02 Chemical Bonding

1 Types of Chemical Bonds

All bonds and intermolecular forces are _____ attractions between ...

Strong bonds	
metallic	positive metal cations and a sea of _____ valence electrons
ionic	oppositely charged _____
covalent	the nuclei of each atom and the _____ of electrons

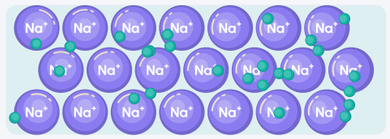
Weak intermolecular forces (IMFs)	
id–id	_____ molecules
pd–pd	_____ molecules
H bond	the _____ of one molecule and a lone pair on F, O or N of another

id–id: instantaneous dipole–induced dipole, pd–pd: permanent dipole–permanent dipole. Structures: giant metallic, giant ionic, giant molecular, simple molecular.

2 Metallic Bonding

2.1 Structure and bonding

Metals have a **giant metallic lattice** structure, with strong electrostatic forces of attraction between a sea of _____ and a lattice of positive metal cations.



2.2 Factors affecting strength

Strength of metallic bond ↑ when

1. Charge of cation ↑ and ionic radius ↓ → _____ of cation ↑
2. No. of valence e^- ↑ → more delocalised e^- in the sea
3. → stronger attraction → _____ required to overcome it → m.p. ↑

WORKED EXAMPLE Explain why the melting point of aluminium (660 °C) is higher than that of sodium (98 °C).

1. Both Al and Na have a _____ structure
2. Al delocalises _____ valence e^- per atom, Na only 1. Al^{3+} has a higher charge and _____ than Na^+
3. → more energy is needed to overcome the stronger electrostatic forces of attraction between Al^{3+} cations and the sea of delocalised e^- than between _____ and its sea of delocalised e^-

2.3 Physical properties

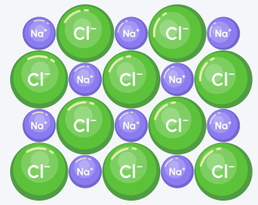
- **Conduct electricity in all states**: delocalised valence e^- become mobile and migrate freely when a potential difference is applied. More delocalised e^- → higher conductivity.
- **Good thermal conductors**: delocalised e^- throughout the structure transfer kinetic energy quickly from one end to the other.
- **Malleable and ductile**: metallic bonds are _____, so layers of cations slide over one another without overcoming the attraction between cations and the sea of e^-.

3 Ionic Bonding

3.1 Structure and bonding

Ionic compounds have a **giant ionic lattice** structure with strong electrostatic forces of attraction between _____ and _____.

DEFINITION **Coordination number**: the number of oppositely charged ions surrounding an ion in a crystal lattice (6 for both Na^+ and Cl^- in NaCl).



Dot-and-cross diagram of MgO

- Show valence e^- only, as dots and crosses
- **Square** brackets with the charge outside
- No. of each ion as a coefficient, e.g. Ca^{2+} 2[F]$^-$



3.2 Factors affecting strength

$$\text{Lattice energy} \propto \frac{q_+ \times q_-}{r_+ + r_-}$$

Greater charge and smaller ionic radii → greater magnitude of lattice energy → _____ required to overcome the attraction.

WORKED EXAMPLE Explain why the melting point of MgO (2852 °C) is higher than that of Na_2O (1132 °C).

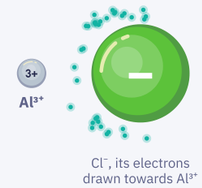
1. Both have a _____ structure
2. Mg^{2+} has a _____ and smaller ionic radius than Na^+ → greater magnitude of lattice energy
3. → more energy is needed to overcome the stronger electrostatic forces of attraction between Mg^{2+} and O^{2-} ions than between _____ ions

3.3 Physical properties

- **Conducts when molten or aqueous**: ions are _____ and migrate to the electrodes when a p.d. is applied. In the solid, ions are held in fixed positions.
- **Hard**: large amount of energy needed to overcome the strong attraction. **Brittle**: under force, layers slide, ions of _____ come together and repel → lattice shatters.
- **Soluble in polar solvents**: energy released forming _____ interactions compensates for overcoming the ionic attraction and the solvent–solvent forces. Insoluble in non-polar solvents.

3.4 Ionic bonds with covalent character

- A small, highly charged cation such as **Al^{3+} polarises** (distorts) the electron cloud of an anion such as **Cl^-** → electron density drawn between the nuclei → partial _____ of e^- → covalent character
- **Polarising power** of cation ↑ with _____ $\propto q_+ / r_+$
- **Polarisability** of anion ↑ with anion size



Cl^-, its electrons drawn towards Al^{3+}

WORKED EXAMPLE Are Al_2O_3 and $AlBr_3$ largely ionic or covalent? Compare with $AlCl_3$.

1. Al^{3+} has a high charge density → high polarising power
2. O^{2-} is smaller and less polarisable than Cl^- → electron density unshared with Al^{3+} → Al_2O_3 largely _____
3. Br^- is larger and more polarisable than Cl^- → electron density largely shared → $AlBr_3$ largely _____

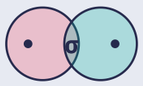
4 Covalent Bonding

4.1 Structure and bonding

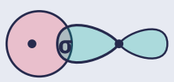
DEFINITION **Covalent bond**: the strong electrostatic forces of attraction between the _____ of each atom and the _____.

DEFINITION **σ bond**: a covalent bond formed by _____ overlap of orbitals. Electron density is concentrated between the nuclei.

DEFINITION **π bond**: a covalent bond formed by _____ overlap of p orbitals, giving two regions of overlap above and below the inter-nuclear axis.



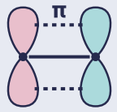
σ: s + s
H_2



σ: s + p
HCl



σ: p + p head-on
Cl_2



π: p + p sideways
after the σ bond

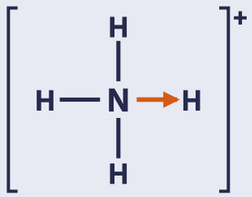
1. π overlap lies above and below the inter-nuclear axis → _____ overlap → π bond weaker than σ
2. A π bond only forms after a σ bond: the σ overlap brings the atoms close enough for the p orbitals to overlap sideways

Bond	σ	π
single	1	0
double	1	1
triple	1	_____

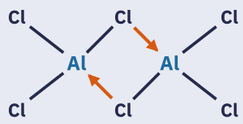
Co-ordinate (dative) bonds

DEFINITION **Dative bond**: a covalent bond formed when an atom donates a _____ of electrons into an _____ of an electron-deficient atom for sharing.

- Shown as an arrow from donor to acceptor, or as 2 e^- of the same type in a dot-and-cross diagram
- Once formed, identical to a normal covalent bond
- **Lewis acid**: electron pair _____. **Lewis base**: electron pair _____. E.g. BF_3 (acid) + NH_3 (base) → $H_3N{\rightarrow}BF_3$



NH_4^+: H^+ accepts the lone pair on N



Al_2Cl_6: 2 dative bonds, each Al gets an octet

4 Covalent Bonding (continued)

4.2 Dot-and-cross diagrams and the octet rule

Drawing steps

1. Central atom: forms the most bonds, or is the least electronegative (not H)
2. Anion: add e^- to the more electronegative atom(s). Cation: remove e^- from the less electronegative atom(s). Square brackets, charge outside
3. Give each atom an octet with single, double or triple bonds
4. Period 2 atoms: _____ valence e^-

Exceptions to the octet rule

Type	Examples (e^- around central atom)
Expanded octet	PCl_5 (10), SF_6 (12), XeF_4 (12)
Electron-deficient	$BeCl_2$ (4), BF_3 (6), $AlCl_3$ (6)
Odd no. of e^- (radicals)	NO, NO_2, ClO_2 (11, 17, 19 valence e^- in all)

KEY IDEA Period 3 and higher atoms have _____ _____, so they can **expand the octet**. Period 2 atoms have no valence d orbitals, so NCl_5 does not exist.



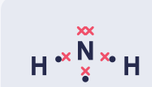
N_2 a triple bond



CO_2 two double bonds



C_2H_4 a C=C double bond



NH_3 one lone pair on N



BF_3 only 6 e^- around B



NH_4^+ dative pair from N

× and • are electrons from different atoms.

4.3 Electronegativity: covalent bonds with ionic character

DEFINITION **Electronegativity**: the measure of an atom's ability to _____ in a bond.

- Across a period ↑: nuclear charge ↑, shielding about constant → bonding e^- more strongly attracted
- Down a group ↓: more shells → bonding e^- further away and more _____
- Different electronegativities → bonding e^- drawn to the more electronegative atom → permanent **dipole**: a _____ bond

4 Covalent Bonding (continued)

4.4 Shapes of molecules (VSEPR)

VSEPR theory

1. Electron pairs around the central atom are arranged as _____ as possible to minimise repulsion
2. Repulsion: lone pair–lone pair > lone pair–bond pair > _____

- A lone pair repels more strongly: it is non-bonding, so its electron density is **closer to the nucleus**
- A double or triple bond counts as **one** region of electron density

2 e^- pairs	 **linear** **180°** CO_2 (2 bp, 0 lp)		
3 e^- pairs	 **trigonal planar** **120°** BF_3 (3 bp, 0 lp)	 **bent** **<120°** SO_2 (2 bp, 1 lp)	
4 e^- pairs	 **tetrahedral** **109.5°** CH_4 (4 bp, 0 lp)	 **trigonal pyramidal** **107°** NH_3 (3 bp, 1 lp)	 **bent** **104.5°** H_2O (2 bp, 2 lp)
5 e^- pairs lone pairs equatorial	 **trigonal bipyramidal** **120°, 90°** PCl_5 (5 bp, 0 lp)	 **see-saw** **<120°, <90°** SF_4 (4 bp, 1 lp)	 **T-shaped** **<90°** ClF_3 (3 bp, 2 lp)  **linear** **180°** XeF_2 (2 bp, 3 lp)
6 e^- pairs lone pairs axial	 **octahedral** **90°** SF_6 (6 bp, 0 lp)	 **square pyramidal** **<90°** BrF_5 (5 bp, 1 lp)	 **square planar** **90°** XeF_4 (4 bp, 2 lp)

ANSWER STRUCTURE **Shape of NH_3**

1. There are _____ bond pairs and _____ lone pair around N
2. To minimise repulsion, the _____ electron pairs are arranged as far apart as possible
3. → NH_3 is _____, bond angle _____

Electronegativity and bond angle

1. **NF_3 102° < NH_3 107°**: F more electronegative → bonding e^- closer to F → _____ around N → less repulsion → smaller angle
2. **H_2O 104.5° > H_2S 92°**: O more electronegative → bonding e^- drawn towards O → more crowding → _____ → larger angle

4 Covalent Bonding (continued)

4.5 Finding the shape of an ion or an unfamiliar molecule

Counting the electron pairs

1. Valence e^- of the central atom + one e^- per surrounding atom bonded to it
2. Add 1 for each negative charge, subtract 1 for each positive charge
3. Divide by 2 for the number of electron pairs. Surrounding atoms give the bond pairs, the rest are lone pairs

ICl_4^-: 7 + 4 + 1 = 12, so 6 pairs: 4 bp, 2 lp, square planar. **PH_4^+**: 5 + 4 − 1 = 8, so 4 pairs: 4 bp, tetrahedral.

Oxygen and substitution

- Try **=O** first (CO_2, SO_2). In an oxoanion the charge gives the number of **$-O^-$** (CO_3^{2-}, SO_4^{2-}). Use **→O** when the central atom cannot take =O (NO_2). O joining two atoms has 2 single bonds (H_2O_2)
- Swap an unfamiliar atom for one with the same **covalency** (number of bonds): $CHCl_3$ as CH_4, F_2O as H_2O, BH_4^- as CH_4, CH_3^+ as BCl_3

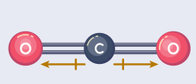
4.6 Polarity of molecules

Steps

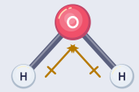
1. Identify any **polar bonds** (bond dipoles)
2. Determine the **shape** of the molecule
3. Resolve the dipoles: net dipole → polar

ANSWER STRUCTURE

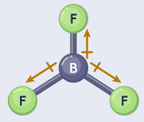
X is a **polar / non-polar** molecule as the dipoles _____ each other out. Hence there _____ an overall dipole moment.



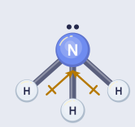
dipoles cancel
CO_2 non-polar



net dipole
H_2O polar



dipoles cancel
BF_3 non-polar



net dipole
NH_3 polar

4.7 Factors affecting strength

DEFINITION **Bond dissociation energy**: the enthalpy change when one mole of a particular covalent bond between atoms in a _____ molecule is broken. **$Cl_2(g) \rightarrow 2Cl(g)$ +244 kJ mol^{-1}**

DEFINITION **Bond length**: the distance between the _____ of the atoms in a covalent bond. Shorter bond = stronger bond.

Factors affecting covalent bond strength

1. **Orbital overlap**: larger bonding atoms → larger, more _____ valence orbitals → less effective overlap → weaker bond. Cl–Cl 244 > Br–Br 193 > I–I 151 kJ mol^{-1}
2. **Polarity**: the more electronegative atom has a larger share of the electron density → dipole, ionic character, may ↑ or ↓ strength (deduce from data). N–H 390 < O–H 460 < F–H 562
3. **Multiplicity**: triple > double > single. C–C 350, C=C 610, C≡C 840. BE(C=C) < 2 × BE(C–C) as the π bond is _____ than σ

Bond strength and reactivity

- A weaker, longer bond breaks more easily → more _____. N≡N 944 kJ mol^{-1}: N_2 is unreactive.
- C–I 240 < C–Br 280 < C–Cl 340 < C–F 485 → R–I hydrolyses fastest: bond strength outweighs polarity.
- A polar bond has a δ+ atom for nucleophiles to attack, e.g. C in C–Cl. Non-polar C–H has none, so alkanes are unreactive.

5 Intermolecular Forces

5.1 Instantaneous dipole–induced dipole (id–id)

DEFINITION **id–id**: weak electrostatic forces of attraction between _____ molecules (present between all molecules).

How id–id forms

1. Continuous movement of e^- → at an instant, one region has slightly _____
2. This instantaneous dipole _____ a dipole in a nearby molecule
3. The two molecules attract by weak electrostatic forces between opposite partial charges

Factors: strength and extent of id–id

- **No. of electrons ↑** (larger M_r) → electron cloud more _____ → stronger id–id. F_2 −188, Cl_2 −34, Br_2 59 °C
- **Surface area ↑** → more extensive id–id. pentane 36 °C > 2,2-dimethylpropane 10 °C

5.2 Permanent dipole–permanent dipole (pd–pd)

DEFINITION **pd–pd**: weak electrostatic forces of attraction between _____ molecules, in addition to id–id.

Strength of pd–pd: the larger the magnitude of the overall _____, the stronger the pd–pd interactions.

Similar vs very different M_r

Compound	M_r	Polarity	b.p. / °C
propene	**42**	non-polar	**−48**
ethanal	**44**	polar	**20**
CH_3Cl	**50.5**	more polar	**−24**
CH_3Br	**94.9**	less polar	**4**

- Similar M_r: polar ethanal has pd–pd as well as id–id → higher b.p.
- Very different M_r: CH_3Br has many more e^- → stronger id–id _____ the pd–pd of CH_3Cl

5 Intermolecular Forces (continued)

5.3 Hydrogen bonding (H bond)

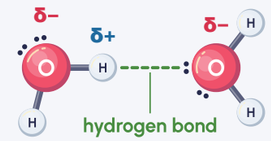
DEFINITION **Hydrogen bond**: weak electrostatic forces of attraction between the _____ _____ of one molecule and a _____ on a highly electronegative atom of another molecule.

Conditions for hydrogen bonding

1. At least one H atom directly bonded to _____
2. The neighbouring molecule has at least one _____ on F, O or N

Why only F, O or N?

They are highly electronegative, so H carries a large δ+, and their lone pair sits in a small 2p orbital with high electron density.



Draw: the lone pair, both δ+ / δ− pairs, and label the hydrogen bond.

Strength of a hydrogen bond

The more _____ the H–X bond, the _____ the hydrogen bond.
Electronegativity F > O > N → H–F is the most polar → strength of one H bond: _____

Extent of hydrogen bonding

Molecule	H on F, O, N	Lone pairs	H bonds / molecule
H_2O	2	2	_____
HF	1	3	1
NH_3	3	1	1

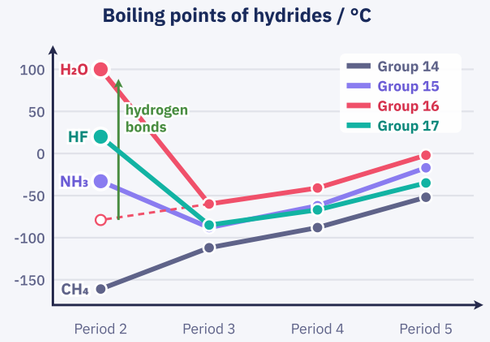
H bonds per molecule = the smaller number (HF: 1 H, NH_3: 1 lone pair).

6 Physical Properties of Covalent Substances

6.1 Simple molecular substances: boiling points

Low m.p. and b.p.: only the **weak IMF** between the discrete molecules are overcome, not the covalent bonds within them.

H_2O, HF and NH_3 boil far higher than the trend in id–id predicts, because of hydrogen bonding.



WORKED EXAMPLE Explain why the boiling points are H_2O (100 °C) > HF (20 °C) > NH_3 (–33 °C), using both the strength and the extent of hydrogen bonding.

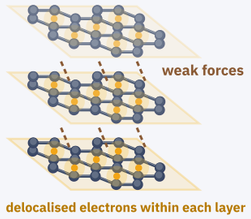
1. All three have hydrogen bonds between molecules, b.p. depends on both their _____ and their _____
2. **Strength**: H–F is the most polar bond, so one H bond between HF molecules is the strongest, then H_2O, then NH_3
3. **Extent**: each H_2O can form _____ H bonds (2 H atoms, 2 lone pairs), but HF and NH_3 form only _____ on average
4. H_2O: more energy is required to overcome the more _____ H bonds between H_2O molecules, which outweighs their slightly lower strength → highest b.p.
5. HF vs NH_3: same extent, but the H bonds between HF molecules are _____ → b.p. HF > NH_3

6.2 Giant molecular structures

Diamond



Graphite



Property	Diamond	Graphite
Bonding	Each C covalently bonded to _____ others, tetrahedrally	Each C bonded to _____ others in hexagonal layers. The 4th valence e^- is _____ within each layer
m.p.	Very high: a large amount of energy is needed to overcome the strong and extensive _____	
Hardness	**Hard**: atoms are held rigidly and do not slide	**Soft**: weak _____ between layers let them slide
Electrical conductivity	**Non-conductor**: all 4 valence e^- are used in covalent bonding → no _____	**Conducts** parallel to the layers: delocalised e^- move when a p.d. is applied
Solubility	Insoluble in all solvents: energy released forming solute–solvent interactions cannot overcome the strong covalent bonds	

NOTE **m.p. diamond (3350 °C) > Si (1410 °C)**: C uses smaller, less diffused $2sp^3$ orbitals than Si ($3sp^3$) → more effective overlap → stronger C–C bonds. Other giant molecular examples: Si, SiO_2, BN.

6 Physical Properties of Covalent Substances (continued)

6.3 Special effects of hydrogen bonding

Ice is less dense than water

1. Ice adopts an _____, crystalline structure with hexagonal holes
2. Each H_2O forms H bonds with _____ other H_2O molecules
3. Each O is surrounded tetrahedrally by 4 H atoms: 2 covalent bonds, 2 H bonds
4. The regular arrangement spaces molecules more widely than in the liquid
5. → water expands on freezing → ice is _____ than water

Intramolecular H bonds lower the boiling point

2-nitrophenol (b.p. 216 °C) < 4-nitrophenol (279 °C)

1. The –OH and $–NO_2$ groups are in close proximity and correctly oriented for an _____ H bond
2. → the H atom of –OH is less available for _____ H bonds
3. Boiling overcomes intermolecular H bonds → less energy needed → lower b.p.

Ethanol, NH_3, HF and ethanoic acid are miscible with water: they form H bonds with water molecules. Ethanoic acid in benzene forms H-bonded **dimers** (apparent M_r 120, not 60).

7 Structure and Physical Properties

Structure	m.p. / b.p.	Electrical conductivity	Solubility	Hardness
Giant metallic **e.g. Cu**	high: strong metallic bonds	good in all states: delocalised e^-	insoluble (some react with water)	malleable, ductile
Giant ionic **e.g. NaCl, MgO**	high: strong ionic bonds	only molten / aqueous: mobile ions	soluble in polar solvents (ion–dipole)	hard, brittle
Giant molecular **e.g. diamond, graphite**	very high: strong, extensive covalent bonds	non-conductor (graphite: along layers)	insoluble in all solvents	diamond hard, graphite soft
Simple molecular **e.g. I_2**	low: _____ between molecules	non-conductor: discrete, uncharged molecules	like dissolves like: polar in polar, non-polar in non-polar	soft: weak IMF easily overcome

ANSWER STRUCTURE **Melting point**

State each structure → more energy is needed to overcome the stronger _____ _____ between the _____ of ZZ than the weaker … of YY.

Same structure? Explain the _____ that makes one attraction stronger, e.g. charge and ionic radius (ionic), no. of valence e^- and cation size (metallic), no. of e^- or surface area (id–id), extent of H bonding.

ANSWER STRUCTURE **Solubility**

Energy released forming _____ interactions is / is not able to compensate for the energy needed to overcome the solute–solute and solvent–solvent interactions → soluble / insoluble.