

The covalent model

International Baccalaureate · IB Diploma · Chemistry · SL

Scope and prerequisites

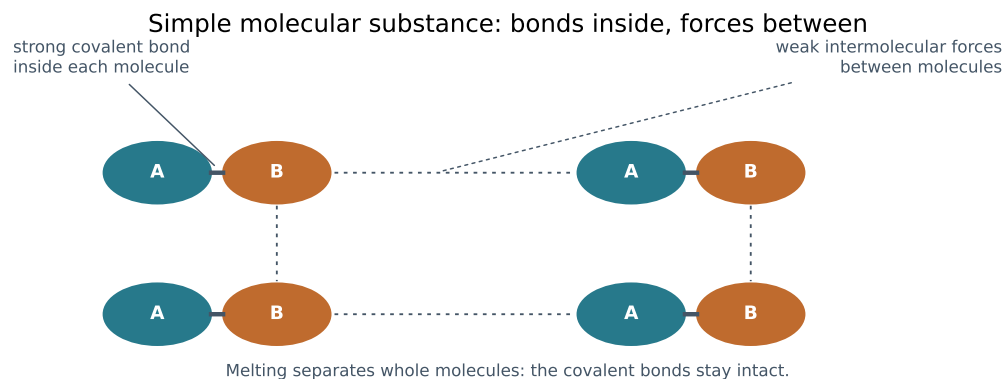
This handout teaches Structure 2.2, The covalent model, for the course first assessed in 2025.

Prerequisites: electron configurations and valence electrons from Structure 1.3, and the ionic model from Structure 2.1. You will use electronegativity values from the data booklet.

The covalent bond

■ Why does iodine melt so easily?

Iodine is made of I_2 molecules. The bond that holds the two iodine atoms together is strong: it takes 151 kJ mol^{-1} to break it. Yet solid iodine melts at only 114°C and turns to a purple vapour with gentle heating. The vapour is still I_2 : no bonds were broken. This unit explains the difference between the strong **covalent bonds** inside a molecule and the weak **intermolecular forces** between molecules.



Bonds inside molecules are strong; forces between them are weak, so melting leaves the molecules intact

■ What a covalent bond is

A covalent bond is the electrostatic attraction between a **shared pair** of electrons and the positively charged nuclei of the two bonded atoms. Covalent bonds form between non-metal atoms, which have similar, high electronegativities: neither atom can take an electron completely, so they share.

- Most atoms in covalent molecules end with eight electrons in their outer shell. This is the **octet rule**. Hydrogen is the exception: it is full with two.
- Some small atoms have fewer than eight. In BF_3 boron has only six outer electrons, and in BeCl_2 beryllium has only four. These are **incomplete octets**.
- Pairs of outer electrons that are not shared are **lone pairs**. They matter for shape and for hydrogen bonding.

■ Lewis formulas

A **Lewis formula** shows every valence electron: shared pairs as lines (or dot-cross pairs) and lone pairs as pairs of dots. To draw one:

- Add up the valence electrons of all the atoms. Add one for each negative charge and subtract one for each positive charge.
- Put the least electronegative atom in the centre (never H) and join each outer atom with a single bond.
- Complete the octets of the outer atoms with lone pairs, then put any electrons left on the central atom.
- If the central atom still has fewer than eight, move a lone pair from an outer atom to make a double or triple bond.

For CO_2 : $4 + 2(6) = 16$ valence electrons. Two C–O single bonds and full octets on both O use all 16, but C has only four. Moving one lone pair from each O gives $\text{O}=\text{C}=\text{O}$, with two lone pairs on each O and eight electrons round C.

■ Single, double and triple bonds

Two atoms can share one, two or three pairs. More shared pairs pull the nuclei closer together and hold them more strongly.

Bond	Shared pairs	Length / pm	Bond enthalpy / kJ mol^{-1}
C–C	1	154	346
C=C	2	134	614
C≡C	3	120	839

So a triple bond is the **shortest** and **strongest**. Note that a double bond is not twice as strong as a single bond.

■ Coordination bonds

In a **coordination bond** (a dative covalent bond) both shared electrons come from the same atom. Once it has formed, it is identical to any other covalent bond.

- $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$: the lone pair on N bonds to the H^+ ion. All four N–H bonds in NH_4^+ are the same.
- $\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{H}_3\text{O}^+$, the oxonium ion in every acid solution.

- Carbon monoxide, $\text{C} \equiv \text{O}$: two of the three shared pairs come from both atoms, but one comes from oxygen alone.

Draw a coordination bond as an arrow from the donor atom to the acceptor atom.

Shapes of molecules: VSEPR

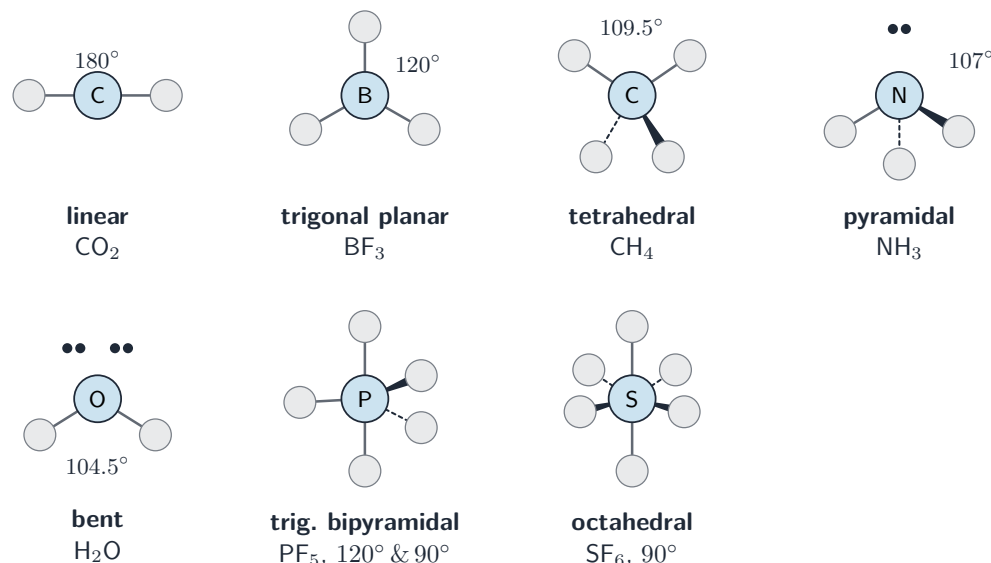
■ Electron domains repel

The **valence shell electron pair repulsion** (VSEPR) model predicts shape from one idea: groups of electrons round the central atom repel and spread as far apart as possible. Each group is an **electron domain**: a single bond, a double bond, a triple bond or a lone pair each counts as **one** domain.

- Draw the Lewis formula.
- Count the electron domains round the central atom: this gives the **electron domain geometry**.
- Count how many domains are bonds: the positions of the atoms give the **molecular geometry** (the shape).

Lone pairs repel more strongly than bonding pairs, because they sit closer to the central atom. Each lone pair squeezes the bond angle by about 2.5° .

Domains	Lone pairs	Shape	Angle	Example
2	0	linear	180°	CO_2 , BeCl_2
3	0	trigonal planar	120°	BF_3 , CO_3^{2-}
3	1	bent (V-shaped)	below 120°	SO_2 , O_3
4	0	tetrahedral	109.5°	CH_4 , NH_4^+
4	1	trigonal pyramidal	107°	NH_3
4	2	bent (V-shaped)	104.5°	H_2O



Wedges point towards you and dashed bonds away. The last two shapes, with five and six domains, are part of the HL course.

■ Worked example: the shape of NH_3

- Valence electrons: $5 + 3(1) = 8$, so four pairs round N.
- Three are N–H bonds and one is a lone pair: four domains, so the electron domain geometry is tetrahedral.
- Only three positions hold atoms, so the shape is **trigonal pyramidal**.
- The lone pair repels more strongly than the bonds, so the angle closes from 109.5° to 107° .

Bond polarity and molecular polarity

■ Polar bonds

Electronegativity is the ability of an atom to attract a shared pair of electrons. When the two bonded atoms have different electronegativities, the shared pair sits closer to the more electronegative atom. That atom gains a small negative charge, δ^- , and the other a small positive charge, δ^+ . The bond is a **polar bond** and has a **bond dipole**.

Atom	H	C	N	O	F	Cl
Electronegativity	2.2	2.6	3.0	3.4	4.0	3.2

The larger the electronegativity difference, the more polar the bond. O–H (difference 1.2) is much more polar than C–H (difference 0.4). With a very large difference, around

1.8 or more, the bonding is mostly ionic: bonding is a continuum, not two separate boxes.

■ Polar molecules

A molecule is **polar** when its bond dipoles do not cancel, so it has a net **dipole moment**. Whether they cancel depends on the shape.

- CO_2 has two polar $\text{C}=\text{O}$ bonds, but the molecule is linear: the two dipoles point in opposite directions and cancel. CO_2 is **non-polar**.
- H_2O has two polar $\text{O}-\text{H}$ bonds, but the molecule is bent: the dipoles add up towards the oxygen. Water is **polar**.
- CH_4 and CCl_4 are symmetrical tetrahedra, so they are non-polar. In CH_3Cl one bond is different, the dipoles no longer cancel, and the molecule is polar.

A quick test: a molecule with no lone pairs on the central atom and all outer atoms the same is non-polar. Anything less symmetrical is usually polar.

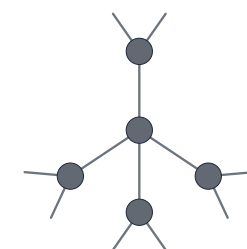
Giant covalent structures

■ Networks instead of molecules

In a **covalent network structure** (giant covalent structure) every atom is joined to its neighbours by covalent bonds in a continuous lattice. There are no separate molecules, so melting means breaking strong covalent bonds. These substances have very high melting points and do not dissolve in any solvent.

Carbon has several **allotropes**: different structural forms of the same element in the same state.

Allotrope	Bonding of each C	Structure	Key properties
diamond	4 C, tetrahedral	3D network	hardest natural substance; does not conduct
graphite	3 C, trigonal planar	flat hexagonal layers, weak forces between them	soft, slippery; conducts along the layers
graphene	3 C, trigonal planar	a single layer of graphite	very strong and light; conducts very well
fullerene C_{60}	3 C	hollow ball of 60 atoms	a molecule, so soft with low melting point; poor conductor



diamond
every C bonded to 4:
rigid 3D network, very hard



graphite
layers slide; spare electrons let it conduct

Diamond is a rigid 3D network. In graphite one electron per carbon is free to move along each layer.

In graphite, graphene and C_{60} each carbon uses three electrons in bonds. The fourth is **delocalized**: spread over many atoms rather than held between two. Mobile delocalized electrons explain why graphite and graphene conduct.

■ Silicon and silicon dioxide

- **Silicon** has the same tetrahedral network as diamond, but the $\text{Si}-\text{Si}$ bond is longer and weaker, so silicon melts lower (1414°C) and is a semiconductor.
- **Silicon dioxide**, SiO_2 (quartz, sand), is a network in which each Si bonds to four O atoms and each O bonds to two Si atoms. The ratio 1 : 2 gives the formula. Compare it with CO_2 : carbon dioxide is a small molecule and a gas at room temperature, while silicon dioxide melts above 1600°C .

Intermolecular forces

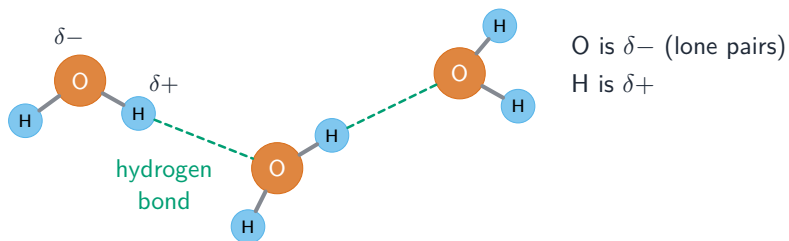
■ Four kinds of attraction between molecules

Intermolecular forces act between molecules in simple molecular substances. From weakest to strongest for molecules of similar size:

1. **London forces** (dispersion forces) act between all molecules. Electrons move, so at any instant one side of a molecule may have more electrons than the other: an **instantaneous dipole**. It induces a dipole in the next molecule, and the two attract. London forces grow with the number of electrons (larger molar mass) and with greater surface contact between molecules.
2. **Dipole-induced dipole forces** act between a polar molecule and a non-polar one: the permanent dipole distorts the electrons of its neighbour.
3. **Dipole-dipole forces** act between polar molecules: the $\delta+$ end of one attracts the $\delta-$ end of the next, in addition to London forces.

4. **Hydrogen bonding** is the strongest. It forms when H is bonded to N, O or F, and is attracted to a lone pair on an N, O or F atom of another molecule.

These three forces together, London, dipole-induced dipole and dipole-dipole, are called **van der Waals forces**.

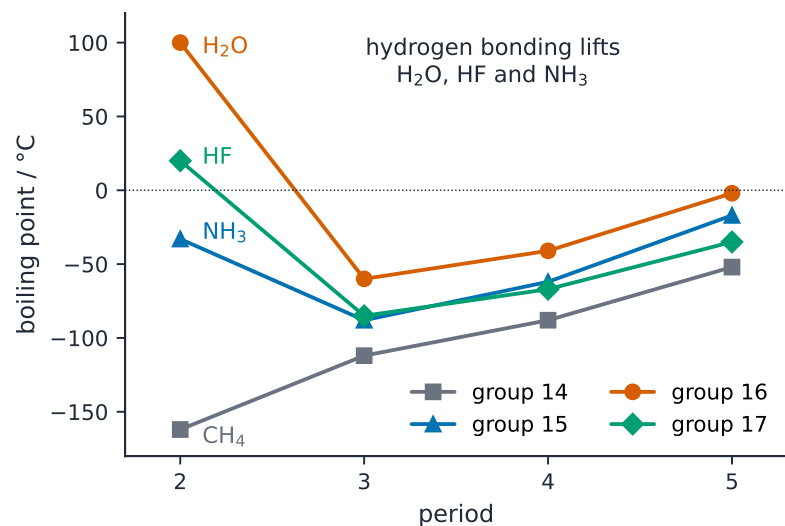


Each water molecule can form up to four hydrogen bonds: two through its H atoms and two through its lone pairs

Hydrogen bonding is strong because N, O and F are very electronegative, which leaves the H almost a bare proton, and because H is so small that the lone pair can come very close.

■ Evidence from boiling points

Down each group the hydrides boil higher, because the molecules have more electrons and stronger London forces. Three hydrides break the pattern.



Hydrogen bonding lifts H₂O, HF and NH₃ far above the trend. CH₄ has no hydrogen bonding and follows it.

Water boils at 100 °C; without hydrogen bonding, the trend in group 16 suggests

about -80 °C.

Properties of covalent substances

■ Explaining a property

To explain a physical property, name the structure, the particles, the forces that must be overcome and any mobile charged particles.

Property	Simple molecular	Covalent network
melting and boiling point	low: only weak intermolecular forces are overcome	very high: strong covalent bonds must break
volatility	often high	very low
conductivity	none: no ions or delocalized electrons (except graphite-like structures)	none, except graphite and graphene
solubility	depends on polarity	insoluble

■ Comparing boiling points: a method

1. Check the type of structure. A network always beats a simple molecular substance.
2. For molecular substances, list every force present, then compare the strongest one.
3. If the strongest force is the same kind, compare London forces through the number of electrons and the shape.

Example: propane, C₃H₈ ($M = 44$), boils at -42 °C; ethanal, CH₃CHO ($M = 44$), at 20 °C; ethanol, C₂H₅OH ($M = 46$), at 78 °C. Similar masses mean similar London forces. Ethanal adds dipole-dipole forces; ethanol adds hydrogen bonding through its O-H group.

Shape matters too: pentane (a straight chain) boils at 36 °C but its branched isomer 2,2-dimethylpropane at 10 °C, because the compact molecules touch over a smaller surface.

■ Solubility: like dissolves like

A substance dissolves well when the new attractions between solvent and solute are similar in strength to the ones that must be broken.

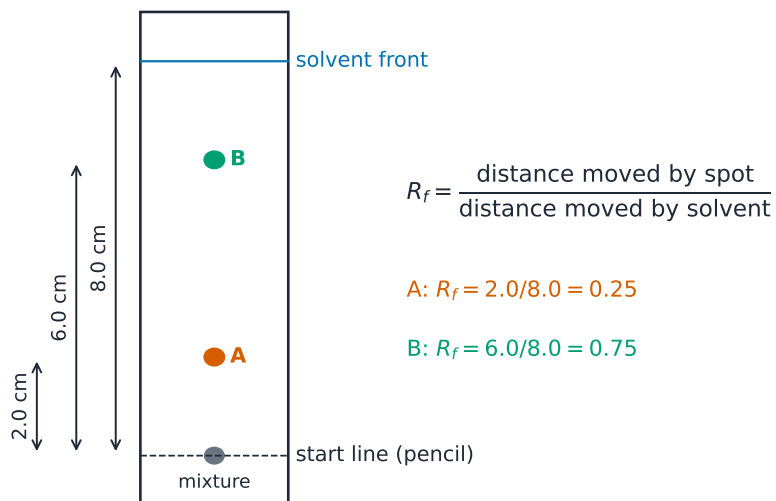
- Polar and hydrogen-bonding substances dissolve in water: ethanol and glucose form hydrogen bonds with water molecules.
- Non-polar substances such as iodine or hexane dissolve in non-polar solvents but hardly in water: they cannot replace the hydrogen bonds between water molecules.
- In a series such as methanol, ethanol, propanol, butanol, solubility in water falls as the non-polar hydrocarbon chain grows longer.

Chromatography

Chromatography separates the components of a mixture by how strongly each one is attracted to two phases:

- the **stationary phase**, which does not move: water held in the fibres of the paper, or a thin layer of silica on a plate in thin-layer chromatography (TLC);
- the **mobile phase**, the solvent that moves through it.

A component that is more attracted to the mobile phase moves further. A component that is more attracted to the stationary phase stays near the start. Because these attractions are intermolecular forces, polarity decides the result: on polar silica with a non-polar solvent, polar components move least.



Measure every distance from the start line, to the centre of each spot

The **retardation factor**, R_f , is

$$R_f = \frac{\text{distance moved by the component}}{\text{distance moved by the solvent front}}$$

R_f always lies between 0 and 1 and has no units. Under the same conditions (paper, solvent, temperature) a substance always has the same R_f , so you can identify a component by comparing it with known samples. Draw the start line in pencil, because ink would itself separate, and keep it above the level of the solvent. Colourless spots are shown with a UV lamp or a locating agent such as ninhydrin.

Practice

- Draw the Lewis formula of: (a) N_2 , (b) HCN , (c) NH_4^+ , showing the coordination bond.
- State and explain which is shorter and stronger: the C–O bond in methanol or the C=O bond in methanal.
- Predict the shape and bond angle of: (a) PH_3 , (b) BCl_3 , (c) H_2S , (d) CS_2 .
- Explain why CCl_4 is non-polar but CHCl_3 is polar.
- Explain why diamond is hard and does not conduct electricity, but graphite is soft and conducts.
- Put these in order of increasing boiling point and explain: CH_3OCH_3 , $\text{C}_2\text{H}_5\text{OH}$, C_3H_8 (all have $M \approx 44\text{--}46$).
- Explain why ethanol mixes with water but hexane does not.
- In a chromatogram the solvent front is 9.0 cm from the start line. Spot X has moved 3.6 cm. Calculate its R_f .

Answers.

- (a) $\text{N} \equiv \text{N}$ with one lone pair on each N. (b) $\text{H} - \text{C} \equiv \text{N}$ with one lone pair on N. (c) N in the centre with four N–H bonds; one is drawn as an arrow from N to H; overall charge +1, shown with square brackets.
- The C=O bond in methanal: two shared pairs pull the nuclei closer together and attract them more strongly than one.
- (a) trigonal pyramidal, less than 109.5° (four domains, one lone pair; VSEPR predicts about 107°). (b) trigonal planar, 120° . (c) bent, less than 109.5° (two lone pairs). (d) linear, 180° .
- Both are tetrahedral. In CCl_4 the four equal C–Cl dipoles cancel by symmetry. In CHCl_3 the C–H bond has a much smaller dipole, so the dipoles do not cancel and there is a net dipole moment.
- In diamond every C forms four strong covalent bonds in a rigid 3D network, and all outer electrons are in bonds, so there are no mobile charged particles. In graphite each C bonds to three others in layers held by weak London forces, so layers slide; the fourth electron of each C is delocalized and moves along the layers.
- C_3H_8 (-42°C) < CH_3OCH_3 (-24°C) < $\text{C}_2\text{H}_5\text{OH}$ (78°C). Similar masses give similar London forces. Methoxymethane is polar and adds dipole–dipole forces. Ethanol has an O–H group and forms hydrogen bonds, the strongest intermolecular force.
- Ethanol forms hydrogen bonds with water molecules through its O–H group, so the new attractions replace the ones broken. Hexane is non-polar and can only form London forces with water, too weak to replace the hydrogen bonds between water molecules.
- $R_f = 3.6/9.0 = 0.40$.

Exam tips

- Define a covalent bond as the attraction between a **shared pair** of electrons and the **nuclei** of the bonded atoms.
- In VSEPR count **domains**, not bonds: a double bond is one domain. Then name the shape from the atoms only.
- Lone pairs repel more than bonding pairs: write this whenever you explain an angle below 109.5° .
- A polar molecule needs polar bonds **and** an unsymmetrical shape; always say whether the dipoles cancel.
- Melting a simple molecular substance overcomes **intermolecular forces**; never write that it breaks covalent bonds.
- Hydrogen bonding needs H bonded **directly** to N, O or F; CH_3F has no hydrogen bonding.
- For R_f , measure to the **centre** of the spot and from the start line, not from the bottom of the paper.