JEE MAIN · PAPER 1 · CHEMISTRY

03 Chemical Bonding & Molecular Structure

Formula & concept sheet

Why atoms bond and what the molecule looks like: Lewis structures, formal charge and resonance, ionic bonds with lattice enthalpy and Fajans' rules, VSEPR shapes and hybridisation, molecular orbital theory for diatomics, dipole moments and hydrogen bonding. Each idea is explained first, then the tables, shortcuts and traps.

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READ ALONGSIDE NCERT XI · Chemical Bonding and Molecular Structure

HOW TO USE THIS SHEET

1. **Skim** — Read the Key ideas, then the formula cards.
2. **Memorise** — Learn the formulas and check every Trap box.
3. **Test** — Do the worked examples, then this chapter's PYQs.
4. **Revise** — Use the last-minute checklist before the exam.

Formula memorise · **Key idea** why it works · **Trap** marks lost here · **PYQ** how it is asked

Practise this chapter with real past-paper questions on Prep Vault. Written for revision, not as a first read.

CHAPTER 03

Chemical Bonding & Molecular Structure

NCERT XI · Chemical Bonding and Molecular Structure

Covers: Kossel-Lewis approach · ionic bond and lattice enthalpy · covalent bond, electronegativity, Fajans' rule, dipole moment · VSEPR shapes · valence bond theory, hybridisation involving s, p and d orbitals, resonance · molecular orbital theory, bond order, magnetism · hydrogen bonding · elementary metallic bonding.

1 Covalent bond: Lewis structures, formal charge, resonance

- Atoms bond to reach a stable noble-gas arrangement of valence electrons (the **octet**, 2 for H). **Ionic** bonds come from complete transfer of electrons, **covalent** bonds from sharing of electron pairs; a **coordinate** bond is a shared pair that both come from one atom (NH_4^+, the adduct $H_3N \rightarrow BF_3$).
- In a Lewis structure each shared pair is a bond and each unshared pair a lone pair. More shared pairs between two atoms means a **shorter, stronger** bond: bond length $C-C > C=C > C\equiv C$ (154, 134, 120 pm).

FORMAL CHARGE

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

V valence electrons of the free atom, L non-bonding electrons, B bonding electrons; the charges add up to the charge of the species

BOND ORDER FROM RESONANCE

$$BO = \frac{\text{bonds in one structure}}{\text{equivalent positions}}$$

all bonds of a hybrid are equal and fractional; CO_3^{2-}: 4 bonds over 3 positions $= 1.33$

BOND ENTHALPY TRENDS

$BO \uparrow \Rightarrow$ length $\downarrow$, energy $\uparrow$

H−F > H−Cl > H−Br > H−I; but F_2 (158) < Cl_2 (242) because lone pairs on small F repel

RESONANCE: BOND ORDERS

SPECIES	STRUCTURES	BOND ORDER
O_3, NO_2^-, SO_2	2	1.5
CO_3^{2-}, NO_3^-, SO_3	3	1.33
SO_4^{2-}	6 (d-orbital forms)	1.5
PO_4^{3-}	4	1.25
ClO_4^-	4	1.75
benzene C−C	2 (Kekulé)	1.5

OCTET RULE EXCEPTIONS

- **Electron-deficient**: $BeCl_2$ (4 e^-), BF_3 (6), $AlCl_3$ (dimerises to Al_2Cl_6 through bridging Cl).
- **Odd-electron**: NO, NO_2, ClO_2.

EXPANDED OCTET

- Only for period 3 and below (they have d orbitals): PCl_5, SF_6, XeF_4, IF_7.
- Period-2 atoms cannot expand: NCl_5 and OF_6 do not exist.

BOND PARAMETERS

PARAMETER	MEANING
bond length	distance between the nuclei; covalent radius < van der Waals radius of the same atom
bond angle	angle between two bonds at an atom; fixed by electron-pair repulsion
bond enthalpy	energy to break one mole of the bond in gaseous molecules, in kJ mol^{-1}; for polyatomics the average over equivalent bonds
bond order	number of bonds between two atoms (1, 2, 3; fractional in resonance hybrids and in MO theory)

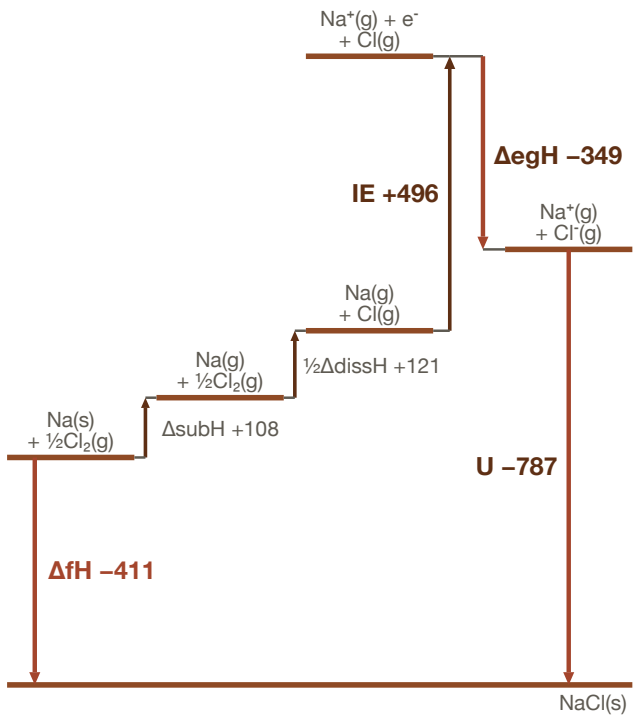
KEY IDEA

Choose the best Lewis structure by formal charge: small charges, negative charge on the more electronegative atom, no adjacent like charges. Ozone: central O $+1$, one terminal O -1, the other 0; sum 0.

TRAP

Resonance structures are not different molecules in equilibrium: the real molecule is one hybrid, lower in energy than any single structure, with **equal** bond lengths. Formal charge is bookkeeping, not the real charge.

2 Ionic bond, lattice enthalpy and Fajans' rules



to scale in kJ mol^{-1}: $+108$, $+121$, $+496$, -349, -787 give $\Delta_f H = -411$

LATTICE ENTHALPY U The energy released when one mole of an ionic solid forms from its gaseous ions, $\mathrm{Na^+\,(g) + Cl^-\,(g) \longrightarrow NaCl\,(s)}$ (quoted as a positive magnitude, NaCl ≈ 787 kJ mol^{-1}). It is the main reason ionic compounds form even though ionisation costs energy.

TREND

$$U \propto \frac{z^+ z^-}{r^+ + r^-}$$

rises with ionic charge, falls with ionic size: MgO (≈ 3800) $\gg$ LiF (1037) $>$ NaCl (787)

BORN-HABER (NACL TYPE)

$$\Delta_f H = \Delta_{sub} H + IE + \tfrac{1}{2}\Delta_{diss} H + \Delta_{eg} H - U$$

Hess's law around the cycle; U positive, $\Delta_{eg} H$ negative for Cl

BORN-HABER STEPS FOR NACL (KJ MOL^{-1})

STEP	EQUATION	ΔH
sublimation of Na	$\mathrm{Na\,(s) \longrightarrow Na\,(g)}$	$+108$
ionisation of Na	$\mathrm{Na\,(g) \longrightarrow Na^+\,(g) + e^-}$	$+496$
half dissociation of Cl_2	$\mathrm{\tfrac{1}{2}\,Cl_2\,(g) \longrightarrow Cl\,(g)}$	$+121$
electron gain of Cl	$\mathrm{Cl\,(g) + e^- \longrightarrow Cl^-\,(g)}$	-349
lattice formation	$\mathrm{Na^+\,(g) + Cl^-\,(g) \longrightarrow NaCl\,(s)}$	-787
overall	$\mathrm{Na\,(s) + \tfrac{1}{2}\,Cl_2\,(g) \longrightarrow NaCl\,(s)}$	-411

$108 + 496 + 121 - 349 - 787 = -411$. The second electron gain of oxygen, $\mathrm{O^-\,(g) + e^- \longrightarrow O^{2-}\,(g)}$, is **endothermic** (repulsion), yet MgO forms because U is huge.

FAJANS' RULES: MORE COVALENT CHARACTER

- **small, highly charged cation** (it polarises the anion): $Li^+ > Na^+$, $Al^{3+} > Mg^{2+}$
- **large, highly charged anion** (easily polarised): $I^- > Cl^-$, $S^{2-} > O^{2-}$
- cation with an **18-electron** (pseudo-noble-gas) shell: Cu^+, Ag^+ more than Na^+ of the same size

RESULTS TO REMEMBER

- $LiCl$ is more covalent than $NaCl$; $AlCl_3$ is covalent; AgI is the least soluble silver halide; LiI dissolves in ethanol.
- Polarisation order of halides: $F^- < Cl^- < Br^- < I^-$, so ionic character $AgF > AgCl > AgBr > AgI$.

PAULING ELECTRONEGATIVITY

ATOM	χ	ATOM	χ
F	4.0	C, S, I	2.5
O	3.5	H, P	2.1
N, Cl	3.0	Si	1.8
Br	2.8	Na	0.9

Rises across a period, falls down a group; rises with s-character of the hybrid ($sp > sp^2 > sp^3$) and with oxidation state. A larger difference means a more polar bond.

IONIC AND COVALENT COMPOUNDS COMPARED

PROPERTY	IONIC	COVALENT
bond	electrostatic, non-directional	shared pairs, directional
state, melting point	hard crystalline solids, high m.p. and b.p. (strong lattice)	gases, liquids, soft solids, low m.p.; network solids (SiO_2, diamond) are the exception
conduction	conduct when molten or dissolved (mobile ions), not as solids	poor conductors; graphite and acid solutions are exceptions
solubility	soluble in polar solvents (water), not in non-polar	soluble in non-polar solvents; polar covalent ones dissolve in water
reactions	fast, ion combination	slow, molecular, often need a catalyst

KEY IDEA

Ionic versus covalent is a scale, not two boxes: no bond is 100% ionic. Ionic character of an A–B bond rises with the electronegativity difference; Fajans' rules tell how an ionic bond turns covalent.

TRAP

Lattice enthalpy goes **up** for higher charge and smaller ions; do not confuse it with hydration enthalpy or ionisation enthalpy. NCl_5 and OF_6 do not exist: period 2 cannot expand its octet.

3 VSEPR: shapes of molecules and ions

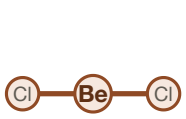
VSEPR Electron pairs (bond pairs and lone pairs) around the central atom repel and take positions of minimum repulsion, so the shape follows from the **steric number** SN = σ bonds + lone pairs on the central atom. Lone-pair repulsion is stronger: lp-$lp > lp$-$bp > bp$-bp, so lone pairs squeeze the bond angles.

SHAPE IN FOUR STEPS

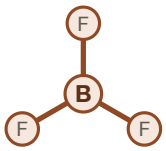
1. Valence electrons V of the central atom; add 1 for each negative charge, subtract 1 for each positive charge.
2. Subtract the electrons used in bonds: 1 per monovalent atom (H, halogen), 2 per terminal O or S (whether drawn single or double bonded).
3. Lone pairs $= \dfrac{\text{what is left}}{2}$; $SN = \sigma$ bonds + lone pairs (σ bonds = number of atoms attached).
4. Read shape and hybridisation from the table below: SN $2, 3, 4, 5, 6, 7$ gives sp, sp^2, sp^3, sp^3d, sp^3d^2, sp^3d^3.

SHAPES BY STERIC NUMBER

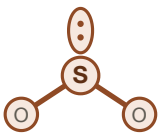
SN	BP + LP	SHAPE	HYBRID	EXAMPLES
2	2 + 0	linear	sp	$BeCl_2$, CO_2, $HgCl_2$, NO_2^+
3	3 + 0	trigonal planar	sp^2	BF_3, SO_3, NO_3^-, CO_3^{2-}
3	2 + 1	bent	sp^2	SO_2, O_3, NO_2^-
4	4 + 0	tetrahedral	sp^3	CH_4, NH_4^+, SO_4^{2-}, ClO_4^-
4	3 + 1	trigonal pyramidal	sp^3	NH_3, PCl_3, H_3O^+, ClO_3^-, XeO_3
4	2 + 2	bent	sp^3	H_2O, OF_2, H_2S
5	5 + 0	trigonal bipyramidal	sp^3d	PCl_5, PF_5, $Fe(CO)_5$
5	4 + 1	see-saw	sp^3d	SF_4, XeO_2F_2
5	3 + 2	T-shaped	sp^3d	ClF_3, BrF_3
5	2 + 3	linear	sp^3d	XeF_2, I_3^-, ICl_2^-
6	6 + 0	octahedral	sp^3d^2	SF_6, PF_6^-, SiF_6^{2-}
6	5 + 1	square pyramidal	sp^3d^2	BrF_5, IF_5, $XeOF_4$
6	4 + 2	square planar	sp^3d^2	XeF_4, ICl_4^-, BrF_4^-
7	7 + 0	pentagonal bipyramidal	sp^3d^3	IF_7
7	6 + 1	distorted octahedral	sp^3d^3	XeF_6



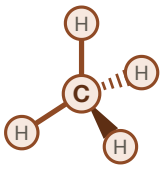
linear
2 bp
$BeCl_2$ 180°



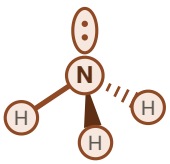
trigonal planar
3 bp
BF_3 120°



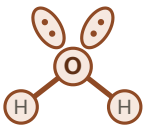
bent
2 bp + 1 lp
SO_2 ~119°



tetrahedral
4 bp
CH_4 109.5°

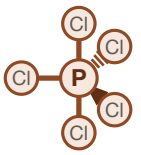


trigonal pyramidal
3 bp + 1 lp
NH_3 107°

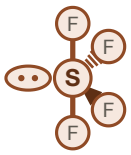


bent
2 bp + 2 lp
H_2O 104.5°

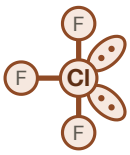
bp = bond pairs, lp = lone pairs; wedge bond toward the viewer, dashed bond away; each lone pair squeezes the bond angle below its ideal value



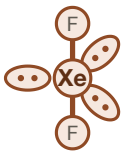
trigonal bipyramidal
5 bp
PCl_5



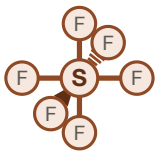
see-saw
4 bp + 1 lp
SF_4



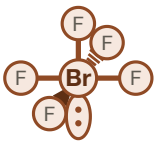
T-shaped
3 bp + 2 lp
ClF_3



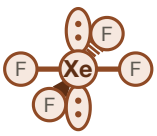
linear
2 bp + 3 lp
XeF_2



octahedral
6 bp
SF_6 90°



square pyramidal
5 bp + 1 lp
BrF_5



square planar
4 bp + 2 lp
XeF_4

in a trigonal bipyramid the lone pairs sit in the equatorial plane (more room); in a square planar molecule the two lone pairs are trans

REMEMBER

Steric number $2, 3, 4, 5, 6$ gives line, triangle, tetrahedron, bipyramid, octahedron. Each lone pair replaces a bonded atom: $CH_4 \to NH_3 \to H_2O$ (tetrahedron to pyramid to bent); $PCl_5 \to SF_4 \to ClF_3 \to XeF_2$; $SF_6 \to BrF_5 \to XeF_4$. Name the **shape** from the atoms only, the **geometry** from atoms plus lone pairs.

QUICK CHECK

Shape and hybridisation of XeF_4 and of ClF_3?

Answer: XeF_4: $SN = 4 + 2 = 6$, sp^3d^2, square planar. ClF_3: $SN = 3 + 2 = 5$, sp^3d, T-shaped.

BOND ANGLE COMPARISONS

SERIES	ANGLES (DEGREES)
$NO_2^+ > NO_2 > NO_2^-$	180, 134, 115
$CH_4 > NH_3 > H_2O$	109.5, 107, 104.5
$NH_3 > PH_3 > AsH_3$	107, 93.5, 92
$H_2O > H_2S > H_2Se$	104.5, 92, 91
$NH_3 > NF_3$	107, 102
$OF_2 < H_2O < Cl_2O$	103, 104.5, 111

REASONS

- More lone pairs (or a lone pair instead of a bond pair) means a smaller angle.
- Down a group the central atom is bigger and hardly hybridises, so the angle falls towards $90°$.
- Electronegative **ligands** pull the bonding pairs away from the central atom: the angle shrinks ($NF_3 < NH_3$); electronegative **central atom**: the pairs are held near it and repel more, the angle rises.
- In trigonal bipyramids and their derivatives the lone pairs go in the **equatorial** positions; in square planar XeF_4 they are trans.

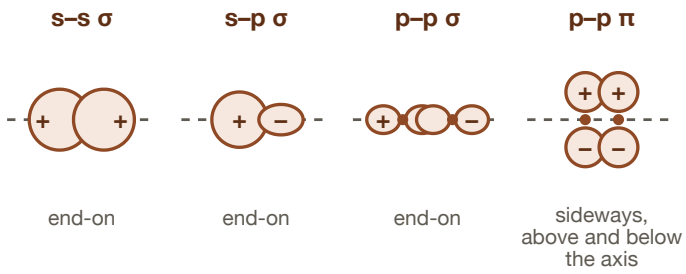
KEY IDEA

Isoelectronic species share a shape: CO_2, NO_2^+, N_3^- are linear; NH_4^+, BF_4^-, CH_4 tetrahedral. SF_4, ClF_3, XeF_2 show how 1, 2, 3 lone pairs turn a bipyramid into see-saw, T and linear.

TRAP

Electron geometry is not molecular shape: NH_3 and H_2O are both tetrahedral in electron geometry. $XeOF_4$ is $SN = 6$ with one lone pair (square pyramid), not octahedral. Hybridisation describes the central atom only.

4 Valence bond theory and hybridisation



sigma: end-on, along the axis; pi: sideways, a nodal plane contains the axis

VALENCE BOND THEORY A covalent bond forms when half-filled orbitals of two atoms overlap with opposite spins; the greater the overlap, the stronger the bond. **Sigma (σ)** bonds come from end-on overlap along the bond axis (free rotation); **pi (π)** bonds from sideways overlap of parallel p orbitals above and below the axis (a nodal plane contains the axis; rotation is blocked).

COUNTING

- Single bond: 1σ; double: $1\sigma + 1\pi$; triple: $1\sigma + 2\pi$. A σ bond is stronger than a π bond.
- Ethane 7σ; ethene $5\sigma, 1\pi$; ethyne $3\sigma, 2\pi$; benzene $12\sigma, 3\pi$; allene $CH_2{=}C{=}CH_2$ $6\sigma, 2\pi$; hex-1,3-dien-5-yne $11\sigma, 4\pi$.

HYBRIDISATION The mixing of atomic orbitals of one atom (of similar energy) into the same number of **equivalent hybrid orbitals** that point to the corners of a regular figure and overlap better than pure orbitals. The number of hybrids equals the steric number.

HYBRIDISATION AND ITS CONSEQUENCES (CARBON)

HYBRID	GEOMETRY	% S	EXAMPLE	C–H BOND (PM)	C–C (PM)
sp	linear, 180°	50	C_2H_2, $BeCl_2$	106	120 (triple)
sp^2	trigonal planar, 120°	33.3	C_2H_4, BF_3, benzene	108	134 (double)
sp^3	tetrahedral, 109.5°	25	CH_4, C_2H_6	109	154 (single)

More s-character gives a shorter, stronger bond and a more electronegative carbon: acidity of C–H, $HC{\equiv}CH > H_2C{=}CH_2 > H_3C{-}CH_3$.

WHICH D ORBITALS ARE USED

HYBRID	ORBITALS MIXED	EXAMPLE
sp^3d	s, three p, d_{z^2}	PCl_5 (trigonal bipyramidal)
sp^3d^2	s, three p, d_{z^2}, $d_{x^2-y^2}$	SF_6 (octahedral)
dsp^2	$(n-1)d_{x^2-y^2}$, s, two p	$[Ni(CN)_4]^{2-}$, $PtCl_4^{2-}$ (square planar)
sp^3d^3	s, three p, three d	IF_7 (pentagonal bipyramidal)

COUNTING HYBRIDISATION

$SN = \sigma$ bonds + lone pairs

each π bond uses an unhybridised p orbital, so it does not change SN: $CH_2{=}CH_2$ carbon has $SN = 3$, sp^2

TRAP

d orbitals are involved only for period 3 and below (SF_6, PCl_5). In PH_3 and H_2S the angle is near 90°: little or no hybridisation. $PtCl_4^{2-}$ and XeF_4 are square planar.

5 Molecular orbital theory

- Atomic orbitals combine (**LCAO**) into molecular orbitals that belong to the whole molecule: adding the waves gives a lower-energy **bonding** MO (σ, π), subtracting them gives a higher-energy **antibonding** MO (σ^*, π^*, with an extra nodal plane between the nuclei). n atomic orbitals give n molecular orbitals.
- Electrons fill the MOs by the Aufbau, Pauli and Hund rules. A molecule is stable if $N_b > N_a$.

BOND ORDER

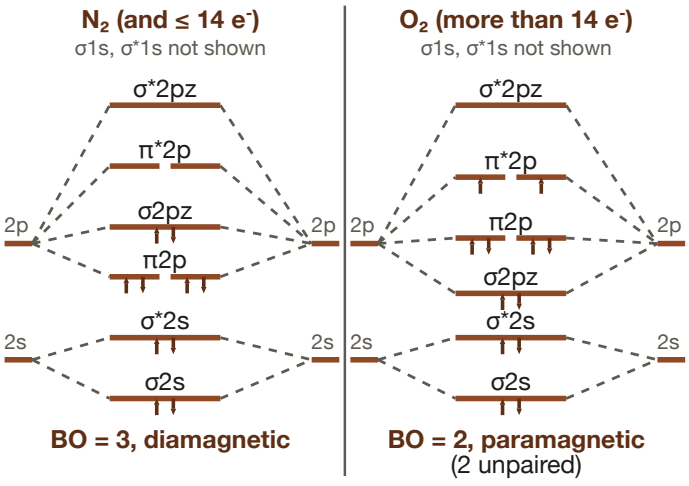
$$BO = \frac{N_b - N_a}{2}$$

N_b, N_a electrons in bonding and antibonding MOs; $BO = 0$ means no molecule (He_2, Be_2, Ne_2)

MAGNETISM

$\mu = \sqrt{n(n+2)}$ BM

n unpaired electrons: any unpaired electron means paramagnetic; none means diamagnetic



at O_2 the order of σ_{2p_z} and π_{2p} changes; bond order $= \frac{1}{2}(N_b - N_a)$

ORDER OF THE MOS

- Up to 14 electrons (B_2, C_2, N_2 and lighter): s-p mixing puts $\pi 2p$ **below** $\sigma 2p_z$: $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_{x,y} < \sigma 2p_z < \pi^* 2p_{x,y} < \sigma^* 2p_z$.
- More than 14 electrons (O_2, F_2, Ne_2 and their ions): $\sigma 2p_z$ is **below** the $\pi 2p$ pair.
- The π and π^* pairs are degenerate: electrons go in singly first (Hund), which is why B_2 and O_2 are paramagnetic.
- N_2: $\sigma 2s^2\, \sigma^* 2s^2\, \pi 2p^4\, \sigma 2p^2$, $BO = 3$.

HOMONUCLEAR AND ISOELECTRONIC SPECIES (ALL ELECTRONS COUNTED)

ELECTRONS	SPECIES	BO	MAGNETISM
1, 2	H_2^+, H_2	0.5, 1	para, dia
3, 4	He_2^+, He_2	0.5, 0	para; He_2 does not exist
6, 8	Li_2, Be_2	1, 0	dia; Be_2 unstable
10	B_2	1	para (2 unpaired)
12	C_2	2	dia (two π bonds, no σ)
13	C_2^-, N_2^+	2.5	para
14	N_2, CO, CN^-, NO^+, C_2^{2-}	3	dia
15	N_2^-, NO, O_2^+	2.5	para
16	O_2, N_2^{2-}	2	para (2 unpaired)
17	O_2^- (superoxide)	1.5	para
18	O_2^{2-} (peroxide), F_2	1	dia
20	Ne_2	0	does not exist

Bond length $\propto 1/BO$: $O_2^+ < O_2 < O_2^- < O_2^{2-}$ (BO 2.5, 2, 1.5, 1). Isoelectronic species have the same bond order and magnetism.

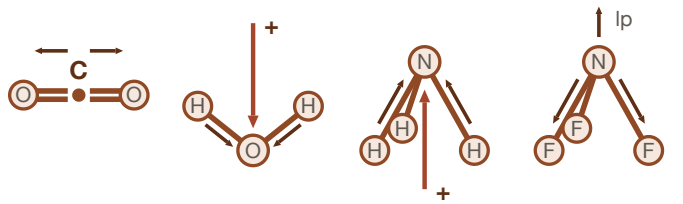
KEY IDEA

Do MO questions in this order: total electrons (add for $-$ charge, remove for $+$); pick the MO order (up to 14 or more); fill with Hund; then BO, unpaired count, bond-length order.

TRAP

O_2 is paramagnetic though its Lewis structure shows none unpaired; B_2 is paramagnetic **because of** s-p mixing; C_2 has two π bonds and no σ bond. Removing an electron from O_2 raises the bond order (O_2^+ 2.5); from N_2 it lowers it.

6 Dipole moment and polarity



μ = 0	μ = 1.85 D	μ = 1.47 D	μ = 0.23 D
CO_2, linear dipoles cancel	H_2O, bent along bisector	NH_3, pyramid along axis to N	NF_3: bond moment oppose the lp

net dipole $\vec{\mu}$ points from $+$ to $-$; bond dipoles add or cancel according to the geometry

DIPOLE MOMENT A polar bond has a dipole moment $\mu = q \times d$ (charge times separation), a vector pointing towards the more electronegative atom. The molecular moment is the **vector sum** of the bond moments (and lone-pair moments): symmetric shapes cancel to zero. Units: debye, $1\ \text{D} = 3.336 \times 10^{-30}$ C m.

RESULTANT

$$\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta}$$

two equal moments at angle θ: $\mu = 2\mu_1 \cos\frac{\theta}{2}$

PERCENT IONIC CHARACTER

$$\%\ \text{ionic} = \frac{\mu_{obs}}{e\,d} \times 100$$

$e\,d$ for 100% ionic ($e = 4.8 \times 10^{-10}$ esu, d in cm; divide by 10^{-18} to get D)

ZERO AND NON-ZERO MOMENTS

ZERO	NON-ZERO (D)
CO_2, BF_3, CH_4, CCl_4	H_2O 1.85, NH_3 1.47
PCl_5, SF_6, XeF_2, XeF_4	NF_3 0.23, $CHCl_3$ 1.0
trans-1,2-dichloroethene, p-dichlorobenzene	cis-isomer 1.9; o- > m- (2.5, 1.5)
$BeCl_2$ (linear)	HF 1.9, HCl 1.0, HBr 0.8, HI 0.4

KEY IDEA

NH_3 (1.47 D) is much more polar than NF_3 (0.23 D): in NH_3 the N−H bond moments point towards N, **along** the lone-pair moment; in NF_3 the N−F moments point to F, **against** it.

TRAP

Polar bonds do not make a polar molecule (CO_2, CCl_4, BF_3 are non-polar); lone pairs can. Draw the arrows to the more electronegative atom before adding vectors.

7 Hydrogen bonding and metallic bonding

- A **hydrogen bond** is the attraction between H, covalently bonded to a small highly electronegative atom (F, O, N), and a lone pair on another such atom: $X{-}H\cdots Y$, about 10 to 40 kJ mol^{-1}, far weaker than a covalent bond but much stronger than van der Waals forces. Strength $F{-}H\cdots F > O{-}H\cdots O > N{-}H\cdots N$.
- **Intermolecular** H-bonds link different molecules (water, HF chains, carboxylic acid dimers, p-nitrophenol) and raise boiling point, viscosity and solubility in water; **intramolecular** H-bonds close a ring inside one molecule (o-nitrophenol, salicylaldehyde) and lower boiling point and water solubility.

BOILING POINTS AND H-BONDING

COMPARISON	REASON
$H_2O > HF > NH_3$ (each far above its group)	each water molecule can form up to four H-bonds (two as donor, two as acceptor)
$H_2S < H_2Se < H_2Te \ll H_2O$	van der Waals rise with mass; only water is H-bonded
$PH_3 < AsH_3 < SbH_3$, NH_3 highest	size for the heavier three; H-bonding for NH_3
p-nitrophenol > o-nitrophenol	intermolecular versus intramolecular

OTHER CONSEQUENCES

- Ice is less dense than water: the open H-bonded cage; water is densest at 4°C.
- Acetic acid is a dimer in benzene; HF is associated and a weak acid.
- H-bonds hold the double helix of DNA and the secondary structure of proteins (see **Biomolecules**).
- **Metallic bond**: metal cations in a sea of delocalised valence electrons, which explains conduction, lustre and malleability; strength rises with the number of valence electrons and falls with atomic size.

8 Worked examples

LONE PAIRS

Total lone pairs on the central atoms of SF_4, ClF_3 and XeF_4?

$\frac{6-4}{2}=1$; $\frac{7-3}{2}=2$; $\frac{8-4}{2}=2$. Total 5

SHAPE

Shape and hybridisation of $XeOF_4$?

Xe 8 e$^-$; 4 F use 4, O uses 2; left 2 is 1 lone pair; σ bonds 5, $SN=6$: square pyramidal, sp^3d^2

FORMAL CHARGE

Formal charges in ozone ($O{=}O^+{-}O^-$ form)?

central: $6-2-\frac{6}{2}=+1$; double-bonded O: $6-4-\frac{4}{2}=0$; single-bonded O: $6-6-\frac{2}{2}=-1$

SPECIES COUNT

How many have square planar shape: XeF_4, SF_4, ICl_4^-, BrF_4^-, $PtCl_4^{2-}$?

XeF_4, ICl_4^-, BrF_4^- ($SN=6$, 2 lp) and $PtCl_4^{2-}$ (dsp^2): 4; SF_4 is see-saw

UNPAIRED ELECTRONS

Total unpaired electrons in O_2, O_2^{2-} and O_2^+?

O_2 (16 e): 2; O_2^{2-} (18 e): 0; O_2^+ (15 e): 1. Total 3

BOND ORDER

Compare NO and NO^+.

NO (15 e): $BO=\frac{10-5}{2}=2.5$, one unpaired, para; NO^+ (14 e): $BO=\frac{10-4}{2}=3$, dia

DIAMAGNETIC SPECIES

How many are diamagnetic: N_2, O_2, C_2, B_2, O_2^{2-}, CO?

N_2, C_2, O_2^{2-}, CO: 4 (O_2 and B_2 have two unpaired electrons each)

RESULTANT DIPOLE

Two bond moments of 1.5 D at $120°$?

$\mu = 2(1.5)\cos 60° = 1.5$ D; check: $\sqrt{2.25 + 2.25 + 2(2.25)(-0.5)} = 1.5$

IONIC CHARACTER

HCl: $\mu = 1.03$ D, bond length 1.27 Å. Percent ionic character?

$e\,d = 4.8 \times 10^{-10} \times 1.27 \times 10^{-8} = 6.10 \times 10^{-18}$ esu cm $= 6.10$ D; $\dfrac{1.03}{6.10} \times 100 \approx 17\%$

BORN-HABER

$\Delta_{sub}H = 108$, $IE = 496$, $\Delta_{diss}H(Cl_2) = 242$, $\Delta_{eg}H = -349$, $U = 787$ kJ mol^{-1}. $\Delta_f H$ of NaCl?

$108 + 496 + 121 - 349 - 787 = -411$ kJ mol^{-1}

DICHLOROBENZENES

Taking each C−Cl bond moment as 1.5 D, estimate μ of the o-, m- and p-isomers.

o ($60°$): $2(1.5)\cos 30° = 2.6$ D; m ($120°$): $2(1.5)\cos 60° = 1.5$ D; p ($180°$): 0. Observed $2.5,\ 1.5,\ 0$

BOND ANGLE ORDER

Arrange NH_3, PH_3, NF_3 in decreasing bond angle.

NH_3 ($107°$) $> NF_3$ ($102°$, electronegative F) $> PH_3$ ($93.5°$, big central atom, little hybridisation)

BOILING-POINT ORDER

Order H_2O, H_2S, H_2Se, H_2Te by boiling point.

only water is strongly H-bonded; the others follow molar mass: $H_2S < H_2Se < H_2Te < H_2O$ (-60, -41, -2, $100°$C)

SIGMA AND PI

Total σ and π bonds in $CH_2{=}C{=}CH_2$ and in $CH_2{=}CH{-}C{\equiv}N$?

allene $6\sigma + 2\pi = 8$; acrylonitrile σ: 3 C−H, 2 C−C, 1 C−N $= 6$; π: $1 + 2 = 3$; total 9

9 Last-minute checklist

BEFORE YOU ANSWER

Total electrons and charge? Which MO order (up to 14 or more)? Lone pairs on the central atom? Do the bond dipoles cancel by symmetry?

- $FC = V - L - B/2$; hybrids from SN (2 sp, 3 sp^2, 4 sp^3, 5 sp^{3}d, 6 sp^{3}d^2, 7 sp^{3}d^3); lone pairs go equatorial in a bipyramid.
- Shapes: bent, pyramidal, see-saw, T, square pyramidal, square planar from lone pairs on SN 3, 4, 5, 6; *lp-lp* > *lp-bp* > *bp-bp*.
- $U \propto z^+z^-/(r^+ + r^-)$; Born-Haber $\Delta_f H = \Delta_{sub}H + IE + \frac{1}{2}\Delta_{diss}H + \Delta_{eg}H - U$; Fajans: small, highly charged cation, large anion, 18-electron cation.
- $BO = (N_b - N_a)/2$; $\pi 2p$ below $\sigma 2p$ up to 14 electrons; B_2, O_2, O_2^+, O_2^-, NO, N_2^+ are paramagnetic; N_2, CO, CN^-, NO^+, C_2^{2-} have $BO = 3$.
- $\mu = q \times d$; vector sum; CO_2, BF_3, CCl_4, XeF_4 zero; $NH_3 > NF_3$; o- > m- > p-dichlorobenzene.
- H-bond needs H on F, O or N; intramolecular lowers boiling point and solubility; $\sigma + \pi$: single 1σ, double $1\sigma 1\pi$, triple $1\sigma 2\pi$.

Now test it. Practise this chapter with past-paper and bank questions on Prep Vault. **Practice this chapter →**