central carbon has no lone pair, so it has only **2 regions** of electron density and the molecule is **linear**. The two polar C=O dipoles point in exactly opposite directions and cancel, so CO_2 is non-polar. In SO_2 the central sulfur carries a **lone pair**, giving **3 regions** and a **bent** molecule. In the bent shape the two polar S–O dipoles do not point in opposite directions, so they do not cancel; there is a net dipole and SO_2 is polar. The contrast is due entirely to the lone pair on sulfur changing the shape.

Question 16 Nitrogen has 3 bonding pairs and 1 lone pair → 4 regions → **trigonal pyramidal**. ΔEN(N–F) $= 3.98 - 3.04 = 0.94$, above 0.4, so each N–F bond is polar (F is δ−). The lone pair makes the arrangement unsymmetrical, so the three dipoles do not cancel; there is a net dipole. ∴ NF_3 is **polar**.

Question 17 Beryllium has 2 bonding pairs and 0 lone pairs → 2 regions → **linear** (Cl–Be–Cl). ΔEN(Be–Cl) $= 3.16 - 1.57 = 1.59$, so each Be–Cl bond is strongly polar (Cl is δ−). But because the molecule is linear and symmetric, the two equal dipoles point in exactly opposite directions and cancel. ∴ gaseous $BeCl_2$ is a **non-polar molecule**.

Question 18 a. For a molecule with four polar bonds to be non-polar, the bond dipoles must cancel exactly. This requires a **symmetric arrangement** — the four identical bonds pointing to the corners of a **tetrahedron** — so that every dipole is balanced by the others. b. If ZY_3 is polar, atom Z must carry a **lone pair** as well as its three bonding pairs. The lone pair makes the molecule **trigonal pyramidal** rather than trigonal planar, so the three bond dipoles no longer cancel and a net dipole remains. c. A molecule that behaves like XY_4 is CCl_4 (or CF_4); a molecule that behaves like ZY_3 is NH_3 (or PCl_3).

Chapter 2 Covalent substances — 2C Properties of covalent compounds and intermolecular forces

Theory

Subtopics 2A and 2B built up a picture of the individual covalent molecule: atoms sharing electron pairs, arranged in a definite shape, and — depending on that shape and on any difference in electronegativity — either polar or non-polar. This subtopic turns from the single molecule to the **bulk substance**: a sample of water, of chlorine gas or of solid iodine contains an enormous number of molecules, and it is the forces *between* those molecules that decide whether the substance is a gas, a liquid or a solid, how easily it melts and boils, whether it conducts electricity and what it dissolves in.

Two very different kinds of attraction. In any molecular substance there are two attractions acting on completely different length scales, and keeping them apart is the key to the whole subtopic. **Intramolecular bonding** is the *covalent bonding within* a molecule — the shared pairs of electrons that hold, say, the two hydrogen atoms and one oxygen atom together as a water molecule. These bonds are **strong**. **Intermolecular forces** (often abbreviated **IMF**) are the much *weaker* attractions *between* one whole molecule and its neighbours. A useful rule of thumb is that intermolecular forces are only a few per cent as strong as covalent bonds. Everything about the physical behaviour of a molecular substance follows from this large difference in strength.

Melting and boiling overcome the weak forces, not the strong ones. When a molecular substance melts or boils, the molecules move apart from one another but each molecule stays intact — the covalent bonds inside it are *not* broken. Melting ice or boiling water separates H_2O molecules from each other by overcoming the intermolecular forces; the steam produced is still made of H_2O molecules, their O–H covalent bonds untouched. Because only the weak intermolecular forces have to be overcome, molecular substances have **low melting points and low boiling points** compared with ionic or metallic substances (whose strong bonding extends through the whole lattice). It also explains the **physical state at room temperature**: substances made of small molecules with the weakest intermolecular forces (such as O_2, N_2, CO_2 and CH_4) are gases at 25 °C, those with somewhat stronger forces are volatile liquids (H_2O, ethanol), and only those with the strongest intermolecular forces or the largest molecules are solids (I_2, glucose) — and even these are usually soft, low-melting solids.

There are **three types of intermolecular force** in the Units 1 & 2 course. They are listed below from weakest to strongest for molecules of *similar size*.

Dispersion forces. Dispersion forces act between **all** molecules and atoms, whether polar or not. The electrons in a molecule are in constant motion, so at any instant they may be spread slightly unevenly, giving the molecule a fleeting, momentary dipole. This temporary dipole attracts the electrons of a neighbouring molecule, inducing a matching dipole in it, and the two weakly attract. Because the effect depends on how many electrons a molecule has and how easily its electron cloud can be distorted, **dispersion forces get stronger as the number of electrons (and hence the size and mass) of the molecule increases**. For a *non-polar* molecular substance, dispersion forces are the *only* intermolecular force present, so its melting and boiling points are governed entirely by molecular size.

Dipole–dipole attraction. A **polar** molecule has a permanent dipole — a δ+ end and a δ− end (established in 2B from the molecule's shape and bond polarity). In the bulk substance these permanent dipoles line up so that the δ+ end of one molecule attracts the δ− end of the next. This **dipole–dipole attraction** acts *in addition to* dispersion forces, so for two substances of similar size the polar one is held together more strongly than the non-polar one and therefore has the higher melting and boiling point. Note that a polar molecule always has dispersion forces as well; dipole–dipole is an *extra* attraction on top.

Hydrogen bonding. Hydrogen bonding is a specially strong dipole–dipole attraction, and it is the **strongest** of the three intermolecular forces. It occurs only when a hydrogen atom is *covalently bonded to nitrogen, oxygen or fluorine* — the three small, highly electronegative atoms. Such a bond (N–H, O–H or F–H) is very strongly polarised, leaving the hydrogen with a large δ+ charge; this hydrogen is then strongly attracted to a lone pair on the N, O or F atom of a neighbouring molecule. Substances that hydrogen bond include water, ammonia (NH_3), hydrogen fluoride (HF) and the alcohols. It is worth stressing the condition: HCl and H_2S do *not* hydrogen bond, because in them the hydrogen is bonded to chlorine and to sulfur, not to N, O or F — they are held together only by dipole–dipole and dispersion forces.

Comparing and ranking substances. To predict the *relative* melting or boiling points of molecular substances, the reasoning always runs in the same chain: **identify the strongest intermolecular force in each substance, then take account of molecular size (number of electrons).** For molecules of *similar* size the order of strength is dispersion < dipole–dipole < hydrogen bonding, so the substance with the strongest *type* of force boils highest. When the molecules differ greatly in size, the rising strength of dispersion forces can outweigh the type of force: a large non-polar molecule can boil at a higher temperature than a small polar one. A good justification therefore names the *type* of force **and** compares molecular size — never one alone. The strength of hydrogen bonding is dramatically illustrated by water: if water were held together only by dispersion and dipole–dipole forces, like its heavier relatives H_2S, H_2Se and H_2Te, it would be expected to boil at about −92 °C; instead it boils at +100 °C, roughly 192 °C higher, entirely because of hydrogen bonding.

Non-conduction of electricity. Electrical conduction requires *mobile charged particles* — free-moving ions or free-moving electrons. A molecular substance is built from whole, electrically neutral molecules; it contains no ions and no delocalised electrons. There are therefore no charge carriers free to move, so **molecular substances do not conduct electricity** as solids, as liquids or (for those that do not react with water) when dissolved. This is a sharp contrast with ionic compounds, which conduct when molten or dissolved because their ions become free to move, and with metals, which conduct because of their delocalised electrons.

Solubility: "like dissolves like". Whether a molecular substance dissolves in a given solvent depends on whether solute–solvent attractions can replace the attractions being broken. **Polar** solutes (and those that can hydrogen bond) dissolve well in **polar** solvents such as water, because the solute molecules can form dipole–dipole attractions or hydrogen bonds with the solvent; ammonia, ethanol and sugars are very soluble in water for this reason. **Non-polar** solutes dissolve in **non-polar** solvents but are almost insoluble in water: a non-polar molecule such as iodine or an oil cannot form strong enough attractions with polar water molecules to break into the extensively hydrogen-bonded water structure. This is the origin of the familiar rule that *like dissolves like*.

Worked examples

Worked Example 1 — State the strongest type of intermolecular force present in each of the following substances, giving a reason: chlorine Cl_2, hydrogen chloride HCl, and ammonia NH_3.

Working	Comment
Cl_2: dispersion forces	Cl_2 is a non-polar molecule, so the only intermolecular force is the dispersion force present between all molecules.
HCl: dipole–dipole attraction	HCl is polar (a permanent dipole), so it has dipole–dipole attraction *as well as* dispersion; the hydrogen is bonded to Cl (not N, O or F), so there is **no** hydrogen bonding.
NH_3: hydrogen bonding	In NH_3 hydrogen is bonded to nitrogen, one of N, O and F, so the molecules hydrogen bond — the strongest intermolecular force.

Worked Example 2 — Methane CH_4, hydrogen sulfide H_2S and ammonia NH_3 have boiling points of −60 °C, −33 °C and −161 °C (not in that order). Match each substance to its boiling point and justify the ranking in terms of intermolecular forces.

Working	Comment
CH_4 is non-polar → dispersion only; it also has the fewest electrons (10)	Weakest intermolecular forces of the three, so it has the **lowest** boiling point: −161 °C.
H_2S is polar → dipole–dipole + dispersion (H on S, so no H-bond); 18 electrons	Stronger than CH_4 (extra dipole–dipole + more electrons), so a **middle** boiling point: −60 °C.
NH_3 is polar and hydrogen bonds (H on N)	Hydrogen bonding is the strongest force, so NH_3 has the **highest** boiling point (−33 °C) even though it has fewer

Working	Comment
	electrons (10) than H_2S.
Ranking of boiling point: $CH_4 < H_2S < NH_3$	Type of force wins here: hydrogen bonding lifts NH_3 above H_2S despite its smaller size.

Worked Example 3 — Solid carbon dioxide ("dry ice") sublimes to a gas at −78 °C and does not conduct electricity. Explain both observations in terms of the structure and bonding of carbon dioxide.

Carbon dioxide is a **molecular** substance: the sample consists of discrete CO_2 molecules, each held together internally by strong covalent bonds, but attracted to one another only by weak intermolecular forces. Because CO_2 is a small, non-polar molecule, those forces are weak **dispersion forces** only. Changing state from solid to gas requires only that these weak dispersion forces be overcome — the strong covalent bonds *within* each molecule are not broken — so very little energy is needed and this happens at a very low temperature (−78 °C). Carbon dioxide does not conduct electricity because it is made of neutral molecules: it contains no ions and no free-moving (delocalised) electrons, so there are no mobile charged particles to carry a current.

∴ the low sublimation temperature reflects the weak dispersion forces *between* molecules, and the lack of conduction reflects the absence of any mobile charged particles.

Worked Example 4 — Water (H_2O) boils at 100 °C, whereas hydrogen sulfide (H_2S) boils at −60 °C, even though an H_2S molecule has more electrons than an H_2O molecule. Explain this difference.

Both molecules are bent and polar, so both have dispersion forces and dipole–dipole attraction. On the basis of size alone H_2S (18 electrons) has *more* electrons than H_2O (10 electrons) and therefore slightly *stronger* dispersion forces, which would tend to give H_2S the higher boiling point. The decisive difference is that in water the hydrogen atoms are bonded to **oxygen**, so water molecules **hydrogen bond** to one another, whereas in H_2S the hydrogen is bonded to sulfur (not N, O or F), so hydrogen bonding cannot occur and the molecules are held only by dipole–dipole and dispersion forces. Hydrogen bonding is much stronger than these, so far more energy is needed to separate water molecules, and this outweighs the greater dispersion forces in H_2S.

∴ water's much higher boiling point is due to hydrogen bonding, an intermolecular force available to H_2O but not to H_2S.

Practice questions

Question 1 — Consider a sample of chlorine, which consists of Cl_2 molecules.

a. Name the type of bonding *within* a Cl_2 molecule (the intramolecular bonding).
b. Name the type of force acting *between* neighbouring Cl_2 molecules.
c. State which of these is overcome when solid chlorine melts, and hence explain why chlorine has a very low melting point.

Question 2 — For each substance below, state the strongest type of intermolecular force present and give a brief reason.

a. oxygen, O_2
b. hydrogen chloride, HCl
c. water, H_2O

Question 3 — The halogens have the following boiling points: fluorine F_2 −188 °C, chlorine Cl_2 −34 °C, bromine Br_2 59 °C, iodine I_2 184 °C.

a. State the only type of intermolecular force present between the molecules of these substances, and explain why it is the only type.
b. Explain the trend in boiling point from F_2 to I_2.

c. Using the boiling points (and noting that bromine melts at −7 °C and iodine at 114 °C), state the physical state of each halogen at 25 °C.

Question 4 — Hydrogen bonding is the strongest of the three intermolecular forces.

a. State the condition that must be met for hydrogen bonding to occur between molecules.
b. For each of HF, CH_4 and NH_3, state whether the pure substance can form hydrogen bonds between its molecules, giving a reason.
c. Hydrogen fluoride (HF) boils at 20 °C but hydrogen chloride (HCl) boils at −85 °C, even though an HCl molecule has more electrons than an HF molecule. Explain this difference.

Question 5 — Solubility of molecular substances follows the rule "like dissolves like".

a. State what this rule means in terms of the polarity of solute and solvent.
b. Iodine (I_2) is a non-polar molecular substance. Predict whether it dissolves readily in water, and explain your prediction.
c. Explain, in terms of intermolecular forces, why ammonia (NH_3) is very soluble in water.

Question 6 — Molecular substances share several characteristic physical properties.

a. Explain why solid glucose, a molecular substance, does not conduct electricity.
b. Explain, in terms of the forces that must be overcome, why molecular substances generally have low melting points.
c. Compare the strength of the covalent bonds *within* a molecule with the strength of the intermolecular forces *between* molecules, and state which is overcome on boiling.

Question 7 — For each of the following molecular substances, state the strongest type of intermolecular force present: carbon dioxide CO_2, methanol CH_3OH, hydrogen bromide HBr, nitrogen N_2.

Question 8 — Explain why molecular substances generally have much lower melting and boiling points than ionic or metallic substances. Your answer should refer to the forces that are overcome when each type of substance melts.

Question 9 — The Group 14 hydrides have the following boiling points: methane CH_4 −161 °C, silane SiH_4 −112 °C, germane GeH_4 −88 °C. All three are non-polar tetrahedral molecules. Rank the three substances in order of increasing boiling point (the data already do this) and justify the trend in terms of intermolecular forces.

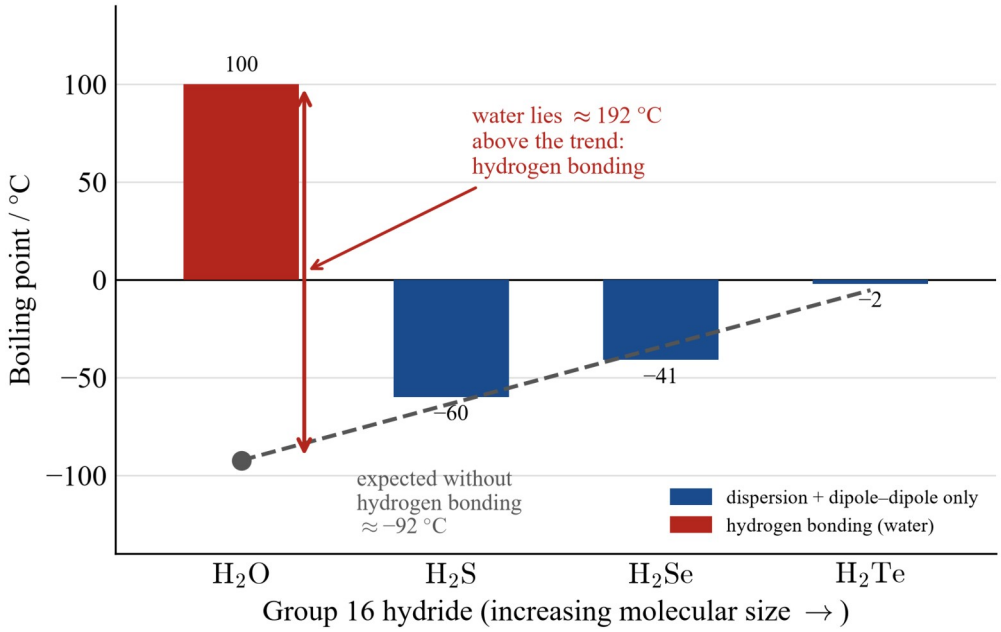
Question 10 — Three substances have similar-sized molecules: fluorine F_2, hydrogen chloride HCl and methanol CH_3OH each contain 18 electrons. Their boiling points are −85 °C, 65 °C and −188 °C (not in that order).

a. Explain why the dispersion forces in the three substances are expected to be very similar.
b. Match each substance to its boiling point.
c. Justify your ranking by referring to the type of intermolecular force in each substance.

Question 11 — Ethanol (CH_3CH_2OH) and dimethyl ether (CH_3OCH_3) have the *same* molecular formula, C_2H_6O, and therefore the same number of electrons, yet ethanol boils at 78 °C while dimethyl ether boils at −24 °C. Explain this large difference in boiling point.

Question 12 — Explain why carbon dioxide does not conduct electricity, either as a gas or as a solid (dry ice). Refer to the particles present.

Question 13 — The figure below shows the boiling points of the Group 16 hydrides. The three heavier hydrides lie on a trend line (dashed); water lies far above it.



a. Describe and explain the trend in boiling point among H_2S, H_2Se and H_2Te.

b. Extrapolating the trend line predicts that water "should" boil at about −92 °C, but it actually boils at 100 °C. Identify the intermolecular force responsible for this difference and explain why it is present in water but not in the heavier hydrides.

c. State what the height of the red arrow (about 192 °C) represents.

Question 14 — Table sugar (sucrose) is a molecular substance whose molecules carry many O–H groups; cooking oil consists of large non-polar molecules. Explain, in terms of polarity and intermolecular forces, why sugar dissolves readily in water but cooking oil does not.

Question 15 — A student claims that "when water boils, the O–H bonds in the water molecules break". Explain why this claim is incorrect, and state correctly what happens to the water molecules and to the forces between them when water boils.

Question 16 — Ammonia (NH_3) boils at −33 °C, whereas phosphine (PH_3) boils at −88 °C, even though a PH_3 molecule has more electrons than an NH_3 molecule. By directly comparing the two substances, explain this difference in boiling point.

Question 17 — Two molecular substances are described below.

- Substance X is a small non-polar gas at room temperature.
- Substance Y is a liquid at room temperature whose molecules contain O–H groups and which mixes completely with water.

a. Identify the strongest type of intermolecular force acting in each of X and Y.

b. Predict which substance has the higher boiling point, and justify your prediction.

c. Predict which substance is the more soluble in water, and justify your prediction.

Question 18 — The table gives data for four molecular substances.

Substance	Formula	Electrons per molecule	Polar?	Boiling point / °C
P	N_2	14	no	−196
Q	HCl	18	yes	−85
R	HBr	36	yes	−67
S	CH_3OH	18	yes	65

a. State the strongest type of intermolecular force present in each of P, Q, R and S.

b. Q and R are both polar and have the same type of intermolecular force, yet R boils at a higher temperature than Q. Explain why, referring to both the type of force and molecular size.

c. Q and S have the same number of electrons, yet S boils about 150 °C higher than Q. Explain this difference.

d. Predict which of the four substances is the most soluble in water, and justify your choice.

Answers

1 a covalent bonding; b dispersion forces; c the dispersion forces between molecules are overcome (not the covalent bonds), and because these forces are very weak the melting point is very low. **2** a dispersion (non-polar); b dipole–dipole (polar, but H on Cl so no H-bond); c hydrogen bonding (H on O). **3** a dispersion forces, because the halogen molecules are non-polar; b boiling point rises $F_2 \rightarrow I_2$ as molecules gain electrons/size, strengthening dispersion forces; c F_2 gas, Cl_2 gas, Br_2 liquid, I_2 solid. **4** a a hydrogen atom must be covalently bonded to N, O or F; b HF yes (H on F), CH_4 no (H on C), NH_3 yes (H on N); c HF hydrogen bonds but HCl only has dipole–dipole/dispersion, and hydrogen bonding outweighs HCl's larger dispersion, so HF boils higher. **5** a polar solutes dissolve in polar solvents, non-polar solutes in non-polar solvents; b no — I_2 is non-polar and cannot form strong attractions with polar water; c NH_3 hydrogen bonds with water, allowing it to mix. **6** a it contains only neutral molecules — no mobile ions or free electrons; b only weak intermolecular forces need be overcome; c covalent bonds (strong) are much stronger than intermolecular forces (weak); boiling overcomes the intermolecular forces only. **7** CO_2 dispersion; CH_3OH hydrogen bonding; HBr dipole–dipole; N_2 dispersion. **8** molecular: only weak intermolecular forces are overcome on melting; ionic/metallic: strong bonding throughout the lattice must be overcome — hence much higher melting/boiling points. **9** $CH_4 < SiH_4 < GeH_4$; all non-polar (dispersion only), and dispersion forces strengthen as the number of electrons/molecular size increases. **10** a each has 18 electrons, so dispersion forces are comparable; b F_2 −188 °C, HCl −85 °C, CH_3OH 65 °C; c dispersion only < dipole–dipole < hydrogen bonding. **11** same electrons → similar dispersion; ethanol has an O–H group so it hydrogen bonds, dimethyl ether (no O–H) has only dipole–dipole, so ethanol boils much higher. **12** it is made of neutral CO_2 molecules with no mobile ions or free electrons, so there are no charge carriers in any state. **13** a boiling point rises $H_2S < H_2Se < H_2Te$ as molecular size/electrons increase → stronger dispersion; b hydrogen bonding, present in water (H on O) but not in the heavier hydrides (H on S/Se/Te); c the extra boiling-point rise (≈192 °C) caused by hydrogen bonding in water. **14** sugar is polar and hydrogen bonds with water (dissolves); oil is non-polar and cannot form strong attractions with water (does not dissolve). **15** incorrect — boiling overcomes the hydrogen bonds *between* molecules, not the O–H covalent bonds; the molecules stay as H_2O and simply move apart into the gas. **16** NH_3 hydrogen bonds (H on N); PH_3 only has dipole–dipole/dispersion; hydrogen bonding is stronger and outweighs PH_3's larger dispersion, so NH_3 boils higher. **17** a X dispersion, Y hydrogen bonding; b Y (hydrogen bonding is stronger than X's dispersion); c Y (it hydrogen bonds with water; X is non-polar). **18** a P dispersion, Q dipole–dipole, R dipole–dipole, S hydrogen bonding; b same force type, but R has more electrons → stronger dispersion → higher boiling point; c S hydrogen bonds while Q only has dipole–dipole, so S boils much higher; d S (it hydrogen bonds with water).

Fully-worked solutions

Question 1 a. The bonding *within* a Cl_2 molecule is **covalent bonding** — a shared pair of electrons between the two chlorine atoms. b. Chlorine molecules are non-polar, so the force *between* neighbouring molecules is the **dispersion force** (the only intermolecular force acting between non-polar molecules). c. Melting separates the molecules from one another, so it is the weak **dispersion forces between molecules** that are overcome — the strong covalent bonds inside each Cl_2 molecule are not broken. Because dispersion forces between these small molecules are very weak, only a little energy is needed, and chlorine melts at a very low temperature.

Question 2 a. O_2 is a non-polar molecule, so the strongest (and only) intermolecular force is the **dispersion force**. b. HCl is a polar molecule with a permanent dipole, so it has **dipole–dipole attraction** (plus dispersion). The hydrogen is bonded to chlorine, not to N, O or F, so there is no hydrogen bonding. c. In H_2O the hydrogen atoms are bonded to oxygen, so water molecules can form **hydrogen bonds** — the strongest of the three intermolecular forces.

Question 3 a. The only intermolecular force is the **dispersion force**. Each halogen molecule (F_2, Cl_2, Br_2, I_2) is a symmetrical diatomic and therefore **non-polar**, so no dipole–dipole attraction or hydrogen bonding is possible. b. Going from F_2 to I_2, each molecule has progressively more electrons and is larger, so its electron cloud is more easily distorted and its **dispersion forces become stronger**. More energy is then needed to separate the molecules, so the boiling point rises steadily down the group. c. At 25 °C a substance is a gas if its boiling point is below 25 °C, a liquid if it melts below 25 °C but boils above it, and a solid if it melts above 25 °C. Hence: F_2 (bp −188 °C) **gas**; Cl_2 (bp −34 °C) **gas**; Br_2 (mp −7 °C, bp 59 °C) **liquid**; I_2 (mp 114 °C) **solid**.

Question 4 a. Hydrogen bonding occurs only when a **hydrogen atom is covalently bonded to a nitrogen, oxygen or fluorine atom**; the strongly δ+ hydrogen is then attracted to a lone pair on an N, O or F atom of a neighbouring molecule. b. HF — **yes**, its hydrogen is bonded to fluorine. CH_4 — **no**, its hydrogens are bonded to carbon (not N, O or F). NH_3 — **yes**, its hydrogens are bonded to nitrogen. c. Both molecules are polar, but HF has its hydrogen bonded to fluorine and therefore forms **hydrogen bonds**, whereas HCl (H bonded to Cl) has only dipole–dipole and dispersion forces. Although HCl has more electrons and so slightly stronger dispersion forces, hydrogen bonding is much stronger than dipole–dipole, so more energy is needed to separate HF molecules and HF boils at the higher temperature.

Question 5 a. The rule "like dissolves like" means that **polar solutes dissolve in polar solvents** and **non-polar solutes dissolve in non-polar solvents**; a polar solute is generally insoluble in a non-polar solvent, and vice versa. b. **No** — iodine is a non-polar molecular substance, whereas water is polar and extensively hydrogen bonded. A non-polar I_2 molecule cannot form strong enough attractions with water molecules to replace the hydrogen bonds that would have to be broken to fit it into the water structure, so iodine is only very slightly soluble in water. (It dissolves much better in a non-polar solvent.) c. Ammonia is a polar molecule whose hydrogens are bonded to nitrogen, so NH_3 molecules can form **hydrogen bonds with water molecules**. These strong solute–solvent attractions readily replace the hydrogen bonds broken in the water, so ammonia is very soluble.

Question 6 a. Solid glucose is a **molecular** substance, made up of whole, electrically neutral glucose molecules. It contains no ions and no free (delocalised) electrons, so there are no mobile charged particles to carry a current — it does not conduct electricity. b. When a molecular substance melts, only the **weak intermolecular forces between the molecules** have to be overcome; the strong covalent bonds inside each molecule stay intact. Because these intermolecular forces are weak, little energy (a low temperature) is needed, so the melting point is low. c. The **covalent bonds within a molecule are strong**, whereas the **intermolecular forces between molecules are weak** (only a few per cent as strong). When a molecular substance boils, it is the weak **intermolecular forces** that are overcome; the covalent bonds are not broken.

Question 7 - CO_2 is a non-polar molecule (linear and symmetrical), so its strongest force is the **dispersion force**. - CH_3OH has an O–H group, so its molecules **hydrogen bond**. - HBr is polar with H bonded to Br (not N, O or F), so its strongest force is **dipole–dipole attraction**. - N_2 is a non-polar molecule, so its strongest force is the **dispersion force**.

Question 8 When a **molecular** substance melts, only the weak **intermolecular forces** between separate molecules are overcome; the strong covalent bonds inside each molecule are not broken, so little energy is required and the melting (and boiling) point is low. In an **ionic** substance, in contrast, the whole solid is one lattice held together by strong electrostatic attractions between oppositely charged ions, and in a **metal** the lattice is held by strong metallic bonding (attraction between the metal cations and the sea of delocalised electrons). Melting these substances means overcoming strong bonding that extends throughout the lattice, which requires a great deal of energy — hence their much higher melting and boiling points.

Question 9 The correct order of increasing boiling point is $CH_4 < SiH_4 < GeH_4$ (−161 °C < −112 °C < −88 °C). All three molecules are **non-polar**, so the only intermolecular force in each is the **dispersion force**. From CH_4 to SiH_4 to GeH_4 the number of electrons per molecule increases (10, 18 and 36), so the molecules are larger and their electron clouds are more easily distorted, making the **dispersion forces progressively stronger**. Stronger dispersion forces require more energy to overcome, so the boiling point rises down the group.

Question 10 a. Dispersion forces depend chiefly on the **number of electrons** in a molecule (and how easily the electron cloud is distorted). Fluorine, hydrogen chloride and methanol each have **18 electrons**, so their molecules are of similar "size" electronically and their dispersion forces are expected to be very similar in strength. b. F_2 −188 °C; HCl −85 °C; CH_3OH 65 °C. c. Because dispersion forces are similar for all three, the differences in boiling point come from the **type** of additional intermolecular force. F_2 is non-polar (**dispersion only**) and boils lowest; HCl is polar and adds **dipole–dipole** attraction, giving a higher boiling point; CH_3OH has an O–H group and so forms **hydrogen bonds**, the strongest force, giving much the highest boiling point. The ranking dispersion < dipole–dipole < hydrogen bonding therefore matches the boiling-point order.

Question 11 The two substances have the same molecular formula C_2H_6O and therefore the same number of electrons, so their **dispersion forces are essentially identical**. The difference lies in the strongest type of force each can form. In **ethanol**, CH_3CH_2OH, a hydrogen atom is bonded to oxygen (an O–H group), so ethanol molecules can **hydrogen bond** to one another. In **dimethyl ether**, CH_3OCH_3, all the hydrogens are bonded to carbon and the oxygen carries none, so no hydrogen bonding is possible and the molecules are held only by **dipole–dipole** and dispersion forces. Because hydrogen bonding is much stronger than dipole–dipole attraction, far more energy is needed to separate ethanol molecules, so ethanol boils about 100 °C higher than dimethyl ether.

Question 12 Carbon dioxide is a **molecular** substance consisting of discrete, electrically neutral CO_2 molecules. Electrical conduction needs mobile charged particles — free ions or free electrons — but CO_2 contains **no ions and no delocalised electrons**. Neither cooling it to a solid nor warming it to a gas creates any mobile charge carriers (changing state only alters how far apart the neutral molecules are), so carbon dioxide does not conduct electricity in any state.

Question 13 a. The boiling point **increases** from H_2S (−60 °C) to H_2Se (−41 °C) to H_2Te (−2 °C). Down the group each molecule has more electrons and is larger, so its **dispersion forces become stronger**; more energy is needed to separate the molecules, raising the boiling point. (Dispersion is the property that changes most down the group, so it dominates the trend.) b. The force responsible is **hydrogen bonding**. In water the hydrogen atoms are bonded to **oxygen**, one of the three N, O and F atoms that permit hydrogen bonding, so water molecules hydrogen bond strongly to one another. In H_2S, H_2Se and H_2Te the hydrogen is bonded to sulfur, selenium or tellurium — none of which are N, O or F — so those substances cannot hydrogen bond and are held only by dipole–dipole and dispersion forces. The extra strength of hydrogen bonding lifts water's boiling point far above the trend set by the heavier hydrides. c. The red arrow (about 192 °C) represents the **extra boiling-point rise caused by hydrogen bonding** — the difference between water's actual boiling point (100 °C) and the value of about −92 °C that the dispersion/dipole–dipole trend of the heavier hydrides predicts.

Question 14 Sugar molecules carry many **O–H groups**, which makes them polar and able to form **hydrogen bonds**. Water is also polar and hydrogen bonded, so sugar molecules can form strong hydrogen bonds with water molecules; these solute–solvent attractions readily replace the attractions broken when the sugar and water mix, so sugar dissolves readily ("like dissolves like"). Cooking oil, by contrast, is made of large **non-polar** molecules. A non-polar oil molecule can only form weak dispersion attractions with water and cannot form the hydrogen bonds needed to break into water's hydrogen-bonded structure, so the oil does not dissolve and separates from the water.

Question 15 The claim is incorrect because boiling overcomes only the forces **between** molecules, not the covalent bonds **within** them. The O–H covalent bonds are strong intramolecular bonds and are **not** broken when water boils. What is overcome on boiling is the **hydrogen bonding between neighbouring water molecules**: this attraction is broken so that the molecules can move apart into the gas phase. The particles in the steam are therefore still intact H_2O molecules; only their separation, not their internal bonding, has changed.

Question 16 Both NH_3 and PH_3 are polar molecules, so both have dispersion and dipole–dipole forces; the comparison must identify what differs between them. In **ammonia** the hydrogens are bonded to **nitrogen**, so NH_3 molecules can form **hydrogen bonds**. In **phosphine** the hydrogens are bonded to **phosphorus** (not N, O or F), so PH_3 **cannot** hydrogen bond and is held only by dipole–dipole and dispersion forces. Although PH_3 has more electrons than NH_3 and therefore slightly stronger dispersion forces, hydrogen bonding is much stronger than that difference, so more energy is needed to separate ammonia molecules and NH_3 boils at the higher temperature (−33 °C versus −88 °C).

Question 17 a. Substance X is small and **non-polar**, so its strongest (and only) intermolecular force is the **dispersion force**. Substance Y has O–H groups, so its strongest force is **hydrogen bonding**. b. **Y** has the higher boiling point. Hydrogen bonding (in Y) is much stronger than the dispersion forces in the small non-polar molecule X, so more energy is needed to separate Y's molecules and it boils at a higher temperature — consistent with Y being a liquid while X is a gas at room temperature. c. **Y** is the more soluble in water. Y can form **hydrogen bonds with water** molecules, so it mixes readily; X is non-polar and can form only weak attractions with polar water, so it is only slightly soluble.

Question 18 a. P (N_2): non-polar → **dispersion**. Q (HCl): polar, H on Cl → **dipole–dipole**. R (HBr): polar, H on Br → **dipole–dipole**. S (CH_3OH): O–H group → **hydrogen bonding**. b. Q and R are both polar with dipole–dipole attraction as their strongest force, so the difference must come from **molecular size**. R (HBr, 36 electrons) has more electrons than Q (HCl, 18 electrons), so R has **stronger dispersion forces**; adding this to the similar dipole–dipole attraction means more energy is needed to separate R's molecules, so R boils higher (−67 °C versus −85 °C). c. Q and S both have 18 electrons, so their dispersion forces are similar, but they differ in the **type** of force. S has an O–H group and so forms **hydrogen bonds**, whereas Q (H on Cl) has only dipole–dipole attraction. Hydrogen bonding is far stronger, so S boils about 150 °C higher than Q. d. **S** (CH_3OH) is the most soluble in water: it has an O–H group and can form **hydrogen bonds with water** molecules. P is non-polar (only dispersion with water) and Q and R are polar but cannot hydrogen bond, so all three are less soluble than S.

Chapter 2 Covalent substances — 2D Covalent network (lattice) substances

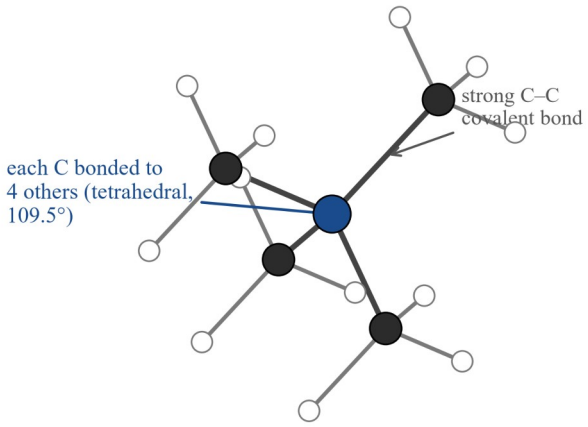
Theory

In 2C we met **covalent molecular** substances: small groups of atoms joined by strong covalent bonds into discrete **molecules** (such as O_2, CO_2 and H_2O), with only *weak* intermolecular forces acting *between* those molecules. This subtopic looks at the other main way covalently bonded atoms can be arranged — a **covalent network (lattice) substance**, in which the covalent bonds do not stop at the edge of a small molecule but continue, atom after atom, throughout the whole sample. There are **no discrete molecules** at all: a single crystal is effectively one giant molecule held together entirely by strong covalent bonds. The two examples set by the study design are the two forms (allotropes) of solid carbon, **diamond** and **graphite**.

A covalent network is sometimes called a **covalent lattice** or a **giant covalent structure**. The single most important idea in this subtopic is this: because the strong covalent bonds run without interruption through the entire lattice, *melting the substance means breaking a huge number of strong covalent bonds*. This one fact explains why covalent network substances are, as a class, substances of **very high melting point** — quite unlike the low-melting covalent molecular substances of 2C.

Hardness, however, is not a class-wide property. Whether a covalent network substance is hard depends on *which directions* the covalent bonds run in. Where they run in all three dimensions (diamond, silicon dioxide) the substance is extremely hard, because deforming it would mean breaking covalent bonds. Where the covalent bonding is confined to flat layers that are stacked on one another and held together only by weak forces (graphite), the substance is **soft**, because those layers slide apart without a single covalent bond being broken. Watch for this distinction throughout the subtopic: high melting point follows from the covalent network in every case, but hardness follows only from a *three-dimensional* one.

Diamond — a three-dimensional tetrahedral network. In diamond every carbon atom uses all **four** of its valence (outer-shell) electrons to form **four** single covalent bonds to four neighbouring carbon atoms. Those four bonds point towards the corners of a **tetrahedron**, so they are spread as far apart as possible. (The angle between neighbouring bonds is then about $109.5°$. Bond-angle **values** — here, in the worked examples and answers that follow, and on the diagrams in this subtopic — are given for interest only and are **not required by the study design**, which asks for the *shape*, not the angle.) Each of those neighbours is itself bonded tetrahedrally to four more carbons, and so on, so the bonding extends in **three dimensions** through the whole crystal. The result is a rigid, continuous, interlocking framework of strong C–C covalent bonds.

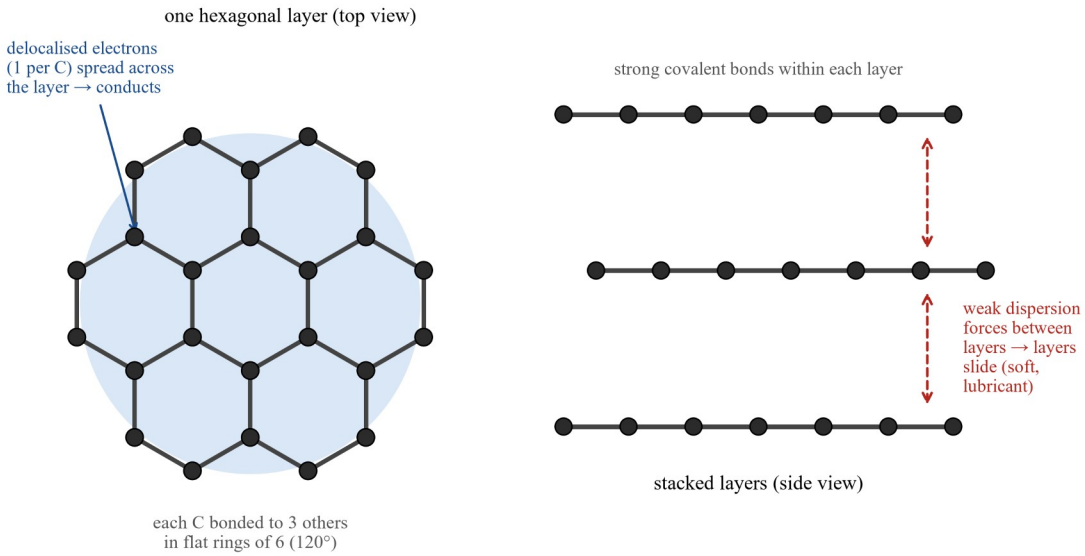


rigid 3-D network — continues in all directions

The properties of diamond follow directly from this structure:

- **Extreme hardness.** To scratch or deform diamond you must break strong covalent bonds, and because the tetrahedral network is rigid in every direction there is no easy plane along which atoms can move past one another. Diamond is the hardest naturally occurring substance.
- **Very high melting point** (above 3500 °C). Melting requires breaking the covalent bonds throughout the lattice; an enormous amount of heat energy is needed to do this, so the melting point is exceptionally high.
- **Does not conduct electricity.** All four of each carbon's valence electrons are **localised** in covalent bonds — none are free to move — so a diamond crystal contains no mobile charge carriers at all (no free electrons, and no mobile ions either) and solid diamond is an electrical insulator.
- **Excellent conductor of heat.** Although it carries no mobile electrons, the stiff, continuous covalent network transmits heat (as lattice vibrations) very efficiently, making diamond one of the best thermal conductors known.
- **Applications.** Its hardness makes diamond ideal for the cutting edges and tips of drills, saws and grinding wheels, and as an industrial abrasive; its high thermal conductivity is used to draw heat away from electronic components (heat sinks).

Graphite — two-dimensional hexagonal layers. Graphite is built from the *same* carbon atoms but arranged completely differently. Here each carbon forms only **three** covalent bonds, to three neighbouring carbons, all in the same plane. This links the carbons into flat **layers** (sheets) of joined **hexagonal rings** — rings of six carbons. (The ring angle is 120 °; as above, this value is enrichment and is **not required**.)



Each carbon has four valence electrons but uses only three of them for bonding within its layer. The **fourth** valence electron of every carbon is **delocalised** — it is not tied to any one atom but is free to move throughout the whole layer, in a shared "sea" of mobile electrons much like the delocalised electrons of a metal. The layers themselves are stacked on top of one another but are **not** covalently bonded together; they are held only by **weak dispersion forces** (the same kind of weak force met in 2C), and the gap between layers is far larger than a C–C bond length.

This layered structure explains graphite's rather surprising set of properties:

- **Soft and slippery — a good lubricant.** Because only weak dispersion forces act between the layers, whole layers can easily **slide** over one another. Graphite therefore feels slippery, marks paper (pencil "lead"), and is used as a solid (dry) lubricant.
- **Conducts electricity.** The delocalised fourth electron of each carbon is a mobile charge carrier, so graphite conducts an electric current **along** its layers — the only common non-metal that is a good electrical conductor. (It conducts much less well in the direction *perpendicular* to the layers, where electrons would have to jump across the gap between sheets.)
- **Conducts heat well.** The same delocalised electrons, together with the strong covalent bonding within each layer, also carry thermal energy efficiently, so graphite is a good conductor of heat. As with its electrical conductivity, this heat conduction is **anisotropic** — heat travels much more readily along the layers than across the wide gap between them.

- **Very high melting point.** As in diamond, melting graphite means breaking the strong covalent bonds *within* the layers, which requires a great deal of energy — so graphite, too, has a very high melting point. (Weak interlayer forces let layers slide, but sliding is not melting.)
- **Applications.** Its electrical conductivity, combined with a high melting point and chemical inertness, makes graphite the standard material for **electrodes** (for example in electrolysis and in batteries); its slipperiness makes it a lubricant and the writing core of pencils.

Other covalent network substances. Diamond and graphite are the two examples named by the study design, but the same "giant covalent" idea describes other materials. **Silicon dioxide** (SiO_2, the main mineral in quartz and sand) is a three-dimensional covalent network in which each silicon atom is covalently bonded to four oxygen atoms and each oxygen to two silicons; like diamond it is very hard, has a very high melting point (about $1710\,°C$) and does not conduct electricity. **Graphene** is simply a *single* layer of graphite — one hexagonal sheet on its own — and, as the model predicts, it conducts electricity (delocalised electrons) and is extremely strong within the sheet.

Covalent network versus covalent molecular — the key contrast. Both classes contain strong covalent bonds, so it is easy to confuse them. The difference is *what has to be overcome to melt the substance*:

Feature	Covalent **network** (2D)	Covalent **molecular** (2C)
Basic unit	one giant lattice — no separate molecules	small, discrete molecules
Forces broken on melting	**strong covalent bonds** throughout the lattice	only **weak intermolecular forces** between molecules
Melting/boiling point	very high	low
Hardness	very hard (diamond, SiO_2) or soft-but-high-melting (graphite)	soft
Electrical conductivity (as a solid)	none (diamond, SiO_2); good along layers (graphite)	none
Examples	diamond, graphite, silicon dioxide	O_2, CO_2, I_2, H_2O

The take-home rule is that a covalent **molecular** substance melts at a low temperature because only weak forces between molecules are overcome — the covalent bonds inside each molecule stay intact — whereas a covalent **network** substance melts at a very high temperature because the covalent bonds *are* the thing that must be broken.

Worked examples

Worked Example 1 — Describe the structure and bonding in diamond, and use them to explain why diamond is extremely hard and has a very high melting point.

Working	Comment
In diamond each carbon atom forms four single covalent bonds to four other carbon atoms.	Carbon has four valence electrons, and all four are used in bonding.
The four bonds point to the corners of a tetrahedron, and this repeats in every direction.	Gives a three-dimensional covalent network — see the diagram above. *(Enrichment, not required: the bonds are about* $109.5°$ *apart.)*
There are no separate molecules; the whole crystal is one giant covalently bonded lattice.	This is what "covalent network (lattice)" means.
Hardness: deforming diamond would mean breaking strong covalent bonds, and the rigid 3-D framework offers no plane for atoms to slip along.	Both the strength *and* the 3-D rigidity of the bonding matter.
Melting point: melting requires breaking a very large number of strong covalent bonds throughout the lattice, needing a great deal of energy.	Hence a very high melting point (above $3500\,°C$).

Worked Example 2 — Graphite is used both as an electrode material and as a dry lubricant. Explain, in terms of its structure and bonding, why graphite conducts electricity yet is soft and slippery.

Working	Comment
In graphite each carbon is covalently bonded to only three others, forming flat hexagonal layers.	Three bonds per carbon, in rings of six — a two-dimensional network within each layer. *(Enrichment, not required: the ring angle is* $120\,°$*.)*
Each carbon's fourth valence electron is delocalised and free to move throughout the layer.	One mobile electron per carbon — a "sea" of delocalised electrons in each sheet.
Conductivity: these mobile delocalised electrons can carry a current along the layers, so graphite conducts electricity.	The mobile charge carriers are the reason it works as an electrode.
The layers are held to each other only by weak dispersion forces, across a relatively large gap.	There are **no** covalent bonds between the layers.
Softness/lubrication: because the interlayer forces are weak, layers slide over one another easily.	So graphite is soft and slippery — a good solid lubricant.

Worked Example 3 — Solid carbon dioxide ("dry ice") and diamond both *contain* carbon — dry ice as the **compound** CO_2 (carbon combined with oxygen), diamond as the **element** carbon alone — and both are solids at low temperature, yet dry ice sublimes at about $-78\,°C$ while diamond does not melt below $3500\,°C$. Explain this enormous difference.

Carbon dioxide is a **covalent molecular** substance: it exists as small, discrete CO_2 molecules, and although the C=O bonds *within* each molecule are strong covalent bonds, the molecules are held to one another only by **weak dispersion forces**. Turning solid CO_2 into a gas requires overcoming only those weak intermolecular forces — the molecules stay intact — so very little energy is needed and this happens at a very low temperature.

Diamond is a **covalent network** substance: there are no separate molecules, and every carbon is joined to its neighbours by strong covalent bonds that run continuously through the whole crystal. To melt diamond you must break an enormous number of these strong covalent bonds, which demands a very large amount of energy.

∴ the two substances differ so greatly because melting/subliming dry ice overcomes only weak forces *between* molecules, whereas melting diamond breaks the strong covalent bonds that make up the network itself.

Worked Example 4 — Diamond and graphite are both pure carbon, yet diamond is the hardest naturally occurring material and an electrical insulator while graphite is soft and conducts electricity. Explain how the same element gives such different properties, and identify which allotrope is better suited to (i) the cutting tip of a drill and (ii) the electrodes of an electrolysis cell.

Both substances are covalent networks of carbon atoms, so both have very high melting points; the differences come entirely from *how* the atoms are bonded. In **diamond** each carbon is bonded to **four** others in a rigid three-dimensional tetrahedral network, and all four valence electrons are locked into covalent bonds. There is no plane for atoms to slide along, so diamond is extremely hard; and because no electrons are free to move, diamond cannot conduct electricity.

In **graphite** each carbon is bonded to only **three** others, forming flat layers. This leaves one delocalised electron per carbon, which is mobile and lets graphite conduct electricity; and because the layers are held together only by weak dispersion forces, they slide easily, making graphite soft.

For the **cutting tip of a drill**, hardness is essential, so **diamond** is chosen — its rigid 3-D network resists being scratched or deformed. For the **electrodes** of an electrolysis cell, the material must conduct electricity and withstand high temperatures, so **graphite** is chosen — its delocalised electrons carry the current while its covalent network gives it a high melting point.

∴ the contrast arises because four-coordinate bonding (diamond) gives a hard insulator, while three-coordinate layered bonding with a delocalised electron (graphite) gives a soft conductor; diamond suits cutting, graphite suits electrodes.

Practice questions

Question 1 — This question is about the structure of diamond.

a. State the number of other carbon atoms to which each carbon atom in diamond is covalently bonded, and name the shape formed by these bonds.
b. State the type of bonding that holds the atoms together throughout a diamond crystal.
c. Classify diamond as a covalent network substance or a covalent molecular substance.

Question 2 — This question is about the structure of graphite.

a. State the number of other carbon atoms to which each carbon atom in graphite is bonded within a layer, and name the shape of the rings formed.
b. State what happens to the fourth valence electron of each carbon atom in graphite.
c. Name the type of force that holds the layers of graphite to one another.

Question 3 — Consider the physical properties of diamond.

a. Explain why diamond has a very high melting point.
b. Explain why diamond is extremely hard.
c. State whether diamond conducts electricity, and explain your answer in terms of its bonding.

Question 4 — Consider the physical properties of graphite.

a. Explain why graphite is able to conduct electricity.
b. Explain why graphite is soft and can act as a lubricant.
c. Explain why graphite, like diamond, has a very high melting point.

Question 5 — Diamond (a covalent network solid) and solid iodine, I_2 (a covalent molecular solid), are compared.

a. State which of the two has the higher melting point, and explain why.
b. State which type of force must be overcome to melt each of the two solids.
c. State whether each solid conducts electricity in the solid state.

Question 6 — Graphite and diamond are each suited to particular uses.

a. Explain why diamond is used on the cutting edges of drills and saws.
b. Explain why graphite is used to make electrodes.
c. Explain why graphite is used as a dry lubricant and as the writing core of pencils.

Question 7 — Describe the structure and bonding of diamond, referring to the number of bonds formed by each carbon atom, the shape of the arrangement, and whether discrete molecules are present.

Question 8 — Diamond and graphite are both made only of carbon atoms, yet graphite conducts electricity and diamond does not. Explain this difference in terms of the electrons in each structure.

Question 9 — Explain, as a step-by-step reasoning chain, why diamond has a very high melting point. Begin with its structure and bonding and end with the melting point.

Question 10 — Explain why graphite is soft and slippery, referring in your answer to both the bonding *within* a layer and the forces *between* the layers.

Question 11 — Diamond is used in some electronic devices as a heat sink because it is an excellent conductor of heat, even though it does not conduct electricity. Explain how the structure of diamond accounts for **both** of these behaviours.

Question 12 — A student claims: “Because diamond and graphite are both made of pure carbon, they must have the same physical properties.” Evaluate this claim, using the structure and properties of the two substances as evidence.

Question 13 — The table lists the melting points of four solids.

Solid	Melting point
diamond	above $3500\,°C$
silicon dioxide	$1710\,°C$
iodine (I_2)	$114\,°C$
carbon dioxide	sublimes at $-78\,°C$

a. Classify each solid as covalent network or covalent molecular.
b. Justify your classification by referring to the forces that must be overcome to melt or sublime each solid.

Question 14 — Silicon dioxide (SiO_2, quartz) is a covalent network substance in which each silicon atom is covalently bonded to four oxygen atoms and each oxygen atom is bonded to two silicon atoms, forming a continuous three-dimensional network. Predict its hardness, its melting point and its electrical conductivity, justifying each prediction from the structure.

Question 15 — Both covalent network and covalent molecular substances contain covalent bonds, yet covalent network substances have far higher melting points. Explain why.

Question 16 — Graphene is a single, isolated layer of graphite. Predict, with reasons, (a) whether graphene conducts electricity and (b) whether it is strong within the plane of the sheet.

Question 17 — The **brushes** of an electric motor are small carbon blocks that are pressed against the spinning contacts of the motor; each brush must carry a large current into those contacts while rubbing against them continuously.

a. Choose diamond or graphite for the brushes, and justify your choice by naming the **two** properties the job demands and the structural feature responsible for each.
b. Explain why the other allotrope of carbon would fail in this application.
c. A **wire-drawing die** is a block with a small hole through it; copper wire is pulled through the hole to make it thinner, and the hole must not widen as thousands of metres of wire pass through. Choose diamond or graphite for the die, and justify your choice.

Question 18 — Explain, as a reasoning chain, why graphite conducts electricity well *along* its layers but poorly in the direction *perpendicular* to the layers.

Answers

1 a 4; tetrahedral. b (Strong) covalent bonding. c Covalent network. **2** a 3; hexagonal rings (rings of six). b It is delocalised and free to move through the layer. c Weak dispersion forces. **3** a Melting breaks many strong covalent bonds throughout the lattice, needing much energy. b Deforming it means breaking strong covalent bonds in a rigid 3-D network with no slip plane. c No — all four valence electrons of each carbon are localised in bonds, so there are no mobile charges. **4** a One delocalised electron per carbon is free to move and carries a current. b Layers are held only by weak dispersion forces, so they slide over one another. c Melting still requires breaking strong covalent bonds within the layers. **5** a Diamond — melting it breaks strong covalent bonds, whereas melting iodine overcomes only weak dispersion forces. b Diamond: strong covalent bonds; iodine: weak dispersion forces (between I_2 molecules). c Neither conducts in the solid state. **6** a It is extremely hard, so it can cut/abrade other materials without being worn away. b It conducts electricity and has a high melting point, so it carries current without melting. c Its layers slide easily (weak interlayer forces), so it is soft and slippery and rubs off onto paper. **7** Each carbon forms four covalent bonds to four other carbons in a tetrahedral, three-dimensional network; there are no discrete molecules — the whole crystal is one giant covalent lattice. **8** Graphite has one delocalised (mobile) electron per carbon that can carry a current; in diamond all four valence electrons are localised in covalent bonds, so there are no mobile charges. **9** Structure (4 bonds/C, tetrahedral 3-D network of strong covalent bonds) → melting needs these bonds broken → very many strong bonds → very large energy needed → very high melting point. **10** Within a layer, strong covalent bonds join each carbon to three others; between layers there are only weak dispersion forces, so layers slide over one another easily, making graphite soft and slippery. **11** Heat is carried efficiently through the rigid, continuous covalent network (as lattice vibrations), so diamond conducts heat well; but all valence electrons are localised in bonds, so there are no mobile charges and it does not conduct electricity. **12** The claim is false: same element, but different bonding arrangements (diamond 3-D 4-bonded network; graphite layered 3-bonded with a delocalised electron) give very different hardness and conductivity. **13** a Diamond and silicon dioxide: covalent network; iodine and carbon dioxide: covalent molecular. b Network solids need strong covalent bonds broken (very high mp); molecular solids need only weak dispersion forces overcome (low mp). **14** Very hard, very high melting point, non-conductor — a rigid 3-D network of strong Si–O covalent bonds with no mobile electrons. **15** In a molecular substance melting overcomes only weak intermolecular forces (bonds stay intact); in a network substance the covalent bonds themselves must be broken, needing far more energy. **16** a Yes — it has delocalised electrons free to move across the sheet. b Yes — it is a continuous network of strong covalent bonds within the plane. **17** a Graphite — its delocalised electrons carry the current, and its weakly held layers slide, so it rubs without seizing. b Diamond: all four valence electrons are localised, so it is an insulator and no current would pass; and its rigid 3-D network has no slip plane, so it would grind the contacts away. c Diamond — a rigid 3-D covalent network with no slip plane makes it extremely hard, so the hole resists wear. **18** Along the layers, delocalised electrons move freely and carry current; perpendicular to the layers, electrons must cross the wide gap held only by weak forces (no delocalisation between layers), so conduction is poor.

Fully-worked solutions

Question 1 a. In diamond each carbon atom is covalently bonded to **4** other carbon atoms, and these four bonds are directed towards the corners of a **tetrahedron**. *(Enrichment, not required: neighbouring bonds are about* $109.5°$ *apart — naming the shape is all that is asked for.)* b. The atoms are held together throughout the crystal by strong **covalent bonding**. c. Diamond is a **covalent network** (giant covalent / lattice) substance — the covalent bonds continue through the whole crystal, so there are no discrete molecules.

Question 2 a. Within a layer each carbon is covalently bonded to **3** other carbon atoms, forming flat **hexagonal rings** (rings of six carbons). *(Enrichment, not required: the ring angle is* $120°$*.)* b. The fourth valence electron becomes **delocalised** — it is not held by any single atom but is free to move throughout the layer. c. The layers are held to one another only by weak **dispersion forces**.

Question 3 a. Diamond is a three-dimensional covalent network in which every carbon is joined to four others by strong covalent bonds. To melt it, a very large number of these strong covalent bonds must be broken, which requires a great deal of energy — hence the very high melting point (above $3500\,°C$). b. Hardness measures resistance to being scratched or deformed. In diamond this would require breaking strong covalent bonds, and because the network is rigid in all three dimensions there is no plane along which atoms can slide past one another, so diamond resists deformation extremely well. c. **No.** Electrical conduction requires mobile charge carriers. In diamond all four valence electrons of every carbon are localised in covalent bonds, so there are no free electrons (or mobile ions) and diamond is an electrical insulator.

Question 4 a. Each carbon in graphite uses only three valence electrons for bonding, leaving one **delocalised** electron per carbon that is free to move through the layer. These mobile electrons act as charge carriers, so graphite conducts an electric current along its layers. b. Within each layer the carbons are strongly covalently bonded, but neighbouring layers are held together only by **weak dispersion forces** across a relatively large gap. Because these interlayer forces are weak, the layers slide over one another easily, so graphite is soft and behaves as a lubricant. c. Melting graphite requires breaking the strong covalent bonds *within* the layers (not merely separating the layers). Breaking so many strong covalent bonds requires a great deal of energy, so graphite has a very high melting point.

Question 5 a. **Diamond** has the higher melting point. Melting diamond breaks the strong covalent bonds of its network, whereas melting solid iodine overcomes only the weak dispersion forces between the discrete I_2 molecules; far more energy is needed for the former. b. Diamond: **strong covalent bonds** (throughout the network). Iodine: **weak dispersion forces** (between I_2 molecules; the covalent bond inside each molecule is not broken on melting).
c. **Neither** conducts electricity in the solid state — diamond has no mobile electrons, and molecular iodine has neither mobile electrons nor mobile ions.

Question 6 a. Diamond is used on cutting edges because it is **extremely hard**: its rigid 3-D covalent network resists scratching and wear, so it can cut or grind softer materials while keeping a sharp edge. b. Graphite is used for electrodes because it **conducts electricity** (via its delocalised electrons) and has a **very high melting point** and good chemical inertness, so it carries current without melting or reacting away. c. Graphite is used as a dry lubricant and pencil core because its layers are held together only by weak dispersion forces and **slide over one another easily**; this makes it soft and slippery, and layers rub off readily onto a surface such as paper.

Question 7 In diamond, every carbon atom forms **four** single covalent bonds to four neighbouring carbon atoms, with the bonds directed towards the corners of a **tetrahedron**. Each of those neighbours is bonded in the same way, so the covalent bonding extends in **three dimensions** throughout the entire crystal. There are **no discrete molecules**: a diamond crystal is a single giant covalent network (lattice) held together entirely by strong covalent bonds.
(Enrichment, not required: the tetrahedral bond angle is about $109.5\,°$*.)*

Question 8 The difference lies in the valence electrons. In **graphite**, each carbon uses only three of its four valence electrons for covalent bonds, so one electron per carbon is **delocalised** and free to move through the layer; these mobile electrons carry an electric current, so graphite conducts. In **diamond**, each carbon uses **all four** valence electrons in covalent bonds to four neighbours, so every valence electron is **localised** and none is free to move. With no mobile charge carriers, diamond cannot conduct electricity — even though both substances contain only carbon.

Question 9 (1) In diamond each carbon atom is covalently bonded to four others in a rigid three-dimensional network of strong covalent bonds. (2) There are no discrete molecules and no weak intermolecular forces to overcome — the covalent bonds *are* the framework of the solid. (3) To melt diamond, these strong covalent bonds must themselves be broken. (4) Because the bonds are both strong and extremely numerous (they run continuously through the whole crystal), an enormous amount of energy is needed to break enough of them to melt the solid. (5) Therefore diamond has a very high melting point (above $3500\,°C$).

Question 10 Graphite is built from flat layers of carbon atoms. *Within* each layer, every carbon is covalently bonded to three others, so the layer itself is strong. *Between* the layers, however, there are only **weak dispersion forces** acting across a relatively wide gap — the layers are not covalently bonded to each other. Because these interlayer forces are weak, one layer can slide over the next with little effort. This easy sliding of layers is what makes graphite soft and slippery, allowing it to act as a lubricant and to rub off onto paper.

Question 11 Both behaviours come from the same rigid covalent network. **Heat conduction:** heat is transmitted through a solid mainly as vibrations of the atoms; diamond's stiff, continuous framework of strong covalent bonds passes these lattice vibrations along very efficiently, making diamond an excellent conductor of heat and a good heat sink. **Electrical (non-)conduction:** an electric current needs *mobile charge carriers*, but in diamond all four valence electrons of every carbon are localised in covalent bonds, so there are no free electrons (and no mobile ions). Diamond therefore conducts heat extremely well yet does not conduct electricity.

Question 12 The claim is **incorrect**. Although diamond and graphite are both allotropes of pure carbon, their carbon atoms are bonded in different arrangements, and it is the arrangement — not just the element — that determines physical properties.

- In **diamond**, each carbon is bonded to four others in a rigid three-dimensional network with all valence electrons localised; this makes it extremely hard and an electrical insulator.
- In **graphite**, each carbon is bonded to only three others in layers, with one delocalised electron per carbon and only weak forces between layers; this makes it soft, slippery and an electrical conductor.

So the two substances differ markedly in hardness and in electrical conductivity (while both, being covalent networks, share a very high melting point). ∴ having the same chemical composition does not guarantee the same properties — structure and bonding matter.

Question 13 a. **Diamond** and **silicon dioxide** are **covalent network** solids; **iodine** and **carbon dioxide** are **covalent molecular** solids. b. The classification follows from the melting points and the forces overcome:

- Diamond (above $3500\,°C$) and silicon dioxide ($1710\,°C$) melt only at very high temperatures because melting them requires breaking the strong **covalent bonds** that run throughout the whole network — this needs a large amount of energy.
- Iodine ($114\,°C$) and carbon dioxide (sublimes at $-78\,°C$) change state at low temperatures because only the **weak dispersion forces** between their discrete molecules must be overcome; the covalent bonds *within* each molecule stay intact.

The huge gap in melting point (thousands of degrees versus around or below $100\,°C$) is exactly what distinguishes a covalent network from a covalent molecular solid.

Question 14 Silicon dioxide is a three-dimensional covalent network of strong Si–O covalent bonds (each Si bonded to 4 O, each O to 2 Si), which is structurally analogous to diamond. Predictions:

- **Hardness — very hard.** Deforming it would require breaking strong covalent bonds in a rigid 3-D framework with no slip plane, so it strongly resists scratching and deformation.
- **Melting point — very high.** Melting requires breaking a very large number of strong Si–O covalent bonds throughout the network, which needs a great deal of energy.
- **Electrical conductivity — does not conduct.** All the valence electrons are localised in the Si–O covalent bonds, so there are no mobile charge carriers.

(These predictions match the real properties of quartz — very hard, melting near $1710\,°C$, and an electrical insulator.)

Question 15 Both types of substance contain covalent bonds, but those bonds are in different places relative to the *unit that moves apart on melting*. In a **covalent molecular** substance the covalent bonds are *inside* the discrete molecules; melting only pulls whole molecules away from each other, so just the **weak intermolecular forces** between molecules are overcome, and the strong covalent bonds are left intact — this needs little energy, giving a low melting point. In a **covalent network** substance there are no separate molecules, so melting can only happen by breaking the **strong covalent bonds** that form the lattice itself. Because breaking many strong covalent bonds requires far more energy than overcoming weak intermolecular forces, covalent network substances have much higher melting points.

Question 16 a. **Yes, graphene conducts electricity.** Like a graphite layer, each carbon in graphene bonds to three others and contributes one **delocalised** electron; these mobile electrons are free to move across the sheet and carry a current. b. **Yes, graphene is very strong within the plane of the sheet.** The sheet is a continuous two-dimensional network of strong covalent bonds joining each carbon to three neighbours, and breaking or tearing the sheet in-plane would require breaking many of these strong covalent bonds.

Question 17 a. **Graphite.** The job demands two things at once. (i) *Electrical conductivity:* each carbon uses only three of its four valence electrons for bonding within a layer, leaving one **delocalised** electron per carbon that is free to move, so graphite carries the current into the contacts. (ii) *Softness / ability to slide:* the layers are held to one another only by **weak dispersion forces**, so they slide over one another easily and the brush rubs smoothly against the moving contact instead of seizing or gouging it. b. **Diamond** would fail on both counts. All four valence electrons of every carbon are **localised** in covalent bonds, so there are no mobile charge carriers and diamond is an electrical insulator — no current could reach the contacts. And because its covalent bonding is rigid in all three dimensions there is no plane along which atoms can slip, so a diamond block pressed against a spinning contact would abrade it rather than slide over it. c. **Diamond.** Widening the hole would mean atoms being torn out of its surface, which in diamond requires

strong covalent bonds to be broken, and the rigid three-dimensional network offers no plane along which material can be pushed aside. Diamond is therefore the hardest naturally occurring substance and the hole keeps its size. Graphite would be useless here: its layers are held together only by weak dispersion forces, so the passing wire would simply shear layers away and the hole would widen immediately.

Question 18 (1) Within each layer, every carbon contributes one delocalised electron that is free to move throughout that layer. (2) When a voltage is applied along the layers, these mobile electrons drift through the sheet and carry a current easily — so graphite conducts well *along* the layers. (3) Between the layers, however, there are no covalent bonds and no delocalisation of electrons from one layer to the next; the layers are separated by a relatively wide gap and held only by weak dispersion forces. (4) For a current to pass *perpendicular* to the layers, electrons would have to cross this gap, which they do only with difficulty. (5) Therefore graphite is a good electrical conductor along its layers but a poor conductor across them.