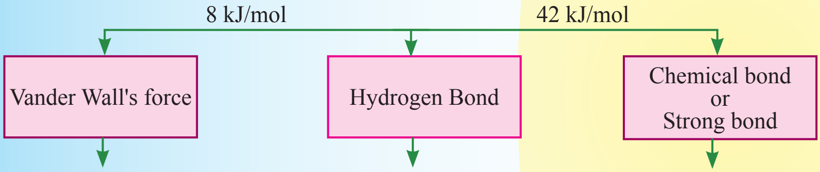
CHAPTER 26

Chemical Bonding

CHEMICAL BOND

The force of attraction which hold together atom, molecule or ions with in chemical species.

It is always exothermic process.



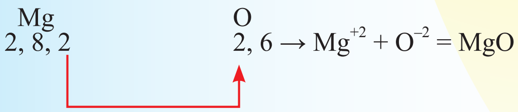
1. Dipole-Dipole (Keesome)
2. Dipole-induce dipole (Debye)
3. Instantaneous diple-induce dipole
4. Ion-dipole
5. Ion-induced dipole

1. Intermolecular hydrogen bond
2. Intramolecular hydrogen bond

1. Ionic bond
2. Covalent bond
3. Co-ordinate bond
4. Metallic bond

ELECTROVALENT OR IONIC BOND

The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electrons from one atom to another is called as Ionic or electrovalent bond.



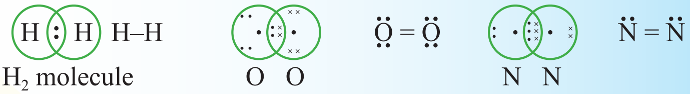
$$\underset{2,\,8,\,2}{Mg} \qquad \underset{2,\,6}{O} \rightarrow Mg^{+2} + O^{-2} = MgO$$

electrovalency of Mg = 2

electrovalency of O = 2

COVALENT BOND

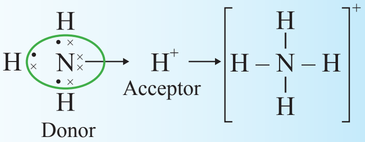
A covalent bond is formed by the mutual sharing of electrons between two atoms to complete their octet. (Except H which completes its duplet)



COORDINATE BOND (DATIVE BOND)

The bond formed between two atom in which contribution of an electron pair is made by one of them while the sharing is done by both.

(i) NH_4^+ (ammonium ion)



(ii) $F_3B + :NH_3 \longrightarrow (F_3B \leftarrow NH_3)$

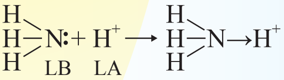
EXCEPTION OF OCTET RULE		
(a) electron deficient Central atom: No. of electron < 8 BeH_2 BF_3, BCl_3, BBr_3, BI_3 $AlCl_3$, $AlBr_3$, AlI_3	**(b)** electron rich Central atom: No. of electron > 8 PCl_5, IF_7 SF_6, XeF_2	**(c)** odd electron species central atom : has odd electron NO, NO_2, ClO_2, ClO_3

CO-ORDINATE BOND (DATIVE BOND)

In this type of bond, shared pair of electron donates by one species but shared by both.

- For this type of sharing.
- One species - must have lone pair - act as donar known as Lewis base - acquire +ve charge.
- Another species - must have orbital act as acceptor known as Lewis acid - acquire –ve charge.

Eg.



Similarly

$$H_2O + H^+ \longrightarrow H_3O^+$$
$$BF_3 + F^- \longrightarrow BF_4^-$$
$$NH_3 + BF_3 \longrightarrow F_3B.NH_3$$

- Donor atom follow octet rule.

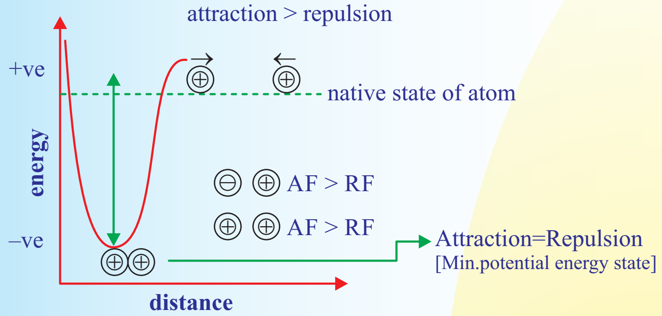
MODERN APPROACH OF COVALENT BOND

Consider wave mechanical model of atom means electron has dual nature; wave nature as well as particle nature considered by these theories, there are two theories in this approach.

1. Valence Bond Theory

Proposed by Heitler & London as per VBT bonding takes place for attaining stability.

$$\text{Stability} \propto \frac{1}{\text{Potential energy}}$$



- Bond formation is an exothermic process.
- During this process some extent of electron cloud merge into each other; this part is known as overlapped region & this process is known as overlapping.

Atom < Nucleus
Atom < Shell - subshell - orbital - electron - cloud

2. Molecular Orbital Theory

- Only those orbitals of valence shell can exhibit overlapping which has Unpaired electron

For example H—Cl bond form by overlapping of 1s - 3p orbitals.
$H \rightarrow 1s^1$
$Cl \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^5$

- Opposite spin
- **Strength of Covalent Bond**

Strength of covalent bond ∝ extent of overlapping.

1. Nature of Orbitals

(a) No. of shell: lower the number of shell higher overlapping.

$$\text{Bond Strength} \propto \frac{1}{\text{No.of shell}} / \text{size of orbitals}$$

$$\boxed{1\text{-}1 > 1\text{-}2 > 2\text{-}2 > 2\text{-}3}$$

- **Exception:** $Cl_2 > Br_2 > F_2 > I_2$ due to
$O—O < S—S$ lp-lp
$N—N < P—P$ repulsion

(b) Type of Sub-shell

Valence shell contain subshell s & p

s-non-directional p-directional	Directional orbital has higher extent of overlapping

Possibler Combination & Strength of Overlapping

s-s < s-p < p-p

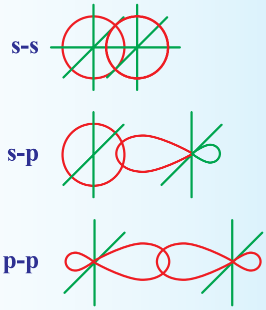
This factor is applicable when number of shell is same otherwise shell factor prominent.

2s - 2s < 2s - 2p < 2p - 2p	sub-shell factor
1s - 1s > 1s - 2s > 1s - 3s	shell factor

2. Pattern of Overlapping

(a) Axial overlapping:

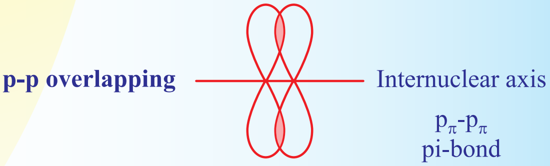
Along the internuclear axis; form sigma (σ) bond, strong bond.

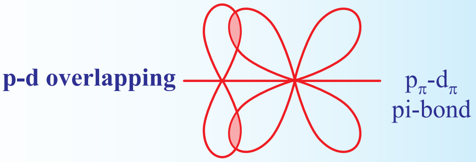


(b) Co-lateral overlapping

Side wise overlapping has less extent of overlapping for π-bond.

Weak bond





HYBRIDISATION

S.No.	Type or orbital	No. of hybrid orbital	3D orientation	Example
1.	one s + one p	2; sp	Linear	BeH_2, $BeCl_2$
2.	one s + two p	3; sp^2	Triangular	BCl_3, BF_3
3.	one s + three p	4; sp^3	Tetrahedral	CH_4, CCl_4
4.	one s + three p + one d	5; sp^3d	Triangular bipyramidal	PCl_5
5.	one s + three p + two d	6; sp^3d^2	Octahedral	SF_6
6.	one s + three p + three d	7; sp^3d^3	Pentagonal bipyramidal	IF_7

VALENCE SHELL ELECTRON PAIR REPULSION THEORY

- **Order of repulsion:** lp-lp > lp-bp > bp-bp mb-mb > mb-sb > sb-sb

(mb = multiple bond; sb = single bond)

TYPE OF HYBRIDISATION & POSSIBLE STRUCTURE

Type of Hybridisation	No. of B.P.	No. of L.P.	Shape	Examples
1. sp-hybridisation	2	-	Linear	BeF_2, CO_2, CS_2, $BeCl_2$
2. (a) sp^2-hybridisation	3	-	Trigonal planar	BF_3, $AlCl_3$, BeF_3^-
(b) sp^2-hybridisation	2	1	V-shape, Angular	NO_2^-, SO_2, O_3
3. (a) sp^3-hybridisation	4	0	Tetrahedral	CH_4, CCl_4, PCl_4^+, ClO_4^-, NH_4^+, BF_4^{-1}, SO_4^{-2}, $AlCl_4^-$,
(b) sp^3-hybridisation	3	1	Pyramidal	NH_3, PF_3, ClO_3^-, H_3O^+, PCl_3, XeO_3, $N(CH_3)_3$, CH_3^-
(c) sp^3-hybridisation	2	2	V-shape Angular	H_2O, H_2S, NH_2^-, OF_2, Cl_2O_2, SF_2, I_3^+
4. (a) sp^3d-hybridisation	5	–	Trigonal bipyramidal	PCl_5, SOF_4, AsF_5
(b) sp^3d-hybridisation	4	1	See-Saw, folded square distorted tetrahedral	SF_4, PF_4^-, AsF_4^- SbF_4^-, XeO_2F_2
(c) sp^3d-hybridisation	3	2	almost T-shape	ClF_3, ICl_3
(d) sp^3d-hybridisation	2	3	Linear	I_3^-, Br_3^-, ICl_2^-, XeF_2
5. (a) sp^3d^2-hybridisation	6	–	Square bipyramidal/ octahedral	PCl_6^-, SF_6
(b) sp^3d^2-hybridisation	5	1	Square pyramidal/ distorted octahedral	$XeOF_4$, ClF_5, SF_5^-,
(c) sp^3d^2-hybridisation	4	2	Square planar	XeF_5^+, XeF_4

Type of Hybridisation	No. of B.P.	No. of L.P.	Shape	Examples
6. (a) sp^3d^3-hybridisation	7	–	Pentagonal bipyramidal	IF_7
(b) sp^3d^3-hybridisation	6	1	Pentagonal pyramidal/ distorted octahedral/ capped octahedral	XeF_6
(c) sp^3d^3-hybridisation	5	2	Pentagonal planar	XeF_5^-

DIPOLE MOMENT

Measurement of Polarity in a molecule

$\boxed{\vec{\mu} = q \times d}$ debye = esu-cm

1D = 10^{-18} esu.cm

(A) Identification of polar or Non-polar molecule.

Molecule: Symmetrical distribution of electron cloud-Non-polar.
Molecule: Unsymmetrical distribution of electron cloud-Polar.

Diatomic Molecule

(a) Homoatomic $\Delta EN = 0 \rightarrow \vec{\mu} = 0 \rightarrow$ Non-polar.

H_2, F_2, Cl_2, N_2 etc.

(b) Heteroatomic $\Delta EN \neq 0 \rightarrow \vec{\mu}_{net} \neq 0 \rightarrow$ polar

$HF > HCl > HBr > HI$

Polyatomic Molecule:

$\mu_R \rightarrow$ vector sum of bond moment

$$\mu_R \rightarrow \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$$

Important Order

$NH_3 > NI_3 > NBr_3 > NCl_3 > NF_3$

$NH_3 > SbH_3 > AsH_3 > PH_3$

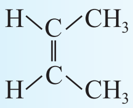
$H_2O > H_2S$

$CH_3Cl > CH_3F > CH_3Br > CH_3I$

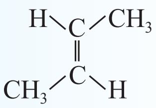
$CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$

Applications

Predict shape and polarity of molecule
Symmetrical geometry → $\mu = 0$ → non-polar
Unsymmetrical geometry → $\mu \neq 0$ → polar
Distinguish between cis & transform

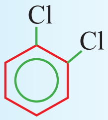


maleic acid
μ ≠ 0



fumaric acid
μ = 0

Dipole moment in Aromatic Compounds



Orthodichloro benzene

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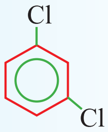

Metadichloro benzene

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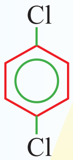


Paradichloro benzene

$$\mu \propto \frac{1}{\text{bond angle}}$$

HYDROGEN BONDING

- It is dipole-dipole type of interaction.
- Electrostatic force of attraction between hydrogen (covalently bond with F/N/O) & highly electronegative atom.
- Hydrogen bond
  - Intermolecular hydrogen bond → between the molecules
  - Intramolecular hydrogen bond → the molecules
- Intromolecular H-bonding takes places mainly in ortho derivatives only.

NOTES

1. Boric acid solid at room temperature (with 2D sheet structure) due to intermolecular hydrogen bonding.
2. In vapour state or in non-polar solvent CH_3COOH as dimer due to intermolecular hydrogen bonding.
3. In vapour phase HF exist as dimer and $(HF)_6$, due to intermolecular hydrogen bonding.
4. Due to intermolecular hydrogen bonding ice has 3D network structure with tetrahedral unit and having open cage structure.
   The density of ice is less than water.
5. DNA having hydrogen bonds.
6. In hydrated chloral intramolecular hydrogen bond is present.

Strength

Intermolecular H-bond > Intramolecular H-bond

Intramolecular H-bonding takes place in ortho derivatives only.

Applications of H-bonding

Physical State (densile nature) $\propto$ H-bond

Melting Point (mp) $\propto$ H-bond

Boiling Point (bp) $\propto$ H-bond

Viscosity $\propto$ H-bond

Surface Tension $\propto$ H-bond

Volatility $\propto$ 1/H-bond

Vapour Pressure $\propto$ 1/H-bond

MOLECULAR ORBITAL THEORY (MOT)

The molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features are:

(i) Just as electrons of any atom are present in various atomic orbitals, electrons of the molecule are present in various molecular orbitals.

(ii) Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.

(iii) An electron in an atomic orbital is influenced by one nucleus, while in a molecular orbital it is influenced by two or more nuclei depending upon the number of the atoms in the molecule. **Thus an atomic orbital is monocentric while a molecular orbital is polycentric.**

(iv) The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals called **bonding molecular orbital** and **anti-bonding molecular orbital** are formed.

(v) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.

Formation of Molecular Orbitals:
Linear Combination of Atomic Orbitals (LCAO)

Case I: When two waves are in same phase (constructive interference) the wave adds up and amplitude of new wave is the sum of wave functions of individual atomic orbitals.

$\psi_{MO} = \psi_A + \psi_B$ (Bonding M.O.)

Case II: When two waves are out of phase, the waves are subtracted from each other so that the amplitude of new wave is:

$\psi^*_{MO} = \psi_A - \psi_B$ (Antibonding M.O.)

Condition for Combination Atomic Orbitals

1. The combining atomic orbitals must have the same or nearly the same energy.
2. The combining atomic orbitals must have the same symmetry about the molecular axis.
3. The combining atomic orbitals must overlap to the maximum extent.

Energy level diagram from MOs:

Molecular orbital energy diagram for up to N_2 (molecule having $\leq$ 14 electrons)

$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \pi_{2p_x} = \pi_{2p_y} < \sigma_{2p_z} < \pi^*_{2p_x} = \pi^*_{2p_y} < \sigma^*_{2p_z}$

Molecular orbital energy diagram for O_2 and F_2 (molecule having > 14 electrons)

$\sigma_{1s} < \sigma^*_{1s} \,; < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2p_z} < \pi_{2p_x} = \pi_{2p_y} < \pi^*_{2p_x} = \pi^*_{2p_y} < \sigma^*_{2p_z}$

σ^*, π^* = antibonding molecular orbital

σ, π = bonding molecular orbital

Rules of Filling up of Molecular Orbital with Electrons

(1) The molecular orbital with lower energy will be filled first. (Aufbau Principle)

(2) The molecular orbital can accommodate maximum only two electrons. (Pauli's exclusion principle)

(3) If the two MOs have same energy then molecular orbital will first get singly filled and after that pairing will start. (Hunds Rule)

BOND ORDER

Bond order (B.O.) is defined as follows Bond order (B.O.) = $\frac{1}{2}(N_b - N_a)$

A positive bond order (i.e., $N_b > N_a$) means a stable molecule while a negative value (i.e., $N_b < N_a$) (i.e., $N_b = N_a$) bond order means an unstable molecule. If bond order zero then molecular does not exist.

NATURE OF THE BOND

Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively.

BOND-LENGTH

The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. The bond length decreases as bond order increases.

MAGNETIC NATURE

If one or more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic filed), e.g.,

1. Boric acid solid at room temperature (with 2D sheet structure) due to intermolecular hydrogen bonding.
2. In vapour state or in non-polar solvent CH_3COOH as dimer due to intermolecular hydrogen bonding.
3. In vapour phase HF exist as dimer and $(HF)_6$, due to intermolecular hydrogen bonding.
4. Due to intermolecular hydrogen bonding ice has 3D network structure with tetrahedral unit and having open cage structure.
   The density of ice is less than water.
5. DNA having hydrogen bonds.
6. In hydrated chloral intramolecular hydrogen bond is present. O_2 molecule. Otherwise diamagnetic (e.g.: N_2)

Fractional bond order it will be always paramagnetic

S.No.	No. of electrons in molecules	N_b	N_a	B.O.	Paramagnetic/ diamagnetic
1.	1	1	0	½	paramagnetic
2.	2	2	0	1	diamagnetic
3.	3	2	1	0.5	paramagnetic
4.	4	2	2	0	does not exist
5.	5	3	2	½	paramagnetic
6.	6	4	2	1	diamagnetic
7.	7	4	3	½	paramagnetic
8.	8	4	4	0	does not exist
9.	9	5	4	½	paramagnetic
10.	10	6	4	1	paramagnetic
11.	11	7	4	1.5	paramagnetic
12.	12	8	4	2	both bond are π C_2 molecule
13.	13	9	4	2.5	paramagnetic
14.	14	10	4	3	diamagnetic
15.	15	10	5	2.5	paramagnetic
16.	16	10	6	2	paramagnetic
17.	17	10	7	1.5	paramagnetic
18.	18	10	8	1	diamagnetic
19.	19	10	9	0.5	paramagnetic
20.	20	10	10	0	does not exist

In case of same bond order, stability depends upon No. of anti-bonding electrons

$$\text{Stabiligy} \propto \frac{1}{\text{No. of anti}-\text{bonding } e^-}$$

BONDING PARAMETER

1. Bond length: Internuclear distance

Factor affecting Bond length

(i) Atomic size: bond length ∝ size```` [No. of shell]

(ii) ΔEN, Bond length $\propto \frac{1}{\Delta EN}$

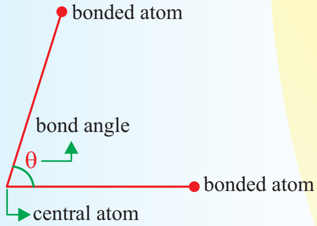
$$\boxed{d_{A-B} = r_A + r_B - 0.09 \times \Delta EN\ \text{Å}}$$

(iii) Bond order: Bond length $\propto \frac{1}{\text{B.O.}}$

(iv) Hybridisation: Bond length $\propto \frac{1}{\%\text{age of s} - \text{character}}$

Bond Angle

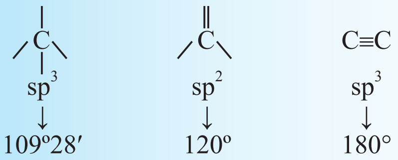
Angle between two adjacent bond is known as bond angle.



FACTORS AFFECTING BOND ANGLE

(i) Hybridisation

Bond angle ∝ % age of s-character



(ii) No. of lp/bp

[when hybridisation is same]

Bond angle $\propto \frac{1}{lp}$ Eg.: $CH_4 > \ddot{N}H_3 > H_2\ddot{O}\!:$

(iii) Type of Central atom: Applicable when:

- hybridisation same
- No. of lp/bp same

Bond angle $\propto$ EN of central atom.

Eg. $NH_3 > PH_3 > AsH_3 > SbH_3$

(iv) Type of bonded atom: Applicable when:

- hybridisation - same
- No. of lp/bp - same
- Central atom - same

Bond angle $\propto$ size of bonded species

Eg. $OF_2 < OCl_2 < OBr_2 < OI_2$

NOTES

Regular geometry / same hybridisation / bond angle same $BF_3 = BCl_3 = BBr_3 = BI_3$

Ionic Bond

Extreme polar covalent bond is an Ionic Bond.

Therefore Ionic Bond ΔEN - Must be higher - one specie - lower EN - metal one specie - higher EN - non metal

Eg. NaCl, KF

Formation of Ionic Bond takes place in following step.

$$\underset{\text{Solid}}{\text{Metal (M)}} \xrightarrow[\substack{\Delta H = +ve \\ \text{S.E.}}]{\text{Sublimation}} M(g) \xrightarrow[\substack{\Delta H = +ve \\ \text{I.E.}}]{\text{Ionisation}} M^+_{(g)}\,; \quad \underset{\substack{\text{Non metal} \\ \text{molecule}}}{X_2} \xrightarrow[\substack{\Delta H = +ve \\ \text{B.D.E.}}]{\text{Dissociation}}$$

$$X \xrightarrow[\substack{\Delta H = -ve \\ \text{electron gain} \\ \text{enthalpy}}]{+e^-} X^-_{(g)} \qquad M^+_{(g)} + X^-_{(g)} \xrightarrow[\substack{\Delta H = -ve \\ \text{lattice energy}}]{} MX_{(solid)}$$

$\Delta H_{formation} = S.E. + I.E. + \frac{1}{2}BDE + \Delta H_{eg} + U$

bond formation is always an exothermic process.

$\Delta H_{formation} = -ve$

S.E.: should be lower
I.E.: should be lower
B.D.E.: should be lower
ΔH_{eg}: should be higher
U: should be higher

PROPERTIES OF IONIC SALT

General Properties

Hard, Solid, Brittle (strong electrostatic attraction between ions)
Non directional nature (ionic compound do not exhibit stereo isomerism)
Higher Melting Point / Boiling Point
Isomorphism: $MgSO_4.\ 7H_2O$; $ZnSO_4.\ 7H_2O$; $FeSO_4.\ 7H_2O$

Specific Properties

- Conduction
  - Molten state
  - Aqueous medium
- Solubility
- Covalent Character

Molten state

Ionic conduction $\propto \dfrac{1}{\text{Ionic radius}}$

Eg. : LiCl, NaCl, KCl, RbCl, CsCl
Ionic Radius: $Li^+ <<< Cs^+$
Conductance: CsCl < RbCl < KCl < NaCl < LiCl

Aqueous medium

Ionic mobility $\propto \dfrac{1}{\text{Ionic radius}}$

Hyd. radius: $Cs^+ <<< Li^+(aq)$
conductance: LiCl < NaCl < KCl < RbCl, CsCl

COVALENT CHARACTER / FAJAN'S RULE

$$\text{Ionic potential of cation } (\phi) \propto \frac{\text{charge of cation}}{\text{size of cation}}$$

Polarisibility of anion $\propto$ size of anion $\propto$ charge of anion

Condition of polarisation
- Smaller cation
- Large anion
- Higher charge

FACTORS AFFECTING POLARISATION

(1) Polarisation $\propto$ charge of cation or anion

Eg. (i) $\overset{+2}{Cr}O < \overset{+3}{Cr_2}O_3 < \overset{+6}{Cr}O_3$ Covalent character ↑

(ii) $\overset{+2}{S}F_2 < \overset{+4}{S}F_4 < \overset{+6}{S}F_6$ Covalent character ↑

(iii) $Li\overset{-1}{F} < Li_2\overset{-2}{O} < Li_3\overset{-3}{N}$ Covalent character ↑
(anion charge↑)

(2) Polarisation $\propto \dfrac{\text{size of anion}}{\text{size of cation}}$

Eg. (i) $LiF < LiCl < LiBr < LiI$ anion size ↑
polarisability ↑
covalent character ↑

(ii) $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$ cation size ↑
polarisation ↓
covalent character ↑

SOLUBILITY

For s-block
Same group cation
Lattice Energy / Hydration Energy

(i) $BaCO_3$, $SrCO_3$, $CaCO_3$, $MgCO_3$, $BeCO_3$
(ii) $Be(OH)_2$, $Sr(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$
(iii) $BaSO_4$, $SrSO_4$, $CaSO_4$, $MgSO_4$, $BeSO_4$
(iv) Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3, Cs_2CO_3
(v) LiOH, NaOH, KOH, RbOH, CsOH
(vi) LiF, LiCl, LiBr, LiI
(vii) LiF, NaF, KF, RbF, CsF
(viii) BaF_2, SrF_2, MgF_2, CaF_2, BeF_2
(ix) CaF_2, $CaCl_2$, $CaBr_2$, CaI_2

$$\left.\begin{array}{l}\text{(x) AgI, AgBr, AgCl, AgF}\\ \text{(xi) PbO}_2\text{, CdI}_2\text{, RbI}\end{array}\right]\ \text{solubility} \propto \frac{1}{\text{covalent char.}}$$

For all solubility $\propto \dfrac{\mathbf{1}}{\textbf{covalent char.}}$

solubility in org. solvent $\propto$ **cov. char** $\propto \dfrac{\mathbf{1}}{\textbf{ionic char.}}$

[CCl_4, benzene, ether, alcohol, acetone]

Eg. (i) $PbF_2 > PbCl_2 > PbBr_2 > PbI_2$
(Anion size↑, cov. char.↑, solubility ↓)

(ii) $Fe^{+2}(OH)_2 > Fe^{+3}(OH)_3$
(+) charge↑, PP↑, CC↑, solubility ↓

(iii) $ZnCl_2 > CdCl_2 > HgCl_2$
Z_{eff}↑, PP↑, CC↑, solubility ↓

(iv) $Na_2SO_4 > MgSO_4$
(+) charge↑, PP↑, CC↑, solubility ↓

(v) $ZnCl_2 > CdCl_2 > HgCl_2$
Z_{eff}↑, PP↑, CC↑, solubility ↓

(vi) NaCl > CuCl

PP↑, CC↑, solubility ↓

(vii) AgF > AgCl > AgBr > AgI

Anionic Size↑, PP↑, CC↑, solubility ↓

HYBRIDISATION OF FOLLOWING SPECIES IN SPECIFIED STATE

Species	Cationic part	Anionic part
PCl_5	PCl_4^+ (sp^3)	PCl_6^- (sp^3d^2)
PBr_5	PBr_4^+ (sp^3)	Br^-
XeF_6	XeF_5^+ (sp^3d^2)	F^-
N_2O_5	NO_2^+ (sp)	NO_3^- (sp^2)
I_2Cl_6 (liquid)	ICl_2^+ (sp^3)	ICl_4^- (sp^3d^2)
Cl_2O_6	ClO_2^+ (sp^2)	ClO_4^- (sp^3)
I_2 (molten state)	I_3^+ (sp^3)	I_3^- (sp^3d)

SILICATES

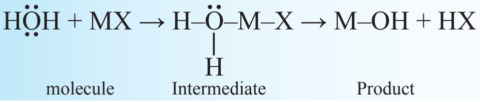
Silicates	Sharing of O-atom/Basic Tetrahedral unit	Contribution of O-atom/Basic Tetrahedral unit	General formula
Ortho	0	4	SiO_4^{4-}
Pyro	1	3.5	$Si_2O_7^{6-}$
Cyclic	2	3	$(SiO_3)_n^{2n-}$
Simple chain (pyroxene)	2	3	$(SiO_3)_n^{2n-}$
Double chain (Amphibole)	(3,2) avg. = 2.5	$\frac{11}{4} = \left(\frac{5.5}{2}\right)$	$(Si_4O_{11})_n^{6n-}$
2D or (Sheet)	3	2.5	$(Si_2O_5)_n^{2n-}$
3D	4	2	$(SiO_2)_n$

HYDROLYSIS

Hydro - Water

lysis - break down

Break down of a molecule through water and formation of new product is known as hydrolysis.

- It is nucleophilic substitution reaction.
- 

$$\underset{\text{molecule}}{H\ddot{\underset{\cdot\cdot}{O}}H} + MX \rightarrow \underset{\text{Intermediate}}{H\text{–}\underset{\underset{H}{|}}{\ddot{O}}\text{–}M\text{–}X} \rightarrow \underset{\text{Product}}{M\text{–}OH + HX}$$

Extent of Hydrolysis ∝ Covalent Character

$BeCl_2 + 2HOH \rightarrow Be(OH)_2 + 2HCl$

$BCl_3 + 3HOH \rightarrow B(OH)_3 + 3HCl$

$AlCl_3 + 3HOH \rightarrow Al(OH)_3 + 3HCl$

$SiCl_4 + 4HOH \rightarrow Si(OH)_4 + 4HCl$

$SF_6 + H_2O \rightarrow$ No hydrolysis due to crowding

$CCl_4 + HOH \xrightarrow[\text{conditions}]{\text{ordinary}}$ No hydrolysis

$BF_3 + 3HOH \rightarrow B(OH)_3 + 3HF$

$3BF_3 + 3HF \rightarrow 3H^+ [BF_4]^-$

$4BF_3 + 3H_2O \rightarrow 3H[BF_4]$

(partially hydrolysis)

Similarly

$SiF_4 + 4HOH \rightarrow Si(OH)_4 + 4HF$

$2SiF_4 + 4HF \rightarrow H_2^+ [SiF_6]^{2-}$

hydrolysis followed by
Lewis acid-base reaction.

15th Group Halides

$NF_3 + HOH \xrightarrow[\text{conditions}]{\text{ordinary}}$ No hydrolysis

$NCl_3 + HOH \rightarrow NH_3 + 3HOCl$

$PCl_3 + HOH \rightarrow H_3PO_3 + 3HCl$

$AsCl_3 + HOH \rightarrow As(OH)_3 + 3HCl$

$SbCl_3 + HOH \rightarrow SbOCl + 2HCl$
(partial hydrolysis)

$BiCl_3 + HOH \rightarrow BiOCl + 2HCl$
(partial hydrolysis)

$PCl_5 + HOH \rightarrow POCl_3 \rightarrow H_3PO_4$
partial completely

Hydrolysis of Higher Covalent Character Containing Salt

$Be_2C + 4HOH \rightarrow 2Be(OH)_2 + CH_4$

$Mg_2C_3 + 4HOH \rightarrow 2Mg(OH)_2 + C_3H_4$

$CaC_2 + 2HOH \rightarrow Ca(OH)_2 + C_2H_2$

$Al_4C_3 + 12HOH \rightarrow 4Al(OH)_3 + 3CH_4$

$Mg_3N_2 + 6HOH \rightarrow 3Mg(OH)_2 + 2NH_3$

$AlN + 3HOH \rightarrow Al(OH)_3 + NH_3$

$Ca_3P_2 + 6HOH \rightarrow 3Ca(OH)_2 + 2PH_3$

$LiH + HOH \rightarrow LiOH + H_2$

$CaH_2 + 2HOH \rightarrow Ca(OH)_2 + H_2$

Hydrolysis of Interhalogen Compounds

$AX + HOH \rightarrow HX + HOA$

$AX_3 + HOH \rightarrow 3HX + HAO_2$

$AX_5 + HOH \rightarrow 5HX + HAO_3$

$AX_7 + HOH \rightarrow 7HX + HAO_4$

HX Hydrohalic acid

HOA, HAO_2, HAO_3, HAO_4
oxyacid of halogen

Some Specific Hydrolysis

$XeF_2 \xrightarrow{HOH} Xe + 2HF + O_2$

$6XeF_4 \xrightarrow{HOH} 4Xe + 2XeO_3 + 24HF + 3O_2$

$$XeF_6 \xrightarrow{HOH} 2HF + \underset{\text{partial}}{XeOF_4} \xrightarrow{HOH} 2HF + \underset{\text{partial}}{XeO_2F_2} \xrightarrow{HOH} 2HF + \underset{\text{complete}}{XeO_3}$$

Back Bonding

It is type of π-interaction between lone pair & vacant orbital of adjacent atom in molecule.

Condition:

(i) One atoms must have lone pair.
(ii) And another atoms must have vacant orbital.

Type of Back Bond:

(i) (pπ - pπ) type of back bond, eg. BF_3, BCl_3, CF_2, CCl_2
(ii) (pπ - dπ) type of back bond
eg. CCl_3^-, $O(SiH_3)$, $N(SiH_3)_2$, SiH_5O^-, etc.

Application of Back Bonding

Lewis acid character:

$BF_3 < BCl_3 < BBr_3 < BI_3$

$BeF_2 < BeCl_2 < BeBr_2 < BeI_2$

$SiF_4 > SiCl_4 > SiBr_4 > SiI_4$

Lewis basic character:

$N(CH_3)_3 > N(SiH_3)_3$

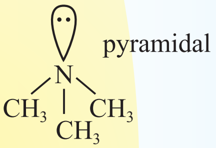
$O(CH_3)_3 > O(SiH_3)_3$

NOTES

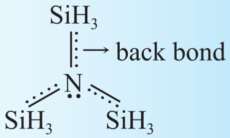
Due to back bonding $\underline{B}_3N_3H_6$, $(\underline{B}O_2)_3^{3-}$, $\underline{N}(SiH_3)_3$ is planar around under lined atom.

Few more examples of Back Bonding

1. Shape of trimethyl amine pyramidal while shape of trisillyl amine is triangular planar.



No back bonding due to no vacant orbital in carbon.

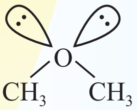


Trigonal Planar

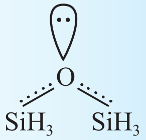
2. Lewis base strength

$$\ddot{N}(CH_3)_3 > \underbrace{\ddot{N}(SiH_3)_3}_{\text{lp involve in back bonding}}$$

3. Bond angle of $(CH_3)_2O$ is very less than $(SiH_3)_2O$



No back bonding
C : No vacant orbital



back bond effect of lp ↓
bond angle ↑

Chemical Species having Multicentered Bond

(3c-2e) bond is also termed as banana bond.

Bridge bond is stronger than terminal bond.

Bridge bond is longer than terminal bond.

	Bridge bond	**Hybridisation of central atom**
Be_2Cl_4	(3c-4e)	sp^2
$(BeCl_2)_n$	(3c-4e)	sp^3
Al_2Cl_6	(3c-4e)	sp^3
I_2Cl_6	(3c-4e)	sp^3d^2
B_2H_6	(3c-2e)	sp^3
Be_2H_4	(3c-2e)	sp^2
$(BeH_2)_n$	(3c-2e)	sp^3
$(AlH_3)_n$	(3c-2e)	sp^3d^2
$Al_2(CH_3)_6$	(3c-2e)	sp^3

Odd e^- species: Total number of electron or valence electron in odd number.

	Hybridisation	**Shape**	**Magnetic behaviour**
NO_2	sp^2	V shape	Para
ClO_2	sp^2	V shape	Para
ClO_3	sp^3	Pyramidal	Para
$^{\bullet}CH_3$	sp^2	Trigonal planar	Para
$^{\bullet}CH_3/^{\bullet}CHF_2/CH_2F$	sp^3	Pyramidal	Para

OXY-ACIDS

- Mainly oxy-acids are hydroxide of Non-metal oxides.
- No. of H^+ ion furnish by an oxy-acid is known as their basicity.

Oxy-acid obtained by dissolving non-metal oxide in water.

Eg. $CO_2 + HOH \rightarrow H_2CO_3$ or $OC(OH)_2$

Here: $CO_2 \rightarrow$ Non metal oxide - Anhydride of carbonic acid $OC(OH)_2 \rightarrow$ Oxyacid

- $NO_2 \rightarrow$ Mixed anhydride
- it gives $\rightarrow HNO_2$ & HNO_3

Oxide		**Acid**		
• N_2O_3	→	HNO_2	–	Nitrous acid
• N_2O_5	→	HNO_3	–	Nitric acid

- P_4O_{10} → H_3PO_4 – Phosphoric acid
- SO_2 → H_2SO_3 – Sulphurous acid
- SO_3 → H_2SO_4 – Sulphuric acid
- Cl_2O_7 → $HClO_4$ – Perchloric acid
- Oxyacids of different elements

Order of acidic strength

$H_3PO_2 > H_3PO_3 > H_3PO_4$

Reducing nature

$H_3PO_2 > H_3PO_3 > H_3PO_4$

Element	Oxide	Oxyacid	Basicity
Boron	B_2O_3	$B(OH)_3$ boric acid	Not protonic acid monobasic Lewis acid
Carbon	CO_2	H_2CO_3 carbonic acid	Two
Nitrogen		$H_2N_2O_2$ Hyponitrous aicd HNO_2 Nitrous acid HNO_3 Nitric acid HNO_4 Pernitric acid	
Phosphorus		H_3PO_2 Hypophosphorus acid H_3PO_3 Phosphorus acid H_3PO_4 Ortho phosphoric acid HPO_3 Meta phosphoric acid $H_4P_2O_5$ Pyrophosphorus acid $H_4P_2O_7$ Pyrophosphoric acid $H_4P_2O_6$ Hypophosphoric acid	

OXYACIDS OF SULPHUR

1. Sulphurous acid - H_2SO_3
2. Sulphuric acid - H_2SO_4
3. Thiosulphuric acid - $H_2S_2O_3$
4. Peroxymonosulphuric (Caro’s acid) - H_2SO_5 (Peroxide bond)

5. Peroxydisulphuric acid (Marshal's acid) - $H_2S_2O_8$ (Peroxide bond)
6. Pyrosulphurous acid - $H_2S_2O_5$ - (S-S linkage)
7. Pyrosulphuric acid - $H_2S_2O_7$ (S-O-S linkage)
8. Thionus acid - $H_2S_2O_4$
9. Thionic acid - $H_2S_2O_6$
10. Polythionus acid - $H_2(S)_nO_4$ (S-S linkage)
11. Polythionic acid - $H_2(S)_nO_6$ (S-S- linkage)

OXYACIDS OF HALOGEN (Cl)

1. Hypochlorous acid - HClO
2. Chlorous acid - $HClO_2$
3. Chloric acid - $HClO_3$
4. Perchloric acid - $HClO_4$

Order of acidic strength: $HClO < HClO_2 < HClO_3 < HClO_4$

Oxidising nature: $HClO > HClO_2 > HClO_3 > HClO_4$

ALLOTROPY

- Those substance which are made up of same elements but having different bonding arrangement are known as allotropes & this phenomenon known as allotropy.
- Those elements which exhibit higher tendency of catenation exhibit higher tendency of allotropy.
- Therefore carbon, phosphorus & sulphur exhibit maximum allotropy.

ALLOTROPES OF CARBON		
Diamond	**Graphite**	**Fullerene**
C-sp^3, tetrahedral structure C-C bond length 1.54Å Compact 3 dimensional structure Hardest substance Very high mp (~ 3400ºC) Very high density Non conductor Very high refractive index Exhibit total internal reflection Shines bright in light	**Hexagonal layer structure** All sp^2 hybrid carbon Unhybrid orbital electron form π-bond. This π-bond exhibit resonance and due to resonance there is mobility of electrons and it becomes conductor of electricity.	**Latest discovered allotrope of carbon it is found in chimney sooty particle.** It contain C_{60}-C_{320}. C : sp^2 hybrid Contain pentagon & hexagonal structure C_{60}: Buckminster fullerene soccer ball (Football) or bucky ball. C_{60}: 20 hexagon rings 12 pentagon rings Purest form of carbon No dangling bond

ALLOTROPES OF PHOSPHOROUS

(a) White phosphorous (b) Red phosphorous (c) Black phosphorous

White phosphorous	Red Phosphorous
Waxy solid	Brittle powder
Poisonous	Non poisonous
Soluble in CS_2, Insoluble in water	Insoluble in water & CS_2
Monomer of P_4	Polymer of P_4
Highly reactive due to bond angle strain	More stable than white phosphorous
It glows in dark due to slow oxidation (phosphorescence)	It does not glow in dark
It gives phosphine (PH_3) on reaction with NaOH	It gives hypo phosphoric acid on reaction with NaOH

Order of stability of MP or density → white < red < black

$$\begin{tikzcd}
\text{Red Phosphorous} \arrow[r, "803K", "\text{high P}"'] & \alpha\text{-Black Phosphorous} \\
\text{White Phosphorous} \arrow[u, "\text{inert medium}"'] \arrow[r, "473K", "\text{high P}"'] & \beta\text{-Black Phosphorous}
\end{tikzcd}$$

ALLOTROPES OF SULPHUR	
Crystalline	**Amorphous**
Rhombic sulphur (α-S) most stable form Monoclinic sulphur (β-S) $\alpha\text{-S} \underset{<95°,6°C}{\overset{>95.6°C}{\rightleftharpoons}} \beta\text{-S}$ 95.6°C = transition Temperature both are soluble in CS_2 but insoluble in water	Milk of sulphur Plastic sulphur (γ-S) Colloidal sulphur $\underset{RA}{H_2S} + \underset{OA}{2HNO_3} \xrightarrow[\text{Redox}]{} S + 2NO_2 + 2H_2O$

(a) Density of $\alpha S > \beta S$.

(b) Both are puckered crown shape having S_8 units.

(c) S_2 is paramagnetic sulphur which exist in vapour form at high temperature.

(d) S_6 is chair form of S.

Effect of Temperature

$S_{8(\alpha)} \xrightarrow{95.5°C} S_{8(\beta)} \xrightarrow{130\text{-}200°C}$ Viscosity of liquid increase $\xrightarrow{>200°C}$ Viscosity decrease

SOME IMPORTANT INCREASING ORDER

1. Acidic property

(i) SiO_2, CO_2, N_2O_5, SO_3
(ii) MgO, Al_2O_3, SiO_2, P_4O_{10}
(iii) $HClO$, $HClO_2$, $HClO_3$, $HClO_4$
(iv) CH_4, NH_3, H_2O, HF
(v) SiH_4, PH_3, H_2S, HCl
(vi) H_2O, H_2S, H_2Se, H_2Te
(vii) HF, HCl, HBr, HI
(viii) $InCl_3$, $GaCl_3$, $AlCl_3$
(ix) BF_3, BCl_3, BBr_3, BI_3

2. Bond Angle

(i) CH_4, C_2H_4, C_2H_2
(ii) H_2O, NH_3, CH_4, CO_2
(iii) H_2O, NH_3, CH_4, BH_3
(iv) NO_2^-, NO_2, NO_2^+
(v) H_2Se, H_2S, H_2O
(vi) AsH_3, PH_3, NH_3
(vii) PF_3, PCl_3, PBr_3, PI_3
(viii) NF_3, NCl_3
(ix) NF_3, NH_3, NCl_3
(x) OF_2, OH_2, Cl_2O

3. Basic Character

(i) $LiOH$, $NaOH$, KOH, $RbOH$, $CsOH$
(ii) $Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$
(iii) BeO, MgO, CaO, SrO
(iv) NiO, MgO, SrO, K_2O, Cs_2O
(v) CO_2, B_2O_3, BeO, Li_2O
(vi) SiO_2, Al_2O_3, MgO, Na_2O
(vii) SbH_3, AsH_3, PH_3, NH_3
(viii) F^-, OH^-, NH_2^-, CH_3^-

4. Thermal Stability

(i) Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3, Cs_2CO_3
(ii) $BeCO_3$, $MgCO_3$, $CaCO_3$, $BaCO_3$

(iii) $Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$
Polarisation

(iv) LiOH, NaOH, KOH, RbOH, CsOH

(v) $BeSO_4$, $MgSO_4$, $CaSO_4$

(vi) CsH, RbH, KH, NaH, LiH

(vii) SbH_3, AsH_3, PH_3, NH_3

(viii) H_2Te, H_2Se, H_2S, H_2O

(ix) HI, HBr, HCl, HF

5. Ionic Character

(i) LiBr, NaBr, KBr, RbBr, CsBr

(ii) LiF, NaF, KF, RbF, CsF

(iii) $BeCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$

(iv) BCl_3, $AlCl_3$, $GaCl_3$

(v) VCl_4, VCl_3, VCl_2

(vi) AlF_3, Al_2O_3, AlF_3

(vii) AlN, Al_2O_3, AlF_3

(viii) HI, HBr, HCl, HF

(ix) CuCN, AgCN

(x) AgCl, KCl

6. Oxidizing Power

(i) $Cr_2O_7^{2-}$, MnO_4^-

(ii) MnO_4^{2-}, MnO_4^-

(iii) WO_3, MoO_3, CrO_3

(iv) $GeCl_4$, $SnCl_4$, $PbCl_4$

(v) I_2, Br_2, Cl_2, F_2

(vi) Zn^{+2}, Fe^{+2}, Pb^{2+}, Cu^{2+}, Ag^+

7. Melting Point

(i) Cs, Rb, K, Na, Li

(ii) Mg, Ba, Sr, Ca, Be

(iii) CaI_2, $CaBr_2$, $CaCl_2$, CaF_2

(iv) $BeCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$

(v) NaI, NaBr, NaCl, NaF

(vi) CsCl, RbCl, KCl, NaCl

(vii) $AlCl_3$, $MgCl_2$, NaCl

8. Density

(i) Na, Al, Fe, Pb, Au

(ii) Li, K, Na, Rb, Cs

(iii) Ca, Mg, Be, Sr, Ba

(iv) Highest Density = Os/Ir

(v) Lowest density = H

(vi) Metal of lowest Density = Li

9. Boiling Point

(i) PH_3, AsH_3, NH_3, SbH_3

(ii) H_2S, H_2Se, H_2O

(iii) HCl, HBr, HI, HF

(iv) NH_3, HF, H_2O

(v) He, Ne, Ar, Kr

(vi) H_2O, D_2O

(vii) H_2, Cl_2, Br_2

10. Electrical Conductivity

Cr, Pt, Fe, Al, Au, Cu, Ag

11. Reactivity with water

(i) Li, Na, K, Rb, Cs

(ii) Be, Mg, Ca, Sr, Ba

12. Extent of Hydrolysis

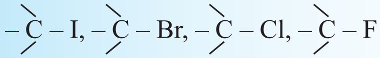
(i) CCl_4, $MgCl_2$, $AlCl_3$, $SiCl_4$, PCl_5

(ii) $BiCl_3$, $SbCl_3$, $AsCl_3$, PCl_3, NCl_3

13. Bond Strength

(i) HI, HBr, HCl, HF

(ii)



$-\overset{\diagdown}{\underset{\diagup}{C}}-I,\ -\overset{\diagdown}{\underset{\diagup}{C}}-Br,\ -\overset{\diagdown}{\underset{\diagup}{C}}-Cl,\ -\overset{\diagdown}{\underset{\diagup}{C}}-F$

(iii) $N-N$, $N=N$, $N\equiv N$

(iv) $As-H$, $Sb-H$, $P-H$, $N-H$

(v) N_2^{2-}, N_2^{-}, N_2^{+}, N_2

(vi) O_2^{2-}, O_2^{-}, O_2, O_2^{+}, O_2^{2+}

LiI, LiBr, LiCl, LiF

NaI, NaBr, NaCl, NaF

CsCl, RbCl, KCl, NaCl

BaO, SrO, CaO, MgO

(vii) F_2, H_2, O_2, N_2

(viii) NO^-, NO, NO^+

(ix) I_2, F_2, Br_2, Cl_2

(x) O – O, S – S

(xi) F – F, O – O, N – N, C – C, H – H

14. Reducing Power

(i) $PbCl_2$, $SnCl_2$, $GeCl_2$

(ii) HF, HCl, HBr, HI

(iii) Ag, Cu, Pb, Fe, Zn

(iv) HNO_3, H_2SO_3, H_2S

(v) H_3PO_4, H_3PO_3, H_3PO_2

15. Covalent Character

(i) LiCl, $BeCl_2$, BCl_3, CCl_4

(ii) $SrCl_2$, $CaCl_2$, $MgCl_2$

(iii) $TiCl_2$, $TiCl_3$, $TiCl_4$

(iv) LiCl, LiBr, LiI

(v) Na_2O, Na_2S

(vi) AlF_3, Al_2O_3, AlN

(vii) HF, HCl, HBr, HI

16. Strength of Hydrogen bonding (X...H–X)

(i) S, Cl, N, O, F

(ii) NH_3, H_2O, HF

17. Reactivity with Hydrogen

(i) Cs, Rb, K, Na, Li

(ii) Ba, Sr, Ca, Mg, Be

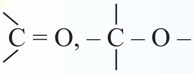
18. Reactivity Towards Air

Be, Mg, Cs, Sr, Ba

19. Bond Length

(i) N_2, O_2, F_2, Cl_2

(ii) N – N, C – N, C – C

(iii) CO, 
$>C=O$, $-\overset{|}{\underset{|}{C}}-O-$

(iv) NO^+, NO, NO^-

(v) O_2, O_3, H_2O_2 (O – O bond length)

(vi) CO, CO_2, CO_3^{-2}

(vii) N_2, N_2^{-}, N_2^{-2}

(viii) $O_2^{+2}, O_2, O_2^{-}, O_2^{-2}$

(ix) HF, HCl, HBr, HI

20. Dipole moments

(i) $CCl_4, CHCl_3, CH_2Cl_2, CH_3Cl$

(ii) NF_3, NH_3, H_2O, HF

(iii) Cis-chloropropene, Trans-chloropropene

(iv) p, m, o-dichlorobenzene

(v) $CH_3I, CH_3Br, CH_3F, CH_3Cl$

(vi) NH_3, SO_2, H_2O, HF

(vii) H_2S, H_2O

(viii) HI, HBr, HCl, HF

(ix) PH_3, ASH_3, SbH_3, NH_3

(x) H_2O, H_2O_2

Group 15	Bond angle	Group 16	Bond angle
NH_3	107°48′	H_2O	104°28′
PH_3	93°36′	H_2S	92°
AsH_3	91°48′	H_2Se	91°
SbH_3	91°18′	H_2Te	90.5°

INERT PAIR EFFECT

Inert pair effect the reluctance of ns electrons to take part in bond formation is called inert pair effect. This effect is more pronounced in heavier elements and that too for 13, 14 and 15 group. It results in the decrease in oxidation state by 2 units. For example, Tl is more stable in oxidation state + 1 than the oxidation state +3.

In p-block elements the stability of the lower oxidation state increases on descending the group.

Group 13	**Group 14**
B (+3)	C (+4)
Al (+3)	Si (+4)
Ga (+3), (+1)	Ge (+4), (+2)
In (+3), (+1)	Sn (+4), (+2)
Tl (+3), (+1)	Pb (+4), (+2)

Order of stability

$Tl^{+1} > In^{+1} > Ga^{+1}$ (due to inert pair effect)

Order of stability

$Pb^{+2} > Sn^{+2} > Ge^{+2}$ (due to inert pair effect)

Molecules that do not Exist

(1) SF_4, SF_6 & PF_5 exist while. OF_4, OF_6, NF_5 do not exist.

(2) (a) PI_5(vap) & SCl_6 do not exist.

  (b) SCl_6 does not exist while $TeCl_6$ exist.

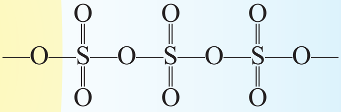
  (c) PI_5 (Solid) exist

(3) SF_6, PF_5, XeF_6, XeF_4 & XeF_2 exist while SH_6, PH_5, XeH_6, XeH_4, XeH_2 do not exist.

ALLOTROPIC FORM OF SO_3

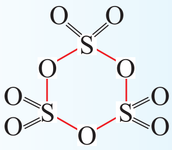
SO_3 have three allotropic form α-SO_3, β-SO_3 and γ-SO_3.

α-SO_3
Cross lined solid



$$-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-$$

Polymeric chain structure
β-SO_3



γ-SO_3
(S_3O_9)
cylic trimer

❑❑❑