

The covalent model

Structure 2.2 · SL and AHL

Why does iodine melt at only 114 °C?

Bonds inside molecules are strong; forces between molecules are weak.

- The I-I bond needs 151 kJ mol^{-1} to break, yet iodine melts easily.
- The vapour is still I_2 molecules.
- This unit: bonds $\rightarrow$ shapes $\rightarrow$ polarity $\rightarrow$ networks $\rightarrow$ forces between molecules.

What a covalent bond is

- Formed between non-metal atoms that share electrons.
- Most atoms end with eight outer electrons (**octet rule**); H is full with two.
- Incomplete octets: B in BF_3 has six, Be in BeCl_2 has four.

Covalent bond the electrostatic attraction between a **shared pair** of electrons and the nuclei of the bonded atoms

Drawing a Lewis formula

- 1 **Count.** CO_2 : $4 + 2(6) = 16$ valence electrons.
- 2 **Connect.** C in the centre, a single bond to each O.
- 3 **Fill.** Complete the O octets; C has only four electrons.
- 4 **Share more.** Move one **lone pair** from each O into the bond.

Decision

$\text{O}=\text{C}=\text{O}$, two lone pairs on each O, eight electrons round C.

More shared pairs, shorter and stronger bonds

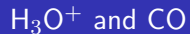
Bond	Length / pm	Enthalpy / kJ mol ⁻¹
C-C	154	346
C=C	134	614
C≡C	120	839

Coordination bonds



The N **lone pair** bonds to H^+ .

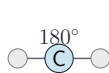
All four N–H bonds are identical.



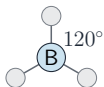
$\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{H}_3\text{O}^+$ in every acid.

In $\text{C}\equiv\text{O}$ one pair comes from O alone.

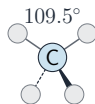
Electron domains repel



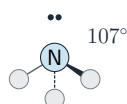
linear
CO₂



trigonal planar
BF₃



tetrahedral
CH₄



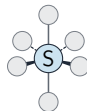
pyramidal
NH₃



bent
H₂O



trig. bipyramidal
PF₅, 120° & 90°



octahedral
SF₆, 90°

Count domains for the geometry; name the shape from the atoms only.

Shapes up to four domains

Domains, lone pairs	Shape	Example
2, 0	linear 180°	CO_2
3, 0	trigonal planar 120°	BF_3
3, 1	bent, below 120°	SO_2
4, 0	tetrahedral 109.5°	CH_4
4, 1	trigonal pyramidal 107°	NH_3
4, 2	bent 104.5°	H_2O

Check: the shape of a molecule

Your turn

What is the shape of PH_3 ?

- ☐ A. trigonal planar
- ☐ B. trigonal pyramidal
- ☐ C. tetrahedral
- ☐ D. bent

Polar bonds

- The more electronegative atom pulls the **shared pair** and becomes $\delta-$.
- O–H (difference 1.2) is far more **polar** than C–H (0.4).
- Bonding is a continuum from pure covalent to ionic.

Electronegativity the ability of an atom to attract a shared pair of electrons

Do the dipoles cancel?

CO_2 , linear

Two $\text{C}=\text{O}$ dipoles point opposite ways.

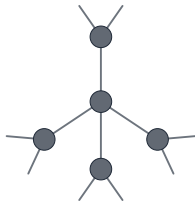
They cancel, so the molecule is non-polar.

H_2O , bent

Two $\text{O}-\text{H}$ dipoles add towards the O.

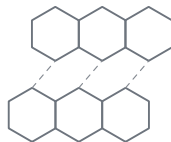
Net **dipole moment**, so water is **polar**.

Giant covalent networks



diamond

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



weak forces

graphite

layers slide; spare
electrons let it conduct

Graphite conducts because one electron per carbon is **delocalized** along each layer.

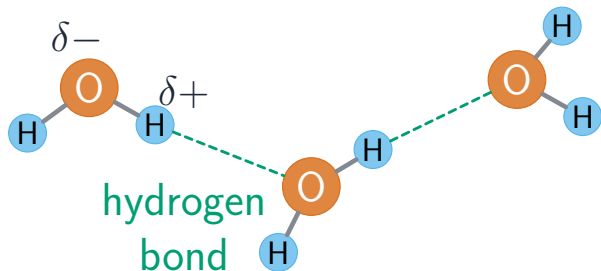
Carbon allotropes, silicon and silica

Substance	Bonding	Property
diamond	4 C, 3D network	very hard, no conduction
graphite	3 C, layers	soft, conducts
graphene	one layer	strong, conducts well
C ₆₀	molecule of 60 C	soft, low melting point
SiO ₂	Si to 4 O, O to 2 Si	melts above 1600 °C

Four forces between molecules

Force	Between	Cause
London	all molecules	instantaneous dipoles
dipole-induced dipole	polar and non-polar	permanent dipole distorts neighbour
dipole-dipole	polar molecules	$\delta+$ attracts $\delta-$
hydrogen bond	H on N, O, F	lone pair on N, O or F

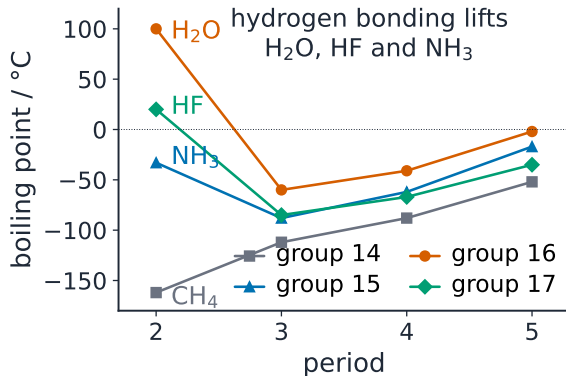
Hydrogen bonding



O is $\delta-$ (lone pairs)
H is $\delta+$

Each water molecule can form up to four hydrogen bonds.

The evidence in boiling points



Without **hydrogen bonding**, water would boil at about $-80\text{ }^{\circ}\text{C}$.

Comparing boiling points

- 1 **Same mass.** Propane, ethanal, ethanol: $M = 44, 44, 46$, so similar London forces.
- 2 **Ethanal. Polar** $\text{C}=\text{O}$ adds dipole–dipole forces.
- 3 **Ethanol.** The $\text{O}-\text{H}$ group adds **hydrogen bonding**.

Decision

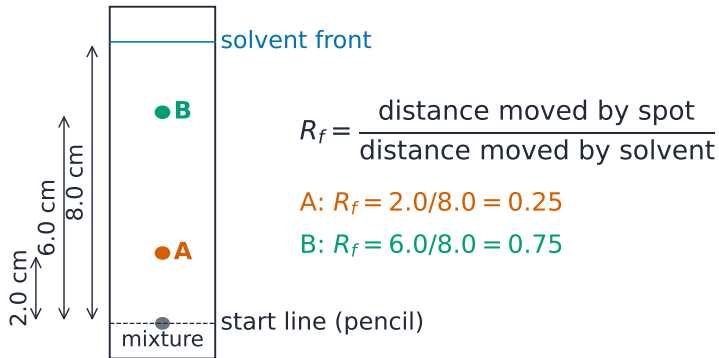
Boiling points: $-42\text{ }^{\circ}\text{C} < 20\text{ }^{\circ}\text{C} < 78\text{ }^{\circ}\text{C}$.

Like dissolves like

Melting a molecular solid overcomes intermolecular forces; it never breaks covalent bonds.

- **Polar** and hydrogen-bonding solutes dissolve in water.
- Non-polar solutes cannot replace the hydrogen bonds between water molecules.
- Longer hydrocarbon chains make alcohols less soluble.

Separating by attraction



R_f is between 0 and 1, has no units and identifies a substance under fixed conditions.

AHL: Resonance structures

Resonance structures are drawings; the molecule never switches between them.

- Both O–O bonds in O_3 are 128 pm: between single (148) and double (121).
- The real structure is one hybrid; electrons are **delocalized**.
- CO_3^{2-} has three structures and **bond order** 4/3.

AHL: Evidence for delocalization in benzene

Evidence	Alternating bonds predict	Benzene shows
bond lengths	154 and 134 pm	six equal, 140 pm
hydrogenation reactions	-360 kJ mol^{-1}	-208 kJ mol^{-1}
1,2-isomers	two	one

AHL: Five and six electron domains

Domains, lone pairs	Shape	Example
5, 0	trigonal bipyramidal	PCl_5
5, 1	see-saw	SF_4
5, 2	T-shaped	ClF_3
5, 3	linear	XeF_2
6, 0	octahedral	SF_6
6, 1	square pyramidal	BrF_5
6, 2	square planar	XeF_4

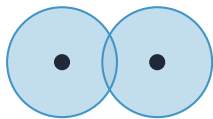
AHL: Formal charge picks the structure

- Prefer formal charges closest to zero.
- A negative **formal charge** belongs on the most electronegative atom.

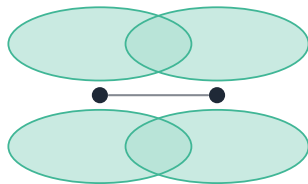
$$FC = V - \frac{1}{2}B - L$$

CO₂: O=C=O gives 0, 0, 0; O≡C-O gives +1, 0, -1. O=C=O is preferred.

AHL: Sigma and pi bonds



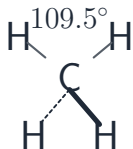
σ bond:
head-on overlap



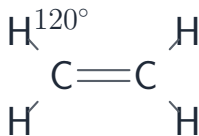
π bond: sideways overlap
of p orbitals

Ethene has five sigma bonds and one **pi bond**.

AHL: Hybridization follows the domains



sp^3 : 4 single bonds
tetrahedral



sp^2 : 1 double + 2 single
planar (flat)



sp : 1 triple bond
linear

Hybrid orbitals hold sigma bonds and lone pairs; leftover p orbitals make pi bonds.

Exam tips

For R_f , measure from the start line to the centre of each spot.

- **Covalent bond**: **shared pair** attracted to both nuclei.
- Count domains, not bonds; lone pairs repel more.
- **Polar** molecule: polar bonds AND dipoles that do not cancel.
- Hydrogen bonding needs H directly on N, O or F.

Check yourself

Try these

Predict the shapes of BCl_3 , H_2S and CS_2 .

Explain why CCl_4 is non-polar but CHCl_3 is polar.

Order C_3H_8 , CH_3OCH_3 and $\text{C}_2\text{H}_5\text{OH}$ by boiling point.

AHL. Count the sigma and pi bonds in propene.