



LOGIC BLOOM • CHEMISTRY • CLASS 11

# Chemical Bonding & Molecular Structure

Tier 1 for **both** NEET and JEE • Built to JEE Advanced depth

*The chapter the rest of Chemistry stands on. Shapes, hybridisation and molecular orbitals, each built so you can predict an answer rather than recall it, with the comparison questions examiners keep returning to worked in full.*

8 Sections

10 Diagrams

14 Worked Questions

NEET Marked

Fact Sheet

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# How to Read This Set

Chemical Bonding is Tier 1 for **both** exams. So this set is built to JEE Advanced depth. Each section carries a badge. It tells a NEET student what they still need.

**IN NEET AND JEE**

Octet and its failures, ionic character, bond parameters, resonance, VSEPR, hybridisation, dipole moment, hydrogen bonding.

**JEE MAIN AND ADVANCED**

Molecular orbital theory in full, bond order comparisons, magnetic behaviour of diatomics.

**JEE ADVANCED MAINLY**

Back bonding, Bent's rule, and the finer bond-angle comparisons.



THINK IT  
THROUGH

**THE ONE HABIT THAT CARRIES THE WHOLE CHAPTER**

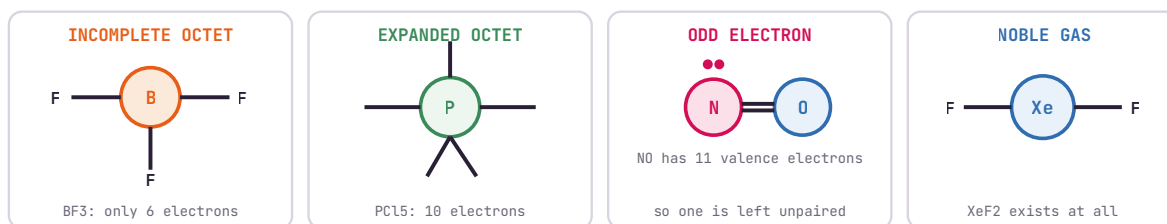
Almost every question here is a **comparison**. Which bond is longer? Which molecule is more polar? Which is more stable? So do not memorise molecules one at a time. Learn the rule that puts them in order. Then apply it. Counting the steric number answers more questions than any list. So does counting bonding electrons minus antibonding ones.

# 1 Why Atoms Bond

IN NEET AND JEE

Atoms combine to reach a lower energy. The **octet rule** works well for the first two short periods. The interesting questions come from where it fails.

## THE OCTET RULE, AND THE FOUR WAYS IT BREAKS



The octet is a guideline, not a law. Expect at least one question a year built on a molecule that breaks it.

Four standard exceptions. Each one has been the subject of an exam question in its own right.

### Incomplete octet

central atom with fewer than eight: BeCl<sub>2</sub>, BF<sub>3</sub>, AlCl<sub>3</sub>

### Expanded octet

period 3 onwards can use d orbitals: PCl<sub>5</sub>, SF<sub>6</sub>, IF<sub>7</sub>

### Odd electron

an unpaired electron remains: NO, NO<sub>2</sub>, ClO<sub>2</sub>

### Formal charge

a way of choosing between Lewis structures; the best one has formal charges nearest zero



TRAP ALERT

### △ FORMAL CHARGE IS A BOOKKEEPING DEVICE, NOT A REAL CHARGE

Formal charge = valence electrons – non-bonding electrons – half the bonding electrons. Use it to rank possible structures. The best one has the smallest charges. Any negative charge should sit on the most electronegative atom. It does not tell you where the electrons really are.

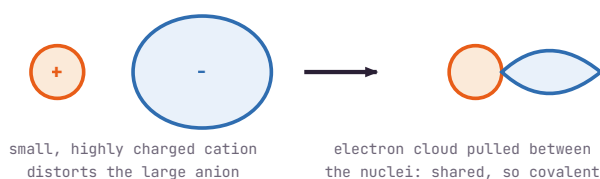
## 2

# The Ionic Bond

IN NEET AND JEE

Electrons transfer completely. The ions are then held together by electrostatic attraction. But no bond is purely ionic. Questions almost always ask **how much covalent character** has crept in.

FAJANS' RULES: how much covalent character an ionic bond picks up



COVALENT CHARACTER RISES

$\text{LiCl} > \text{NaCl} > \text{KCl} > \text{CsCl}$   
(cation gets smaller)

$\text{LiI} > \text{LiBr} > \text{LiCl} > \text{LiF}$   
(anion gets larger)

More covalent character when: the cation is **SMALL** and highly charged, the anion is **LARGE** and highly charged, and when the cation has a pseudo noble gas configuration such as  $\text{Cu}^+$ ,  $\text{Ag}^+$  or  $\text{Zn}^{2+}$ .

*A small, highly charged cation distorts a large anion. That distortion is covalent character.*

## ★ FAJANS' RULES

Covalent character rises with a **smaller cation**. It rises with a **larger anion**. It rises with a **higher charge** on either ion. It also rises when the cation has a **pseudo noble gas** shell, such as  $\text{Cu}^+$ ,  $\text{Ag}^+$  or  $\text{Zn}^{2+}$ .

|                         |                                                                                                               |
|-------------------------|---------------------------------------------------------------------------------------------------------------|
| <b>Lattice enthalpy</b> | energy released when gaseous ions form one mole of solid; it rises with higher charge and smaller ions        |
| <b>Born-Haber cycle</b> | applies Hess's law to obtain lattice enthalpy, which cannot be measured directly                              |
| <b>Melting point</b>    | tracks lattice enthalpy, so $\text{MgO}$ melts far above $\text{NaCl}$ (higher charges, smaller ions)         |
| <b>Solubility</b>       | generally falls as covalent character rises, which is why $\text{AgCl}$ is insoluble but $\text{NaCl}$ is not |



MYTH CHECK

#### MYTH

Ionic and covalent are two separate kinds of bond, and every compound is one or the other.

#### THE SCIENCE

They are the two ends of one continuous scale. Every ionic bond has some covalent character (Fajans) and every bond between unlike atoms has some ionic character. Asking *how much* is the right question; asking *which one* usually is not.

## 3

# The Covalent Bond

IN NEET AND JEE

Shared pairs. Four measurable parameters describe the result, and they all move together in a way you can reason from.

**BOND PARAMETERS: four numbers that move together**



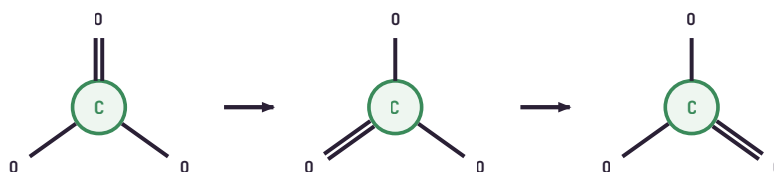
bond order rises, length falls, enthalpy rises

Bond length also falls as the atoms get smaller, and as the s-character of the hybrid orbital rises.

*Higher bond order means shorter and stronger. This single trend answers a surprising number of questions.*

|                      |                                                                                            |
|----------------------|--------------------------------------------------------------------------------------------|
| <b>Bond length</b>   | falls as bond order rises and as the atoms get smaller                                     |
| <b>Bond enthalpy</b> | rises with bond order; it is the energy needed to break one mole of bonds in the gas phase |
| <b>Bond angle</b>    | set by the geometry, then squeezed by lone pairs                                           |
| <b>Bond order</b>    | number of shared pairs; in molecular orbital terms, half of bonding minus antibonding      |

**RESONANCE: one real structure, drawn as several**



all three C-O bonds are IDENTICAL, 129 pm

The molecule is not flicking between these. It is a single hybrid, lower in energy than any one drawing, and the more equivalent structures you can draw, the more stable it is.

*Carbonate. All three C-O bonds are identical in length, which no single Lewis structure can show.*



### ⚠️ RESONANCE IS NOT OSCILLATION

The molecule does not flip between the drawings. It is one structure, called the resonance hybrid. It is **more stable** than any single drawing. That extra stability is the resonance energy. It grows with the number of equivalent structures you can draw.



▶ PLAY

### BOND DIAGRAMS STILL ABSTRACT?

#### Build the molecule and watch the bond lengths settle.

Add and remove shared pairs. Watch the bond shorten as the order rises. Then drill the comparison questions while it is fresh.

[logicbloom.co.in/download](https://logicbloom.co.in/download) · Free to start.



SCAN

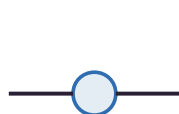
## 4

## VSEPR: Predicting Shape

IN NEET AND JEE

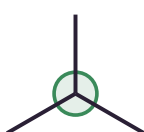
The highest-yield section in the chapter. Electron pairs around the central atom repel each other. They settle as far apart as they can. So counting them gives you the shape, with nothing to memorise.

## THE FIVE PARENT GEOMETRIES: set by the STERIC NUMBER



## 2 LINEAR

sp,  $180^\circ$   
BeCl<sub>2</sub>, CO<sub>2</sub>



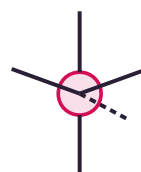
## 3 TRIGONAL PLANAR

sp<sup>2</sup>,  $120^\circ$   
BF<sub>3</sub>, SO<sub>3</sub>, NO<sub>3</sub><sup>-</sup>



## 4 TETRAHEDRAL

sp<sup>3</sup>,  $109.5^\circ$   
CH<sub>4</sub>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>



## 5 TRIGONAL BIPYRAMIDAL

sp<sup>3</sup>d,  $90^\circ$  and  $120^\circ$   
PCl<sub>5</sub>



## 6 OCTAHEDRAL

sp<sup>3</sup>d<sup>2</sup>,  $90^\circ$   
SF<sub>6</sub>

Steric number = number of atoms bonded to the central atom + number of lone pairs on it.

The five parent geometries. Everything else is one of these with lone pairs taking some of the positions.

## ★ THE WHOLE METHOD IN ONE LINE

**Steric number = atoms bonded to the central atom + lone pairs on it**

The steric number gives the parent geometry. The lone pairs then tell you the actual shape.

## LONE PAIRS PUSH HARDER THAN BONDING PAIRS

CH<sub>4</sub>

0 lone pairs  
 $109.5^\circ$

NH<sub>3</sub>

1 lone pair  
 $107^\circ$

H<sub>2</sub>O

2 lone pairs  
 $104.5^\circ$

## REPULSION ORDER

lone-lone  
> lone-bond  
> bond-bond

Same tetrahedral parent, three different shapes and three different angles, because lone pairs push harder.

|                                   |                                                                                                    |
|-----------------------------------|----------------------------------------------------------------------------------------------------|
| <b>SN 4, 0 lone pairs</b>         | tetrahedral, 109.5°: $\text{CH}_4$ , $\text{NH}_4^+$ , $\text{SO}_4^{2-}$                          |
| <b>SN 4, 1 lone pair</b>          | trigonal pyramidal, about 107°: $\text{NH}_3$ , $\text{ClO}_3^-$ , $\text{XeO}_3$                  |
| <b>SN 4, 2 lone pairs</b>         | bent, about 104.5°: $\text{H}_2\text{O}$                                                           |
| <b>SN 5, 1 / 2 / 3 lone pairs</b> | see-saw ( $\text{SF}_4$ ), T-shaped ( $\text{ClF}_3$ ), linear ( $\text{XeF}_2$ , $\text{I}_3^-$ ) |
| <b>SN 6, 1 / 2 lone pairs</b>     | square pyramidal ( $\text{BrF}_5$ ), square planar ( $\text{XeF}_4$ , $\text{ICl}_4^-$ )           |



TRAP ALERT

**▲ IN A TRIGONAL BIPYRAMID, LONE PAIRS ALWAYS TAKE EQUATORIAL POSITIONS**

An equatorial site has only two neighbours at 90°. An axial site has three. So a lone pair feels less repulsion in the equator. This is why  $\text{SF}_4$  is a see-saw, not a trigonal pyramid. It is also why  $\text{ClF}_3$  is T-shaped.



▶ PLAY

**SHAPES NOT COMING AUTOMATICALLY?**

**Count the steric number and watch the shape snap into place.**

The VSEPR game gives you a formula, you count, and the molecule builds itself in front of you. Twenty rounds and you will stop needing the table. [logicbloom.co.in/download](https://logicbloom.co.in/download) · Free to start.

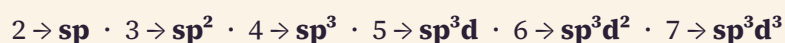


SCAN

IN NEET AND JEE

Valence bond theory mixes atomic orbitals of similar energy. This makes new, identical orbitals called hybrids. They point exactly where VSEPR said they would. The two theories agree. Hybridisation explains the **why**.

★ STERIC NUMBER GIVES THE HYBRIDISATION DIRECTLY



|                    |                                                                                                                            |
|--------------------|----------------------------------------------------------------------------------------------------------------------------|
| <b>Sigma bond</b>  | head-on overlap, strong, and it allows free rotation                                                                       |
| <b>Pi bond</b>     | sideways overlap of unhybridised p orbitals, weaker, and it locks the geometry                                             |
| <b>Counting</b>    | a single bond is one sigma; a double is one sigma and one pi; a triple is one sigma and two pi                             |
| <b>s-character</b> | sp has 50%, $\text{sp}^2$ has 33%, $\text{sp}^3$ has 25%; more s-character means shorter, stronger bonds and larger angles |

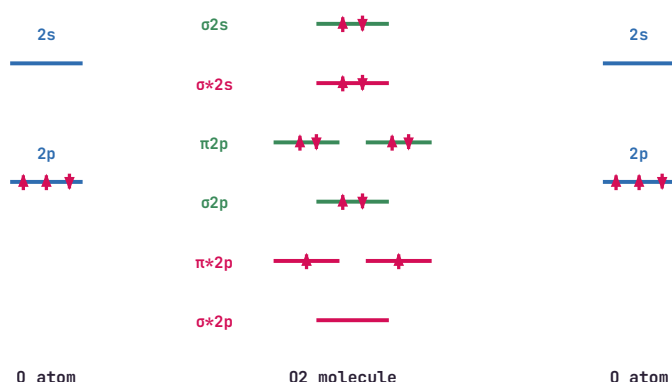
THINK IT  
THROUGH

## WHY BOND ANGLE TRACKS S-CHARACTER

An s orbital is spherical. It holds its electrons closer to the nucleus. So more s-character pulls the bonding pair in closer. The other orbitals then spread wider apart. That is why the angle runs  $180^\circ$  for sp,  $120^\circ$  for  $\text{sp}^2$  and  $109.5^\circ$  for  $\text{sp}^3$ . It is also why an sp C-H bond is shorter than an  $\text{sp}^3$  one.

## JEE MAIN AND ADVANCED

Valence bond theory cannot explain why oxygen is attracted to a magnet. Molecular orbital theory can. It combines the atomic orbitals into new ones. These new orbitals spread over the whole molecule.

MOLECULAR ORBITAL DIAGRAM FOR O<sub>2</sub>: why oxygen is magnetic

Two unpaired electrons sit in the antibonding pi orbitals, so O<sub>2</sub> is PARAMAGNETIC.

**Bond order**

$$= \frac{(\text{bonding} - \text{antibonding})}{2}$$

$$= \frac{(10 - 6)}{2} = 2$$

The MO diagram for oxygen. Two electrons sit unpaired in the antibonding pi orbitals, which is paramagnetism.

## ★ BOND ORDER AND MAGNETISM

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

Any unpaired electron makes the species paramagnetic. All paired means diamagnetic.

Filling order up to N<sub>2</sub>

$\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \pi 2p, \pi 2p, \sigma 2p$ , then the antibonding set

From O<sub>2</sub> onwards

$\sigma 2p$  drops **below** the  $\pi 2p$  pair, because s-p mixing weakens

## Paramagnetic examples

O<sub>2</sub> (2 unpaired), B<sub>2</sub> (2 unpaired), NO and O<sub>2</sub><sup>+</sup> (1 each)

## Diamagnetic examples

N<sub>2</sub>, C<sub>2</sub>, F<sub>2</sub>, CO and NO<sup>+</sup>

THE OXYGEN SERIES: add electrons and the bond weakens

| SPECIES                      | BOND ORDER | MAGNETISM    | BOND LENGTH (pm) |
|------------------------------|------------|--------------|------------------|
| O <sub>2</sub> <sup>+</sup>  | 2.5        | paramagnetic | 112              |
| O <sub>2</sub>               | 2.0        | paramagnetic | 121              |
| O <sub>2</sub> <sup>-</sup>  | 1.5        | paramagnetic | 133              |
| O <sub>2</sub> <sup>2-</sup> | 1.0        | diamagnetic  | 149              |

Every electron added goes into an ANTIBONDING orbital, so bond order falls and the bond gets longer.

Adding electrons to oxygen fills antibonding orbitals, so the bond order falls and the bond lengthens.



TRAP ALERT

▲ REMOVING AN ELECTRON DOES NOT ALWAYS WEAKEN THE BOND

From N<sub>2</sub> you remove a *bonding* electron. The bond order falls from 3 to 2.5, so the bond weakens. From O<sub>2</sub> you remove an *antibonding* electron. The bond order rises from 2 to 2.5. The bond gets stronger and shorter. Same action, opposite result. It is asked almost every year.



▶ PLAY

NO DIAGRAMS FEEL LIKE BOOKKEEPING?

Fill the orbitals yourself and watch the magnetism flip.

Add and remove electrons and see the bond order and the unpaired count update live. The N<sub>2</sub> versus O<sub>2</sub> contrast becomes obvious instead of something to memorise. [logicbloom.co.in/download](https://logicbloom.co.in/download) · Free to start.



SCAN

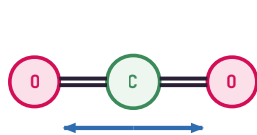
## 7

# Polarity and Hydrogen Bonding

IN NEET AND JEE

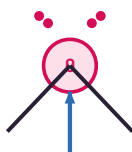
Individual bonds can be polar while the molecule is not. Dipole moments are vectors, so the shape from Section 4 decides the answer.

**DIPOLE MOMENT:** bond moments are **VECTORS**, so geometry decides



CO<sub>2</sub>: Linear, the two moments cancel exactly

$$\mu = 0$$



H<sub>2</sub>O: bent, so they add to a resultant

$$\mu = 1.85 \text{ D}$$

**SAME SHAPE, DIFFERENT ANSWER**

BF<sub>3</sub> trigonal planar:  $\mu = 0$

NF<sub>3</sub> pyramidal:  $\mu = 0.24 \text{ D}$

NH<sub>3</sub> = 1.47 D but NF<sub>3</sub> = 0.24 D:  
in NH<sub>3</sub> the lone pair moment ADDS to the bond moments; in NF<sub>3</sub> it OPPOSES

Identical bonds, opposite outcomes. In CO<sub>2</sub> the moments cancel; in the bent water molecule they add.

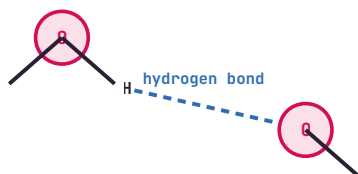
## ★ DIPOLE MOMENT

$$\mu = q \times d$$

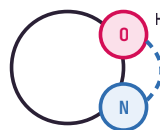
Measured in debye (D). A symmetrical molecule has  $\mu = 0$  no matter how polar its individual bonds are.

|                                                      |                                                                                                                          |
|------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------|
| <b><math>\mu = 0</math> despite polar bonds</b>      | CO <sub>2</sub> , BF <sub>3</sub> , CCl <sub>4</sub> , SF <sub>6</sub> , XeF <sub>4</sub> : all symmetrical              |
| <b><math>\mu \neq 0</math></b>                       | H <sub>2</sub> O, NH <sub>3</sub> , SO <sub>2</sub> , CHCl <sub>3</sub> : lone pairs or asymmetry break the cancellation |
| <b>The NH<sub>3</sub> versus NF<sub>3</sub> case</b> | 1.47 D against 0.24 D, because in NF <sub>3</sub> the lone pair moment opposes the bond moments                          |
| <b>Percentage ionic character</b>                    | the ratio of the observed dipole moment to the value calculated for complete transfer                                    |

### HYDROGEN BONDING: the strongest of the weak forces



**INTERMOLECULAR:** between molecules  
raises boiling point and solubility



**INTRAMOLECULAR:** inside one molecule  
lowers boiling point, as in o-nitrophenol

#### WHY IT MATTERS

H<sub>2</sub>O boils far above H<sub>2</sub>S  
HF boils above HCl

o-nitrophenol is **MORE** volatile  
than p-nitrophenol

Hydrogen bonding needs H attached to N, O or F. Whether it forms between molecules or inside one changes the physical properties completely.



TRAP ALERT

#### ⚠ INTRAMOLECULAR HYDROGEN BONDING DOES THE OPPOSITE OF WHAT YOU EXPECT

Normal hydrogen bonding between molecules **raises** boiling point and solubility. But sometimes the bond forms *inside* one molecule. **o-nitrophenol** does this. That molecule can then no longer bond to its neighbours. So o-nitrophenol is more volatile and less soluble than p-nitrophenol. This is the reverse of the usual rule.

Fourteen questions, tagged by exam. Every one is a comparison or a prediction that needs a rule applied, not a fact recalled. Try each before reading the working.

### Q1 Three shapes from one parent geometry

NEET

Predict the shape and bond angle of  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , and explain why they differ although all three have the same steric number.

**CORE** Count the steric number for each, then let the lone pairs squeeze the angle.

**WORKING**

All three:  $\text{SN} = 4 \Rightarrow$  tetrahedral parent,  $sp^3$

$\text{CH}_4$  : 0 lp  $\Rightarrow$  tetrahedral,  $109.5^\circ$

$\text{NH}_3$  : 1 lp  $\Rightarrow$  pyramidal,  $107^\circ$ ,  $\text{H}_2\text{O}$  : 2 lp  $\Rightarrow$  bent,  $104.5^\circ$

**TRAP** The hybridisation is  $sp^3$  for all three, so hybridisation alone never explains the difference. Lone pair repulsion does. Note  $\text{NH}_4^+$  is back to  $109.5^\circ$  because the lone pair is used up.

### Q2 Shapes of the interhalogens

JEE MAIN

Give the shape and hybridisation of  $\text{ClF}_3$ ,  $\text{SF}_4$ ,  $\text{XeF}_2$ ,  $\text{BrF}_5$  and  $\text{XeF}_4$ .

**CORE** Steric number from the central atom's valence electrons plus the bonded atoms, then place the lone pairs.

**WORKING**

$\text{SN} = 5$  :  $\text{ClF}_3$  (2 lp)  $\rightarrow$  T-shaped,  $\text{SF}_4$  (1 lp)  $\rightarrow$  see-saw,  $\text{XeF}_2$  (3 lp)  $\rightarrow$  linear

$\text{SN} = 6$  :  $\text{BrF}_5$  (1 lp)  $\rightarrow$  square pyramidal,  $\text{XeF}_4$  (2 lp)  $\rightarrow$  square planar

$sp^3d$  for SN 5,  $sp^3d^2$  for SN 6

**TRAP** In the trigonal bipyramid the lone pairs must go equatorial, which is what turns  $\text{SF}_4$  into a see-saw rather than a pyramid. In the octahedron two lone pairs go opposite each other, giving square planar.

### Q3 Which chloride is most covalent

NEET

Arrange LiCl, NaCl, KCl and CsCl in order of increasing covalent character, and explain.

**CORE** Fajans: a smaller cation polarises the anion more, so it gives more covalent character.

**WORKING**

cation size:  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$

polarising power is largest for the smallest cation

$\text{CsCl} < \text{KCl} < \text{NaCl} < \text{LiCl}$

**TRAP** The order of covalent character is the **reverse** of the order of cation size, so read the question carefully: increasing covalent character means decreasing cation size.

### Q4 Bond order, magnetism and length together

JEE MAIN

For  $\text{O}_2$ ,  $\text{O}_2^+$ ,  $\text{O}_2^-$  and  $\text{O}_2^{2-}$ , find the bond order and the magnetic behaviour, and arrange them by bond length.

**CORE** Fill the MO diagram; every extra electron goes into an antibonding  $\pi^*$  orbital.

**WORKING**

$\text{O}_2^+ : 2.5$ , para  $\text{O}_2 : 2.0$ , para (2 unpaired)

$\text{O}_2^- : 1.5$ , para  $\text{O}_2^{2-} : 1.0$ , diamagnetic

bond length  $\propto \frac{1}{\text{bond order}} \Rightarrow \text{O}_2^+ < \text{O}_2 < \text{O}_2^- < \text{O}_2^{2-}$

**TRAP** Only the peroxide ion is diamagnetic, because that is the point at which both  $\pi^*$  orbitals finally fill. Bond length runs opposite to bond order, so the shortest is the one with the highest order.

## Q5 Same action, opposite result

JEE ADVANCED

Explain why removing one electron from  $N_2$  weakens the bond, while removing one electron from  $O_2$  strengthens it.

**CORE** Ask which orbital the electron leaves from: a bonding orbital or an antibonding one.

**WORKING**

$N_2$  : the highest occupied MO is  $\sigma 2p_z$ , BONDING

3.0  $\rightarrow$  2.5, bond lengthens 110  $\rightarrow$  112 pm  $\Rightarrow$  weaker

$O_2$  : the highest occupied MO is  $\pi^* 2p$ , ANTIBONDING

2.0  $\rightarrow$  2.5, bond shortens 121  $\rightarrow$  112 pm  $\Rightarrow$  stronger

**TRAP** The instinct that ionisation always weakens a bond is wrong. What matters is only whether the electron came out of a bonding or an antibonding orbital, which is exactly what MO theory is for.

## Q6 Why $NH_3$ is far more polar than $NF_3$

JEE ADVANCED

Both  $NH_3$  and  $NF_3$  are pyramidal, yet their dipole moments are 1.47 D and 0.24 D. Explain.

**CORE** The lone pair on nitrogen has its own moment. Compare its direction with the resultant of the bond moments in each case.

**WORKING**

$NH_3$  : N is more electronegative than H, so bond moments point TOWARD N  
the lone pair moment also points away from N on the same axis  $\Rightarrow$  they ADD

$NF_3$  : F is more electronegative, so bond moments point AWAY from N  $\Rightarrow$  they OPPOSE the lone pair

$$\mu(NH_3) = 1.47 \text{ D} \gg \mu(NF_3) = 0.24 \text{ D}$$

**TRAP** Judging by electronegativity difference alone would predict  $NF_3$  to be the more polar, since N-F is more polar than N-H. The lone pair is what flips the answer.

## Q7 Zero dipole from polar bonds

NEET

Explain why  $\text{CO}_2$  has zero dipole moment while  $\text{H}_2\text{O}$  has 1.85 D, although both contain polar bonds and the same central-atom family.

**CORE** Dipole moments add as vectors, so the shape decides whether they cancel.

**WORKING**

$\text{CO}_2$  : SN = 2, linear  $\Rightarrow$  two equal moments at  $180^\circ \Rightarrow \mu = 0$

$\text{H}_2\text{O}$  : SN = 4 with 2 lp, bent at  $104.5^\circ \Rightarrow \mu \neq 0$

**TRAP** Zero dipole moment never means non-polar bonds. It means a symmetrical arrangement. The same logic makes  $\text{BF}_3$ ,  $\text{CCl}_4$ ,  $\text{SF}_6$  and  $\text{XeF}_4$  all non-polar overall.

## Q8 The volatile isomer

JEE ADVANCED

o-nitrophenol boils lower and is less soluble in water than p-nitrophenol, even though they have the same formula and mass. Explain.

**CORE** Ask whether the hydrogen bonding is between molecules or inside one.

**WORKING**

ortho: the -OH and -NO<sub>2</sub> are adjacent  $\Rightarrow$  INTRAmolecular H bond (chelation)

para: they are far apart  $\Rightarrow$  INTERmolecular H bonding between molecules

ortho is more volatile and less soluble; para is the opposite

**TRAP** This reverses the usual rule that hydrogen bonding raises boiling point. An intramolecular bond uses up the OH internally, so the molecule cannot bond to its neighbours or to water.

## Q9 Bond angle from s-character

JEE ADVANCED

Explain why the bond angle falls along  $\text{NH}_3$  ( $107^\circ$ ),  $\text{PH}_3$  ( $93.5^\circ$ ),  $\text{AsH}_3$  ( $91.8^\circ$ ) and  $\text{SbH}_3$  ( $91.3^\circ$ ).

**CORE** As the central atom gets larger and less electronegative, the extent of hybridisation falls and the bonding pairs move further from the central atom.

**WORKING**

N is small and electronegative  $\Rightarrow$  good  $sp^3$  hybridisation  
down the group the atom is larger, hybridisation is poorer

bonds become nearly pure  $p \Rightarrow$  angle approaches  $90^\circ$

**TRAP** The angles converge on  $90^\circ$ , the angle between pure  $p$  orbitals, rather than falling without limit. The same reasoning explains  $\text{H}_2\text{O}$   $104.5^\circ$  against  $\text{H}_2\text{S}$   $92^\circ$ .

## Q10 The weaker Lewis acid

JEE ADVANCED

$\text{BF}_3$  is a weaker Lewis acid than  $\text{BCl}_3$ , even though fluorine is far more electronegative than chlorine. Explain.

**CORE** Consider back bonding: donation from a filled halogen  $p$  orbital into the empty  $p$  orbital on boron.

**WORKING**

B is  $sp^2$  with an empty  $2p$  orbital

F  $2p$  overlaps well with B  $2p$  (same shell) so back bonding is STRONG

Cl  $3p$  overlaps poorly with B  $2p \Rightarrow$  weak back bonding

$\text{BF}_3$  has less empty orbital left, so it is the weaker acid

**TRAP** Electronegativity alone predicts the opposite order. Back bonding is also why the B-F bond is shorter than a pure single bond, and why  $\text{BF}_3$  is planar rather than pyramidal.

### Q11 Counting sigma and pi

NEET

How many sigma and pi bonds are present in (a)  $\text{CH}_2 = \text{CH}-\text{C} \equiv \text{N}$  and (b) benzene?

**CORE** Every bond, single or multiple, contains exactly one sigma. The rest are pi.

**WORKING**

(a)  $\text{CH}_2 = \text{CH}-\text{C} \equiv \text{N}$ : bonds = 3 C-H + 3 skeletal = 6  $\sigma$

extras: one from C=C, two from  $\text{C} \equiv \text{N} \Rightarrow$  6  $\sigma$ , 3  $\pi$

(b) benzene: 6 C-C + 6 C-H = 12  $\sigma$ , 3  $\pi$

**TRAP** A double bond is one sigma plus one pi, not two pi. Counting bonds rather than counting lines is the reliable method here.

### Q12 Which is more stable

JEE MAIN

Explain, using resonance, why the carbonate ion has three identical C-O bonds of 129 pm, between a single bond (143 pm) and a double bond (122 pm).

**CORE** Draw the contributing structures and note that the double bond is not fixed on any one oxygen.

**WORKING**

three equivalent structures, each with one C=O and two C-O<sup>-</sup>

$$\text{bond order} = \frac{4 \text{ bonds shared}}{3 \text{ positions}} = 1.33$$

129 pm, between a single and a double bond

**TRAP** The hybrid is not an average of the drawings in a loose sense, it is a single real structure lower in energy than any of them. The equal bond lengths are the experimental proof.

### Q13 Magnetic behaviour across the second period

JEE ADVANCED

Which of  $B_2$ ,  $C_2$ ,  $N_2$ ,  $O_2$  and  $F_2$  are paramagnetic? Give bond orders.

**CORE** Remember the filling order changes at  $O_2$ : before it,  $\pi 2p$  lies below  $\sigma 2p_z$ .

**WORKING**

$B_2$ : BO 1, 2 unpaired in  $\pi 2p \Rightarrow$  paramagnetic

$C_2$ : 2,  $N_2$ : 3,  $F_2$ : 1  $\Rightarrow$  all diamagnetic

$O_2$ : BO 2, 2 unpaired in  $\pi^* 2p \Rightarrow$  paramagnetic

**TRAP**  $B_2$  is the one students miss. Its two electrons enter the **degenerate  $\pi 2p$  pair** singly by Hund's rule, so it is paramagnetic despite a bond order of only 1.

### Q14 Assertion and reason on hybridisation

JEE ADVANCED

**Assertion:**  $H_2O$  has a smaller bond angle than  $NH_3$ . **Reason:** Oxygen is  $sp^2$  hybridised while nitrogen is  $sp^3$ . Judge both statements.

**CORE** Check the steric number of each central atom before accepting the reason.

**WORKING**

$H_2O$ : 2 bonds + 2 lp = SN 4  $\Rightarrow sp^3$

$NH_3$ : 3 bonds + 1 lp = SN 4  $\Rightarrow sp^3$

Assertion true, Reason false

**TRAP** Both are  $sp^3$ . The angle difference comes from the **number of lone pairs** (two against one), not from different hybridisation. Questions that offer hybridisation as the reason are usually wrong on purpose.

# ★ Chemical Bonding • Fact Sheet

Every rule for revision day. Print this page alone.

## OCTET EXCEPTIONS

**Incomplete: BF<sub>3</sub>, BeCl<sub>2</sub>**

Expanded: PCl<sub>5</sub>, SF<sub>6</sub>, IF<sub>7</sub>  
Odd electron: NO, NO<sub>2</sub>.

## FAJANS

**Small cation, large anion,**

high charge, pseudo noble gas  
= more covalent.

## BOND PARAMETERS

**Order up: length down,**

enthalpy up.  
single 154, double 134,  
triple 120 pm.

## STERIC NUMBER

**SN = bonded atoms +  
lone pairs**

2 sp, 3 sp<sup>2</sup>, 4 sp<sup>3</sup>,  
5 sp<sup>3</sup>d, 6 sp<sup>3</sup>d<sup>2</sup>.

## LONE PAIR ANGLES

**CH<sub>4</sub> 109.5°, NH<sub>3</sub> 107°,**

H<sub>2</sub>O 104.5°  
lp-lp > lp-bp > bp-bp.

## SN 5 SHAPES

**1 lp see-saw (SF<sub>4</sub>)**

2 lp T-shaped (ClF<sub>3</sub>)  
3 lp linear (XeF<sub>2</sub>, I<sub>3</sub><sup>-</sup>).

## SN 6 SHAPES

**1 lp square pyramidal  
(BrF<sub>5</sub>)**

2 lp square planar (XeF<sub>4</sub>)  
lone pairs go opposite.

## BOND ORDER

**BO = (Nb - Na) / 2**

Unpaired electron =  
paramagnetic.

## MO FILLING

**Up to N<sub>2</sub>: π2p below  
σ2pz**

From O<sub>2</sub>: σ2pz below π2p  
because s-p mixing weakens.

## PARAMAGNETIC LIST

**O<sub>2</sub>, B<sub>2</sub>, NO, O<sub>2</sub><sup>+</sup>, O<sub>2</sub><sup>-</sup>**

Diamagnetic: N<sub>2</sub>, C<sub>2</sub>, F<sub>2</sub>,  
CO, NO<sup>+</sup>, O<sub>2</sub><sup>2-</sup>.

## N<sub>2</sub> VS O<sub>2</sub> ON IONISING

**N<sub>2</sub> → N<sub>2</sub><sup>+</sup> : 3 → 2.5,  
weaker**

O<sub>2</sub> → O<sub>2</sub><sup>+</sup> : 2 → 2.5, stronger  
bonding vs antibonding.

## DIPOLE MOMENT

**μ = 0: CO<sub>2</sub>, BF<sub>3</sub>, CCl<sub>4</sub>,  
SF<sub>6</sub>**

NH<sub>3</sub> 1.47 D but NF<sub>3</sub> 0.24 D  
lone pair adds, then opposes.



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★ SHAPES STILL NOT OBVIOUS?

**Play it. Then practice it.**

Open Chemical Bonding in the Logic Bloom app: count the steric number and watch the molecule build itself, fill an MO diagram and see the magnetism flip, then drill the comparison questions. Free to start.

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