Chemical bonding

Electronegativity, ionic, metallic and covalent bonding, orbital overlap and hybridisation, VSEPR shapes, intermolecular forces and hydrogen bonding, and dot-and-cross diagrams.

3.1 Electronegativity and bonding

Electronegativity is the power of an atom to attract electrons to itself in a covalent bond (the Pauling scale).

- It **increases across a period** (greater nuclear charge, smaller radius, the same shielding) and **decreases down a group** (more shielding and a larger radius).
- A large difference in electronegativity (roughly above 1.8) predicts an **ionic** bond, a small difference a **covalent** bond, and an intermediate difference a **polar covalent** bond.

Bonding is a model of attraction

Bond formation lowers energy because attractions outweigh repulsions at the equilibrium separation. Electron transfer explains how ions can form; the **ionic bond itself** is the attraction between oppositely charged ions. Similarly, a shared electron pair is attracted to both nuclei in a covalent bond. At very short distances, nucleus–nucleus and electron–electron repulsions become important, so bonded atoms do not collapse into one another.

Electronegativity differences are a guide rather than a rigid numerical boundary. Many bonds have mixed ionic/covalent character. For a polar bond, place δ^- on the more electronegative atom and δ^+ on the other; these are partial charges, not the full charges of separate ions.

> **TRY IT**
>
> Explain why HCl has a polar covalent bond rather than describing it as a hydrogen ion next to a chloride ion in the gas.

Answer: The atoms share an electron pair, but chlorine attracts it more strongly, giving $H^{\delta+}-Cl^{\delta-}$. Unequal sharing does not by itself mean complete electron transfer.

3.2 Ionic bonding

Ionic bonding is the electrostatic attraction between oppositely charged ions (positive cations and negative anions). Electrons are transferred from the metal to the non-metal.

- Sodium chloride: Na^+ and Cl^- in a 1 : 1 giant lattice.

Note Academy

- Magnesium oxide: Mg^{2+} and O^{2-}, with stronger attraction and a higher melting point than NaCl.
- Calcium fluoride: Ca^{2+} and two F^{-} per cation, CaF_2.

From ion charge to lattice properties

An ionic lattice extends in three dimensions: there is no isolated NaCl molecule with a single bond. Each ion attracts several neighbouring oppositely charged ions. Higher charges and smaller interionic distances normally produce stronger attractions, so more energy is needed to separate ions on melting.

Worked comparison: MgO and NaCl both form ionic lattices, but MgO contains 2+ and 2− ions instead of 1+ and 1− ions. The stronger electrostatic attractions help explain its higher melting point. Saying "magnesium has more electrons" does not identify the force holding the solid together.

> TRY IT
>
> Why does solid NaCl fail to conduct even though it contains charged particles?

Answer: Its ions are held in fixed lattice positions and cannot move through the solid to carry charge. On melting, ions become mobile. Electrical conduction needs mobile charge carriers, not merely the existence of charge.

3.3 Metallic bonding

Metallic bonding is the electrostatic attraction between **positive metal ions** and a sea of **delocalised electrons**. It is stronger with more delocalised electrons per atom, a higher ionic charge and a smaller ion.

Explaining metallic properties

The positive ions occupy a regular arrangement while delocalised electrons move through the structure. An applied potential difference produces a net electron flow, accounting for electrical conductivity. When layers of ions slide under a force, the electrons still attract the ions; the bonding is not restricted to a particular pair of neighbours. This explains malleability without claiming the metal has no strong bonding.

Compare Na, Mg and Al cautiously in terms of increasing charge and number of delocalised electrons, alongside changes in ionic size. Metallic bond strength is not determined solely by the atomic mass. Link a melting-point explanation to the energy needed to overcome attractions, and a conductivity explanation to moving electrons.

3.4 Covalent bonding and coordinate (dative covalent) bonding

Covalent bonding is the electrostatic attraction between the nuclei of two atoms and a shared pair of electrons. Examples are H_2, O_2 (a double bond), N_2 (a triple bond), Cl_2, HCl, CO_2, NH_3, CH_4, C_2H_6 and C_2H_4.

Note Academy

- **Expanded octet:** elements in Period 3 and below can have more than eight electrons in the outer shell, as in SO_2, PCl_5 and SF_6.
- **Coordinate (dative covalent) bond:** both electrons of the shared pair come from one atom. Examples are $NH_3 + HCl \rightarrow NH_4^+ + Cl^-$ (the lone pair on N is donated) and the Al_2Cl_6 dimer, where each Al accepts a lone pair from a Cl atom of the other $AlCl_3$.

Orbital overlap, σ and π bonds, hybridisation

- A **σ bond** is formed by direct (head-on) overlap of orbitals along the bond axis.
- A **π bond** is formed by sideways overlap of adjacent p orbitals, above and below the σ bond.
- A double bond is one σ and one π bond (C_2H_4). A triple bond is one σ and two π bonds (N_2, HCN).

Hybridisation	Mixing	Geometry	Example
sp^3	one s + three p	tetrahedral, 109.5°	CH_4, C_2H_6
sp^2	one s + two p	trigonal planar, 120°	C_2H_4
sp	one s + one p	linear, 180°	HCN, CO_2

Following lone pairs and orbital overlap

For a coordinate bond, identify a donor with a lone pair and an acceptor able to receive that pair. In $NH_3 + H^+ \rightarrow NH_4^+$, nitrogen supplies the pair. After formation, the four N–H bonds in ammonium are equivalent; the donation history does not leave one permanently weaker bond. The coordinate-bond arrow points from donor to acceptor and records pair donation, whereas a dipole arrow represents a different idea.

In ethene, each carbon uses three sp^2 orbitals for sigma bonds in one plane. The remaining unhybridised p orbitals overlap sideways, giving electron density above and below that plane. Rotation about C=C would destroy this sideways overlap, explaining restricted rotation and geometrical isomerism. A sigma bond lies along the internuclear axis and allows rotation much more readily when no other constraints operate.

Worked example: ethyne, $HC \equiv CH$, has three sigma bonds (two C–H and one C–C) and two pi bonds. Count **one sigma bond for every connected pair of atoms**, then count the additional components of multiple bonds. Do not count a triple bond as three sigma bonds.

> **TRY IT**
>
> How many sigma and pi bonds are present in CH_3CHO?

Note Academy

Answer: Six sigma bonds: four C–H, one C–C and one C–O. The C=O contributes one additional pi bond. It contains seven bonding pairs in total, but only six sigma bonds.

Comparing bond energies and lengths

Bond energy is the energy required to break one mole of a particular covalent bond in the gaseous state. **Bond length** is the internuclear distance of two covalently bonded atoms. Shorter bonds (more bonds between the same atoms) are stronger. A stronger bond makes a molecule less reactive: $N{\equiv}N$ is very strong, so nitrogen is unreactive.

3.5 Shapes of molecules

VSEPR theory: electron pairs around a central atom repel one another and take up positions as far apart as possible. **Lone pairs repel more than bonding pairs**, which reduces bond angles.

Shape	Bonding / lone pairs	Angle	Example
Linear	2 / 0	180°	CO_2
Trigonal planar	3 / 0	120°	BF_3
Tetrahedral	4 / 0	109.5°	CH_4
Pyramidal	3 / 1	107°	NH_3
Non-linear	2 / 2	104.5°	H_2O
Trigonal bipyramidal	5 / 0	120° and 90°	PF_5
Octahedral	6 / 0	90°	SF_6

Predict the shapes of similar species by counting pairs: NH_4^+ is tetrahedral (109.5°) and H_3O^+ is pyramidal. A multiple bond counts as one region of electron density.

A step-by-step shape prediction

Draw the electron arrangement, count regions of electron density around the central atom, arrange those regions to minimise repulsion, then name the positions of the **atoms**. A double or triple bond counts as one region for geometry, even though it contains several electron pairs. The number of regions determines the electron arrangement; lone pairs determine how the molecular shape differs from it.

Worked example: NH_4^+ has four N–H bonding regions and no lone pair on N, giving tetrahedral geometry. NH_3 has four regions but one is a lone pair, so the three atoms form a pyramidal shape. H_2O also has four regions, now with two lone pairs, producing a bent shape. Greater lone-pair repulsion compresses the bond angle along this sequence.

Note Academy

> **TRY IT**
>
> Predict the shape of CO_2 and explain why it is not bent merely because oxygen has lone pairs.

Answer: Carbon is the central atom and has two bonding regions with no lone pairs. They lie opposite one another, giving a linear shape, 180°. The relevant lone pairs for this prediction are those on the **central** atom.

3.6 Intermolecular forces, electronegativity and bond properties

A bond is **polar** when the atoms differ in electronegativity, giving a dipole ($\delta+$ and $\delta-$). A molecule has a **permanent dipole moment** only if the bond dipoles do not cancel. CO_2 and BF_3 are non-polar overall; H_2O and NH_3 are polar.

van der Waals' forces is the general term for all intermolecular forces:

- **Instantaneous dipole–induced dipole (id–id)** forces (London dispersion forces) act between all molecules and increase with the number of electrons, so with M_r.
- **Permanent dipole–permanent dipole (pd–pd)** forces act between polar molecules.
- **Hydrogen bonding** is a special, stronger case of pd–pd forces. It occurs where H is bonded to N, O or F and is attracted to a **lone pair** on another N, O or F atom.

Anomalous properties of water

Hydrogen bonding explains the relatively **high melting and boiling points** of water, its high **surface tension**, and why **ice is less dense than liquid water**: in ice each molecule is held in an open lattice by four hydrogen bonds.

In general, ionic, covalent and metallic bonds are much stronger than intermolecular forces.

Bond polarity versus molecular polarity

Treat bond dipoles as vectors. In linear CO_2, two equal C=O dipoles point in opposite directions and cancel. In bent water, the O–H dipoles do not cancel, so the molecule has a permanent dipole. Symmetry is the reason: a molecule can contain polar bonds and still be non-polar overall.

Dispersion forces arise from temporary fluctuations in electron density which induce dipoles in neighbours. They act in **all** molecules, including polar and hydrogen-bonded ones. Their strength depends on polarizability and molecular contact, so comparisons based on electron number are most convincing for similarly shaped species. Hydrogen bonding requires a suitable donor bond and acceptor lone pair; merely containing hydrogen and oxygen somewhere in a molecule is insufficient for self-hydrogen-bonding.

Note Academy

Worked comparison: ethanol can hydrogen-bond to other ethanol molecules because it has an O–H bond and oxygen lone pairs. Dimethyl ether has oxygen lone pairs but no O–H donor, so it cannot form the same hydrogen-bond network with itself. Both can accept hydrogen bonds from water. Boiling separates molecules; it does not normally break their C–O or C–H covalent bonds.

> TRY IT
>
> Why does boiling water require energy even though water molecules remain chemically intact?

Answer: Energy is needed to overcome intermolecular attractions, particularly hydrogen bonds. The covalent O–H bonds within individual molecules remain; breaking them would be a chemical reaction.

3.7 Dot-and-cross diagrams

Show the outer-shell electrons only, using dots for the electrons of one atom and crosses for those of the other. Show ionic compounds with square brackets and charges (for MgO, $[Mg]^{2+}$ and $[O]^{2-}$ with eight electrons around the oxide ion), covalent molecules with shared pairs and any lone pairs, and a dative bond with both shared electrons drawn from one atom. Expanded-octet species (SF_6, PCl_5) and odd-electron species (NO, NO_2) are included.

Checking an electron diagram

Add all available valence electrons, including extra electrons for a negative charge and subtracting for a positive charge. Place bonding pairs, complete appropriate outer shells, and account for every remaining electron. In NH_4^+ there are $5 + 4 - 1 = 8$ valence electrons, all in four N–H bonding pairs. In NO there are 11 valence electrons, so a diagram with only paired electrons cannot be correct. Dots and crosses indicate electron origin; they do not mean electrons remain physically distinguishable after bonding.

Chapter check: every property explanation should identify the particles, the attraction or charge carrier, and what happens during the stated process. Link these models to the solid structures in **states of matter** and to **lattice and hydration enthalpies**.

References and further reading

Scope follows section 3 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

Note Academy