Unit 5 · Chemical Bonding and Shapes of Molecules

STUDY NOTES

WHAT NEB'S GRADE 11 EXAM ASKS

- **CDC's grid (2077):** Physical Chemistry (Units 1–8 together): 28 of 75 marks
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** MCQ: why ammonia is so soluble in water (hydrogen bonding with water)
- **MCQ (1 mark)**
  - true of hydrogen bonding; its effect on properties; lowest boiling point; soluble in water
  - 4 bond pairs, no lone pair: shape; largest bond angle; NH_4^+ shape and hybridization
  - more delocalized electrons → stronger metallic bond; what VBT describes
  - strongest London forces; σ and π in benzene; atoms on the axis of an orbital picture
- **Short (5 marks, in parts)**
  - differences: ionic/covalent network solid, sp^2/sp^3, σ/π
  - reasons: $CuSO_4$ brittle, Cu malleable; iodine sublimes; glycerol viscous; CO_2 linear, SO_2 bent; NH_3 polar, BH_3 not; σ stronger than π; petrol sealed
  - octet rule, three that follow and three that don't; an ionic crystal hammered, conducting only molten
  - resonance: define, cause, stability (SO_3, CO_3^{2-}, SO_2); dipole moment, its unit, polar bonds in a non-polar molecule
  - CH_3Cl, BF_3 vs NF_3, dichlorobenzenes: which bond is more polar, which molecule is polar
  - **Lewis structures**: H_2O, CCl_4, PCl_5, NO_3^-, SO_4^{2-}, O_3, I_3^-, ClO_3^-, SiH_4, IF_5, HNO_3, NO_2^-
  - lone pairs, bond pairs and shape from a picture; a table for $BeCl_2$, BF_3, CH_4, PCl_5
  - ethene and ethyne orbital pictures; NH_3's shape and solubility; HCl, HBr, HI: dipole, length, strength; halides' boiling points
- **Long (8 marks)**: VSEPR postulates, BF_3 vs PF_3 (shape, hybridization, angle, polarity); methane and CCl_4; benzene's σ, π and equal bonds; N_2 by VBT (why unreactive); odd-electron molecules; sp^2 hydrocarbon; VBT postulates, H_2, HF, why not He_2; group 16 hydrides' boiling points; σ vs π, O_2's orbitals; Mg_3N_2 from 2, 8, 2 and 2, 5; four kinds of solid; dipole moment table

Key terms

Valence electrons: electrons of the outermost (valence) shell.

Octet rule (Lewis, Kossel, 1916): atoms gain, lose or share electrons to have eight in the valence shell (H, He two).

Ionic (electrovalent) bond: attraction between oppositely charged ions formed by the transfer of electrons.

Lattice energy: energy released when gaseous ions come together from infinity to form 1 mol of crystal (NaCl 787 kJ/mol).

Covalent bond: mutual sharing of a pair of electrons; single, double, triple.

Coordinate (dative) bond: both shared electrons from one atom (donor → acceptor).

Lone pair: valence pair not in a bond; **bond pair**: in a bond.

Polar covalent bond: unequal sharing, $\delta+$ and $\delta-$ ends; **non-polar**: equal sharing.

Resonance: one molecule described by several Lewis structures; the real one is their **hybrid**.

Resonance energy: how much more stable the hybrid is than its best structure (benzene ~150 kJ/mol).

Sigma (σ) bond: head-on overlap along the axis; **pi (π) bond**: sideways overlap of parallel p orbitals.

Hybridization: mixing of orbitals of slightly different energy on one atom into as many identical hybrid orbitals.

Dipole moment μ: $q \times d$; a vector; unit debye.

Bond length: distance between the nuclei of two bonded atoms.

Van der Waals forces: weak forces between molecules (London, dipole–dipole).

Hydrogen bond: attraction between H bonded to F, O or N and a lone pair on another F, O or N.

Metallic bond: attraction between positive metal ions and the sea of delocalized electrons.

Formulas

$\mu = q \times d$	$1\ \text{D} = 3.336 \times 10^{-30}$ C m **Use:** dipole moment
$\%\ \text{ionic} = \dfrac{\mu}{ed} \times 100$	μ measured; $e = 1.602 \times 10^{-19}$ C **Use:** ionic character
$\text{formal charge} = \text{V} - \text{L} - \text{B}/2$	V valence, L lone-pair, B bonding electrons **Use:** choosing a Lewis structure

The octet and its exceptions

- incomplete: $BeCl_2$, BeH_2 (4 e on Be), BF_3, BCl_3 (6 on B)
- expanded (period 3 on, d orbitals, room): PCl_5 (10), SF_6 (12), H_2SO_4; NCl_5 can't exist (no 2d)
- odd-electron: NO (11), NO_2 (17), ClO_2 (19): an unpaired electron, paramagnetic
- follow it: NaCl, CH_4, H_2O, NH_3, CO_2

Ionic bonding

- metal (low IE) → electrons → non-metal (high EA); Na (2, 8, 1) + Cl (2, 8, 7) → Na^+ (2, 8) Cl^- (2, 8, 8); Ca + 2Cl → $CaCl_2$; Mg + O → MgO
- conditions: ΔEN over ~1.7, low IE, high EA, high lattice energy
- non-directional: no NaCl molecules; each Na^+ has six Cl^- round it (rock-salt cube)

Properties

- hard crystals, high mp (NaCl 801 °C, MgO 2852 °C)
- soluble in water (ions hydrated), not in petrol
- conduct only molten or dissolved (ions then free to move)
- brittle: a blow brings like charges face to face

Covalent bonding

- H_2: attraction balances repulsion at 74 pm, energy lowest (436 kJ/mol released)
- conditions: similar, high EN (non-metals), high IE and EA, half-filled orbitals
- H–H, O=O, N≡N; NH_3 three bond pairs, one lone pair
- **dative**: $NH_3 + H^+ \rightarrow NH_4^+$ (four identical N–H); $H_2O + H^+ \rightarrow H_3O^+$; $H_3N \rightarrow BF_3$
- polar bond ≠ polar molecule (CO_2)

Properties: low mp and bp (weak forces between molecules; diamond, SiO_2 are networks); like dissolves like; don't conduct (graphite does)

Lewis structures

1. count valence electrons (+1 per minus charge, −1 per plus)
2. central atom: least electronegative, never H; single bonds to it
3. outer octets with lone pairs
4. leftover electrons on the central atom
5. still short: lone pairs into double bonds

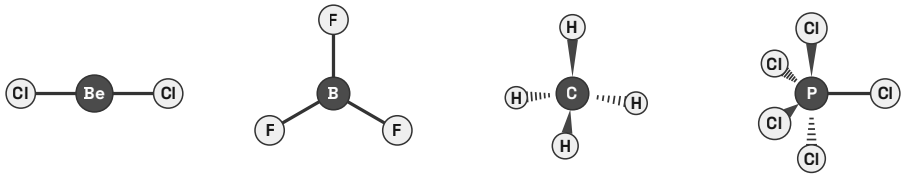
- H_2O 8 e: 2 bp, 2 lp; CO_2 16 e: O=C=O
- NO_3^- 24 e: one N=O, two N–O^-; SO_4^{2-} 32 e; NH_4^+ 8 e
- ions in square brackets with the charge outside
- formal charges add up to the ion's charge (N in NH_4^+: 5 − 0 − 4 = +1)

Resonance

- O_3: two structures; both O–O 128 pm (single 148, double 121)
- CO_3^{2-}: three; C–O all 129 pm, −⅔ on each O
- benzene: two Kekulé; C–C all 139 pm (154, 134)
- SO_2, SO_3, NO_3^-, NO_2^- resonate too; H_2O_2 doesn't
- cause: electrons delocalized; the hybrid is more stable
- ↔ (not ⇌): one real molecule, never switching

VSEPR

1. bond pairs and lone pairs round the central atom; a multiple bond counts as one
2. repulsion: **lp–lp > lp–bp > bp–bp**
3. pairs get as far apart as possible → shape

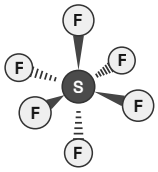


$BeCl_2$
linear
180°

BF_3
trigonal planar
120°

CH_4
tetrahedral
109.5°

PCl_5
trigonal bipyramidal
120°, 90°



SF_6
octahedral
90°

2 to 6 bond pairs: linear, trigonal planar, tetrahedral, trigonal bipyramidal, octahedral.

bp	lp	Shape	Angle	Example
2	0	linear	180°	$BeCl_2$, CO_2
3	0	trigonal planar	120°	BF_3
4	0	tetrahedral	109.5°	CH_4, CCl_4, NH_4^+
3	1	trigonal pyramidal	107°	NH_3, PF_3
2	2	bent	104.5°	H_2O (H_2S 92°)
2	1	bent	~119°	SO_2
5	0	trigonal bipyramidal	120°, 90°	PCl_5
6	0	octahedral	90°	SF_6

- lone pair held by one nucleus: wider cloud, pushes harder
- H_2S 92° < H_2O: S larger, less electronegative, bond pairs farther apart
- 5 pairs: SF_4 seesaw (1 lp), ClF_3 T-shaped (2), XeF_2 linear (3)
- BF_3 planar (no lp), PF_3 pyramidal (1 lp)

Valence bond theory

1. a bond = overlap of two half-filled orbitals, electrons of opposite spin
2. more overlap, stronger bond
3. head-on → σ; sideways (parallel p) → π

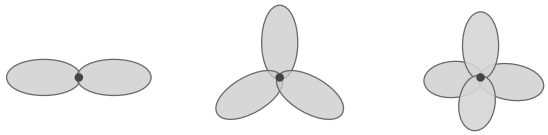
4. energy falls as they overlap

- s–s σ (H_2), s–p σ (HCl, HF), p–p σ (F_2, Cl_2)
- O_2: $\sigma + \pi$; N_2: $\sigma + 2\pi$ (946 kJ/mol, unreactive)
- He_2: both 1s full, nothing to pair

σ bond	π bond
head-on, along the axis	sideways, above and below it
strong, more overlap	weaker
free rotation	no rotation
alone; s, p or hybrid	only with a σ; only p

Hybridization

- C: $2s^2\ 2p^2 \rightarrow$ excited $2s^1\ 2p^3 \rightarrow$ four sp^3 (four identical C–H)
- number of hybrids = orbitals mixed; equivalent; definite directions; σ bonds only



sp 180° linear — **sp²** 120° trigonal planar — **sp³** 109.5° tetrahedral

sp linear 180°, sp^2 flat 120°, sp^3 tetrahedral 109.5°.

	Mixed	Shape	Examples
sp	s + p	linear, 180°	$BeCl_2$, CO_2, C_2H_2
sp^2	s + 2p	trigonal planar, 120°	BF_3, BCl_3, C_2H_4, benzene
sp^3	s + 3p	tetrahedral, 109.5°	CH_4, CCl_4, NH_3, H_2O, NH_4^+

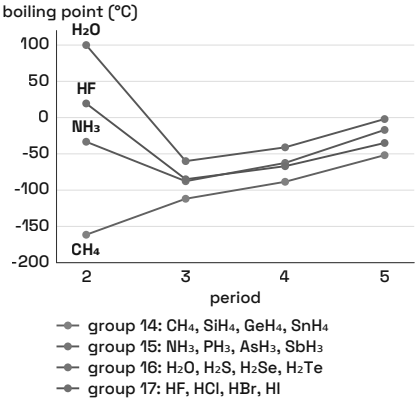
- ethene: $5\sigma + 1\pi$; ethyne: $3\sigma + 2\pi$; benzene: $12\sigma + 3\pi$
- single bond σ; double $\sigma + \pi$; triple $\sigma + 2\pi$

Bond characteristics

- symmetric shapes cancel bond dipoles: CO_2, BeF_2, BF_3, CH_4, CCl_4, PCl_5, SF_6 $\mu = 0$
- polar: H_2O 1.85 D, NH_3, CH_3Cl 1.87 D, $CHCl_3$, NF_3; 1,2-dichlorobenzene most polar, 1,4- zero
- bond length rises with atom size (F–F 142, Cl–Cl 199 pm), falls with ΔEN and with more bonds
- C–C 154 pm, 347 kJ/mol; C=C 134, 614; C≡C 120, 839
- HCl < HBr < HI in length; HI < HBr < HCl in dipole and strength
- ionic character with $\Delta\chi$: LiF 89%, C–F 39%, F–F 0; ~1.7 is a guide (HF 1.78, covalent)

Forces between molecules

- **London**: temporary dipoles; stronger for bigger molecules (CH_4 gas, petrol liquid, wax solid)
- **dipole–dipole**: permanent dipoles (HCl, SO_2)
- molecular solids: dry ice, iodine, naphthalene: soft, low mp, sublime
- **hydrogen bond** (H on F, O, N ··· lone pair); intermolecular (water, HF chains, ethanol) or intramolecular (o-nitrophenol, lower bp than p-)
- raises bp: NH_3 −33 °C vs PH_3 −88; HF 20 vs HCl −85; H_2O 100 vs H_2S −60
- dissolves alcohols, acids, NH_3, sugar, urea in water; glycerol viscous; ice floats (open rings)



NH_3, H_2O and HF boil far above the trend of their groups.

Metallic bonding

- metal ions in a sea of delocalized electrons
- stronger with higher charge, smaller ion, more electrons (Na < Mg < Al)
- conduct heat and electricity; malleable and ductile (layers slide, the sea moves with them); shiny
- $CuSO_4$ brittle (ions), Cu malleable (electron sea)

COMMON MISTAKES

✗ SO_2's resonance with "carbon"
✓ its central atom is sulphur.

✗ CH_3• as an sp^3 example
✓ planar, near sp^2; use CH_4, NH_3, H_2O.

✗ NH_4Cl a molecular solid
✓ ionic.

✗ C–C 147 pm
✓ 154 pm.

✗ PCl_5 and BF_3 polar
✓ symmetric: $\mu = 0$.

✗ H_2O_2 shows resonance
✓ one Lewis structure.

✗ high lattice energy makes a salt dissolve
✓ solubility balances lattice and hydration energy.

✗ 1.7 is a law
✓ a guide: HF (1.78) is covalent.