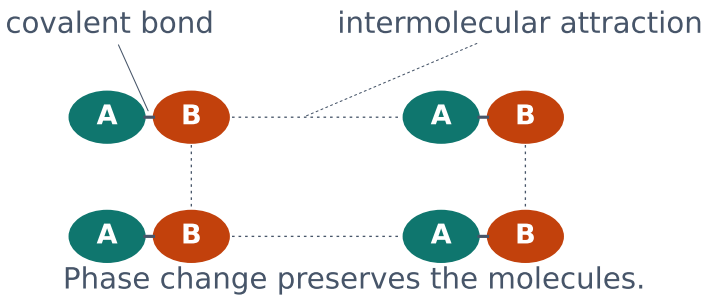
The covalent model

Structure 2.2 · SL and AHL

Why does iodine melt at only 114 °C?



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

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

O=C=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

NH_4^+

The N lone pair bonds to H^+.

All four N–H bonds are identical.

H_3O^+ and CO

$H_2O + H^+ \rightarrow H_3O^+$ is an aqueous hydrated-proton representation.

In C≡O one pair comes from O alone.

Why nitrogen is unreactive



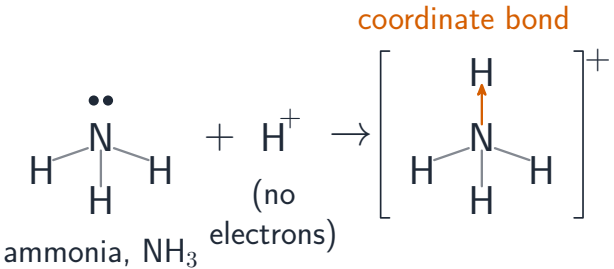
N≡N

strong triple bond: very high bond energy ⇒ hard to break

symmetrical molecule ⇒ no polarity ⇒ nothing pulls it into a reaction

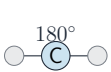
> The strong bond needs a lot of energy to break

A coordinate bond

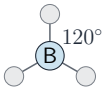


The ammonium ion, NH_4^+

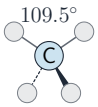
Electron domains repel



linear
CO_2



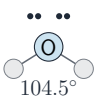
trigonal planar
BF_3



tetrahedral
CH_4



pyramidal
NH_3



bent
H_2O

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 C=O dipoles point opposite ways.

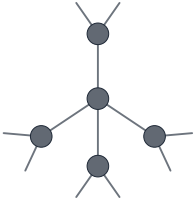
They cancel, so the molecule is non-polar.

H_2O, bent

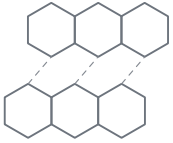
Two O–H dipoles add towards the O.

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

Giant covalent networks



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



graphite
layers slide; spare
electrons let it conduct

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

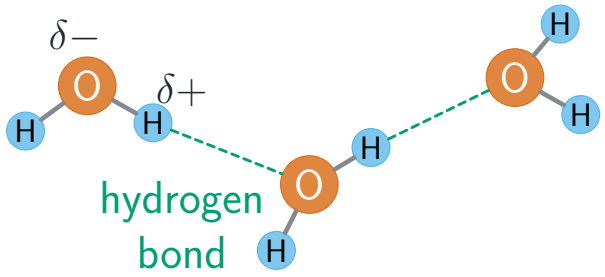
Carbon allotropes, silicon and silica

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	molecular solid; relatively soft
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

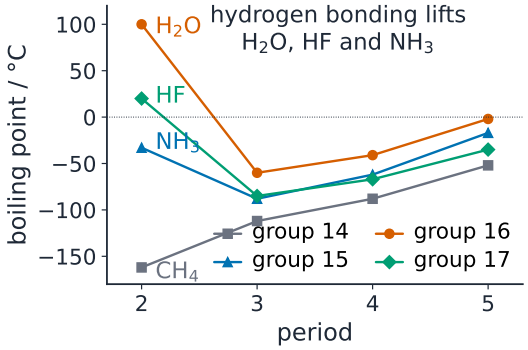
Hydrogen bonding



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

Each water molecule can form up to four hydrogen bonds.

The evidence in boiling points



Hydrogen bonding raises H_2O, HF and NH_3 above their group trends.

Comparing boiling points

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

Decision

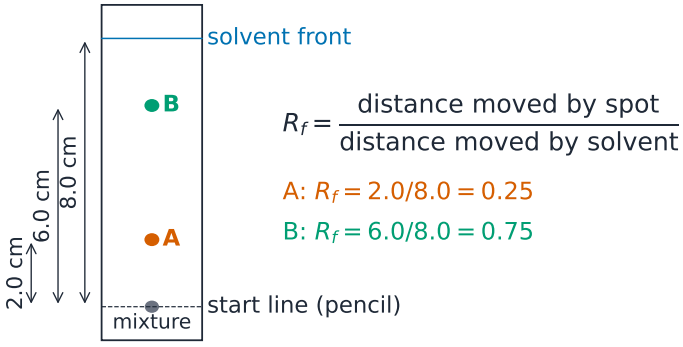
Boiling points: $-42\ ^\circ\text{C} < 20\ ^\circ\text{C} < 78\ ^\circ\text{C}$.

Like dissolves like

> A normal molecular phase change preserves the molecular covalent structure.

- **Polar** groups can favour water solubility; entropy and the whole structure also matter.
- Non-polar solutes cannot replace the hydrogen bonds between water molecules.
- Longer hydrocarbon chains make alcohols less soluble.

Separating by attraction



$$R_f = \frac{\text{distance moved by spot}}{\text{distance moved by solvent}}$$

A: $R_f = 2.0/8.0 = 0.25$

B: $R_f = 6.0/8.0 = 0.75$

R_f is dimensionless and condition-dependent; a match supports, but does not prove, identity.

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** $4/3$.

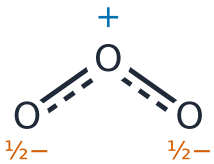
AHL: Evidence for delocalization in benzene

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

Resonance in ozone



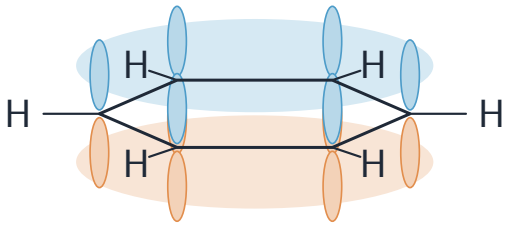
two resonance structures
(lone pairs omitted)



the real molecule (hybrid):
both O–O bonds identical

Both O–O bonds are the same length

Delocalisation in benzene



one **delocalised** π system above and below the ring

sp^2 σ framework;
all six C–C bonds equal

All six C–C bonds are the same length

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

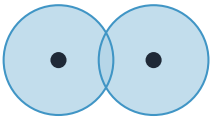
AHL: Formal charge picks the structure

- Prefer formal charges closest to zero.
- For comparable candidate formulas, negative **formal charge** is generally favoured on the more electronegative atom.

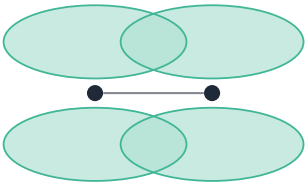
$$\mathrm{FC} = V - \tfrac{1}{2}B - L$$

CO_2: O=C=O gives 0, 0, 0; O≡C–O gives $+1$, 0, -1. O=C=O is preferred.

AHL: Sigma and pi bonds



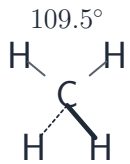
σ bond
head-on



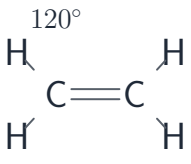
π bond
sideways

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

AHL: Hybridization follows the domains



sp^3
4 single
tetrahedral



sp^2
double + 2 single
planar



sp
triple + single
linear

Hybrid orbitals form sigma bonds; unhybridized p orbitals form 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.

A donor can also be an acceptor

Pure methoxymethane

No usual N–H/O–H/F–H donor.

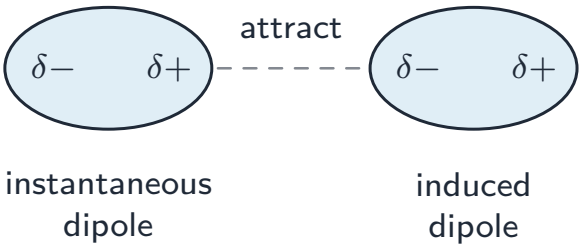
Dispersion and permanent dipole interactions.

With water

Water supplies an O–H donor.

The ether oxygen can accept a hydrogen bond.

London dispersion forces



The two attract

VSEPR predicts arrangements, not exact universal angles

A lone pair does not subtract the same angle in every molecule.

- NH_3 is pyramidal with an angle near 107°; PH_3 is pyramidal near 93.3°.
- A multiple-bond domain can compress angles between neighbouring single bonds.
- Count domains, predict geometry, then use evidence for exact angles.

A matching Rf is evidence with limits

1. **Calculate.** $R_f = 3.6/9.0 = 0.40$, with no unit.
2. **Compare.** A matching ratio supports, but does not prove, identity.
3. **Improve.** Control solvent, **stationary phase** and temperature; seek another independent separation.

Decision

One spot can contain unresolved components.

AHL: Ligand donation in a complex

1. **Donors.** $[Co(NH_3)_6]^{3+}$ has six N donor atoms: arrows point N $\rightarrow$ Co.
2. **Charge.** NH_3 is neutral, so the central cobalt oxidation state is $+3$.
3. **Geometry.** Coordination number six; octahedral in this example.

Decision

Coordination number and oxidation state are different counts.

AHL: Five- and six-domain examples



linear
CO_2



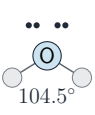
trigonal planar
BF_3



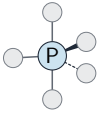
tetrahedral
CH_4



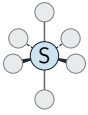
pyramidal
NH_3



bent
H_2O



trig. bipyramidal
PF_5, $120° \,\&\, 90°$



octahedral
SF_6, $90°$

Use electron-domain geometry and the model limits together.

Choosing a Lewis structure

✓ O=C=O

FC: 0 0 0

preferred

O≡C−O

FC: $+1$ 0 -1

charges further from zero

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

sum of FC $=$ charge on species; prefer FCs closest to zero

> Prefer the structure with formal charges nearest zero

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 C_2H_5OH by boiling point.

AHL. Count the sigma and pi bonds in propene.