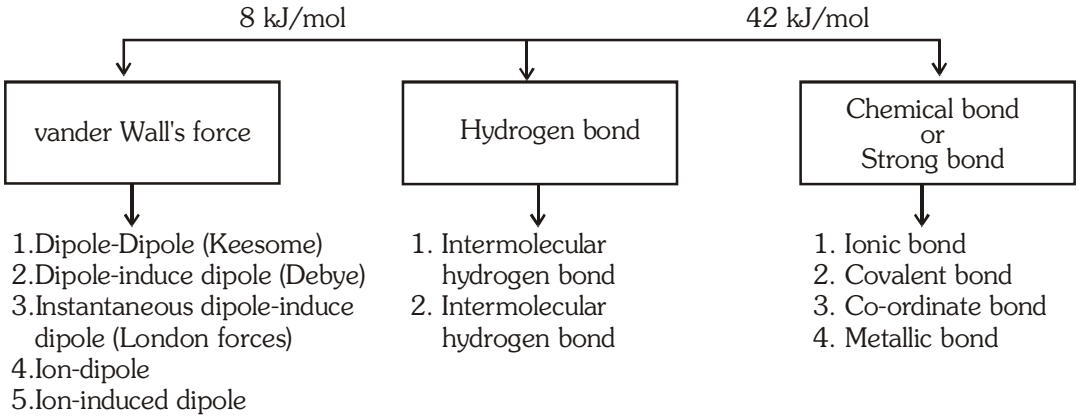
CHAPTER 2

CHEMICAL BONDING

CHEMICAL BOND :

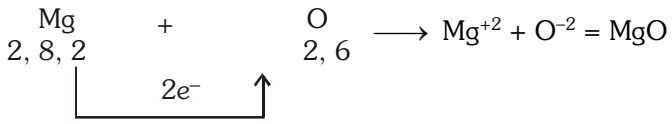
1. The force of attraction which hold togather atom, molecule or ions with in chemical species.
2. It is always exothermic process.



❑ ELECTROVALENT OR IONIC BOND

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

Ionic bonds are non-directional.



electrovalency of Mg = 2

electrovalency of O = 2

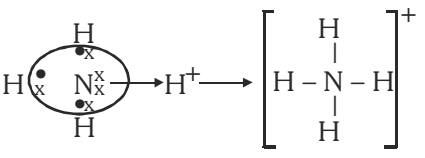
❑ COVALENT BOND

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)



Donor Acceptor

(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 vacant orbital act as acceptor known as Lewis acid - acquire -ve charge.

Eg. $H_3N: + H^+ \rightarrow H_3N \rightarrow H^+$ (LB LA)

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

- Donor atom follow octet rule

MODERN APPROACH OF COVALENT BOND

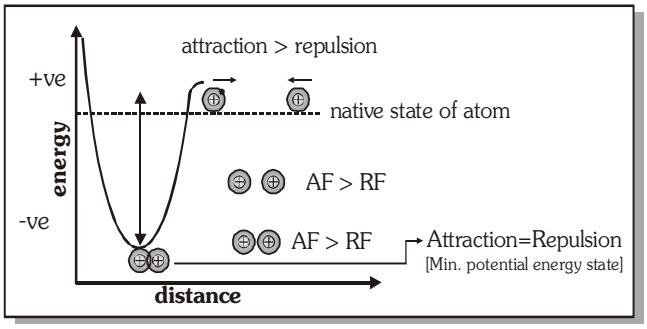
Consider wave mechanical model of atom means electron has dual nature; wave nature as well as particle nature considered by these theories, there are two theories in this approach.

1. Valence Bond Theory | **2. Molecular Orbital Theory**

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
Shell - subshell - orbital - electron - cloud

- 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.

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

1-1 > 1-2 > 2-2 > 2-3

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

(b) Type of Sub-shell

Valence shell contain subshell s & p

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

Possible combination & strength of overlapping

s-s < s-p < p-p

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

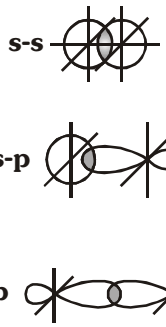
2s - 2s < 2s-2p < 2p-2p sub-shell factor

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.

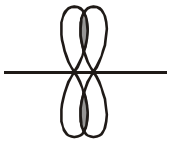


(b) Co-lateral overlapping

Side wise overlapping has less extent of overlapping form π- bond

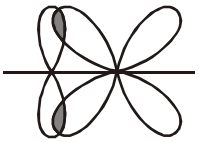
Weak bond

p-p overlapping



Internuclear axis
pπ - pπ bond

p-d overlapping



pπ - dπ bond

- In case of multiple bond between two atom one bond is sigma and rest are pi-bonds.
- VBT was not able to define geometry of molecule therefore a new concept came into existence known as hybridisation.

HYBRIDISATION

- Intermixing of atomic orbitals and formation of new orbital, these orbitals are known as hybrid orbital and this concept is known as hybridisation.
- It is hypothetical concept.
- Only those orbitals can participate in hybridisation which has slight difference in energy.
- No. of hybrid orbitals : No. of atomic orbitals participate in intermixing
- Hybrid orbitals oriented at maximum possible distance three dimensionally.
- On the basis of type of orbitals participating in hybridisation, we can divide hybridisation into following categories.

S.No.	Type of 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

- Given by Nyholm & Gillespie to define shape of molecule.
- Shape of molecule define on the basis of electron pairs orientation present on central atom.
- Electron pairs present on central atom repel each other therefore these electron pair occupy such position on central atom; where they experience minimum repulsion at maximum possible distance three dimensionally.
- **Order of replusion :** 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, NH_2^- OF_2, Cl_2O, 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^-, ClF_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^-, XeF_5^+
(c) sp^3d^2-hybridisation	4	2	Square planar	XeF_4
6. (a) sp^3d^3-hybridisation	7	-	Pentagonal bipyramidal	IF_7
(b) sp^3d^3-hybridisation	6	1	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

$\vec{\mu} = q \times d$ | 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 $\Delta EN \neq 0 \rightarrow \vec{\mu}_{net} = 0 \rightarrow$ polar
HF > HCl > HBr > HI

Polyatomic molecule :

$\mu_R \rightarrow$ Vector sum of bond moment

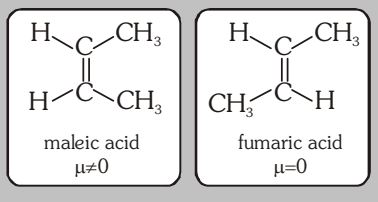
$\mu_R \rightarrow \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$

Important Order

$NH_3 > NI_3 > NBr_3 > NCl_3 > NF_3$
$NH_3 > SbH_3 > AsH_3 > PH_3$
$H_2O > H_2S$
$CH_3Cl > CH_3F > CH_3Br > CH_3I$
$CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$

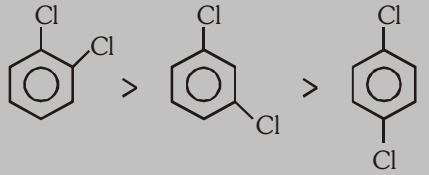
Applications

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



maleic acid $\mu \neq 0$ | fumaric acid $\mu = 0$

Dipole moment in Aromatic Compounds



Orthodichloro benzene | **metadichloro benzene** | **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
Hydrogen bond → Interamolecular hydrogen bond → within the molecules

* Intromolecular H-bonding takes places mainly in ortho derivatives of benzene.

Note :

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

O Intramolecular H-bonding takes place in ortho derivatives only.

Applications of H-bonding

Physical State (densile nature)	∝	H-bond
Melting Point (mp)	∝	H-bond
Boiling Point (bp)	∝	H-bond
Viscosity	∝	H-bond
Surface Tension	∝	H-bond
Volatility	∝	1/H-bond
Vapour Pressure	∝	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 substracted 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 ≤ 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)

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

$\sigma *, \pi *$ = 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 field), e.g., O_2 molecule. Otherwise diamagnetic (eg : $N_{2)}$

Fractional bond order it will be always paramagnetic.

Sr. 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	——
5	5	3	2	½	paramagnetic
6	6	4	2	1	diamagnetic
7	7	4	3	½	paramagnetic
8	8	4	4	0	——
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	——

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

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

BONDING PARAMETER

1. Bond length : Internuclear distance

Factor affecting Bond length

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

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

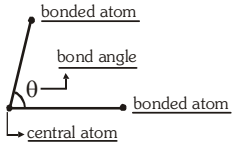
$$d_{A-B} = r_A + r_B - 0.09 \times \Delta EN \text{ Å}$$

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

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

Bond Angle :

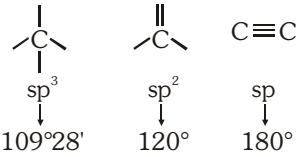
Angle between two adjacent bond is known as bond angle.



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 ∝ 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 ∝ size of bonded species

Eg. $OF_2 < OCl_2 < OBr_2 < OI_2$

Note :

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.

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

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

$\Delta H_{formation} = \Delta H_{Sub}$ + I.E. + ½ BDE + ΔH_{eg} + U
bond formation is always an exothermic process.
$\Delta H_{formation}$ = —ve

ΔH_{Sub}: 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 — Solubility — Covalent Character

Conduction:
- Molten state: Ionic conduction $\propto \frac{1}{\text{Ionic radius}}$
  Eg. : LiCl, NaCl, KCl, RbCl, CsCl
  Ionic Radius : $Li^+ <<< Cs^+$
  Conductance : CsCl < RbCl < KCl < NaCl < LiCl
- Aqueous medium: Ionic mobility $\propto \frac{1}{\text{Ionic radius}}$
  Hyd. radius : $Cs^+ <<< Li^+(aq)$
  conductance : LiCl < NaCl < KCl < RbCl < CsCl

COVALENT CHARACTER / FAJAN'S RULE

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

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

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

FACTORS AFFECTING POLARISATION

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

Eg. (i) $\overset{+2}{CrO} < \overset{+3}{Cr_2O_3} < \overset{+6}{CrO_3}$ Covalent character ↑

(ii) $\overset{+2}{SF_2} < \overset{+4}{SF_4} < \overset{+6}{SF_6}$ Covalent character ↑

(iii) $\overset{-1}{LiF} < \overset{-2}{Li_2O} < \overset{-3}{Li_3N}$ Covalent character ↑ (anion charge↑)

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

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 depends upon Lattice Energy and Hydration Energy

Increasing order of solubility

(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, $CsCO_3$

(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

For all $\textbf{solubility} \propto \frac{1}{\text{cov. char.}}$

solubility in org. solvent $\propto$ **cov. char** $\propto \frac{1}{\text{ionic char}}$

[CCl_4, benzene, ether, alcohol, acetone]

Eg. (i) $PbF_2 > PbCl_2 > PbCl_2 > PbI_2$
(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	$(SiO_3)_n^{2n-}$
Single 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.
- $H\ddot{O}H + MX \longrightarrow H—\ddot{O}(H)—M—X \longrightarrow M—OH + HX$

molecule — Intermediate — Product

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

$NCl_3 + HOH \longrightarrow NH_3 + 3HOCl$

$PCl_3 + HOH \longrightarrow H_3PO_3 + 3HCl$

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

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

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

$PCl_5 + HOH \longrightarrow \underset{\text{partial}}{POCl_3} \xrightarrow{H_2O} \underset{\text{completely}}{H_3PO_4}$

Hydrolysis of higher covalent character containing salt

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

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

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

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

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

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

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

$LiH + HOH \longrightarrow LiOH + H_2$

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

Hydrolysis of Interhalogen Compounds

$AX + HOH \longrightarrow HX + HOA$

$AX_3 + HOH \longrightarrow 3HX + HAO_2$

$AX_5 + HOH \longrightarrow 5HX\ HAO_3$

$AX_7 + HOH \longrightarrow 7HX + HAO_4$

HX Hydrohalic acid
HOA, HAO_2, HAO_3 HAO_4
oxyacid of halogen

Some specific hydrolysis

$XeF_2 \xrightarrow{HOH} Xe + 2HF + \frac{1}{2}O_2$

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

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

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 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 :

* $BF_3 < BCl_3 < BBr_3 < BI_3$
$BeF_2 < BeCl_2 < BeBr_2 < BeI_2$
$SiF_4 > SiCl_4 > SiBr_4 > SiI_4$

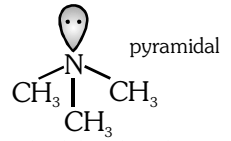
Lewis basic character :

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

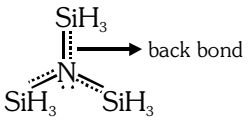
Note : Due to back bonding $\underline{B}_3N_3H_6$, $(\underline{B}O_2)_3^{3-}$, $\underline{N}(SiH_3)_3$ is planar around under lined atom.

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.



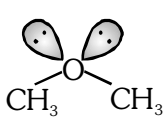
Trigonal Planar

2. Lewis base strength

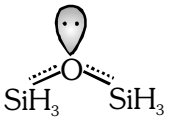
$\ddot{N}(CH_3)_3 > \underline{\ddot{N}(SiH_3)_3}$

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 bannana bond.

Bridge bond is stronger than terminal bond.

Bridge bond is longer than terminal bond.

	Brigde 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 valance electron in odd number.

	Hybridisation	**Shape**	**Magnatic 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	Pramidal	Para

OXY-ACIDS

- Mainly oxy-acids are hydroxide of Non-metal oxides.
- No. of H^+ ion furnish by an oxyacid is known as their basicity.
  Oxyacid 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
- $NO_2 \longrightarrow$ Mixed anhydride
- it gives $\longrightarrow$ 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

	Element	Oxide	Oxyacid	Basicity
1	Boron	B_2O_3	$B(OH)_3$ boric acid	Not protonic acid monobasic Lewis acid
2	Carbon	CO_2	H_2CO_3 carbonic acid	Two
3	Nitrogen		$H_2N_2O_2$ Hyponitrous acid HNO_2 Nitrous acid HNO_3 Nitric acid HNO_4 Pernitric acid	
4	Phosphorus		H_3PO_2 Hypophosphorus acid H_3PO_3 Ortho 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	

Order of acidic strength
$H_3PO_2 > H_3PO_3 > H_3PO_4$

Reducing nature
$H_3PO_2 > H_3PO_3 > H_3PO_4$

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. Dithionus acid - $H_2S_2O_4$
9. Dithionic acid - $H_2S_2O_6$
10. 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

C-sp^3, tetrahedral structure
C-C bond length 1.54 Å
Compact 3 dimensional structure
Hardest substance
Very high mp (~ 3400°C)
Very high density
Non conductor
Very high refractive index
Exhibit total internal reflection
Shines brighty in light

GRAPHITE

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.

FULLERENE

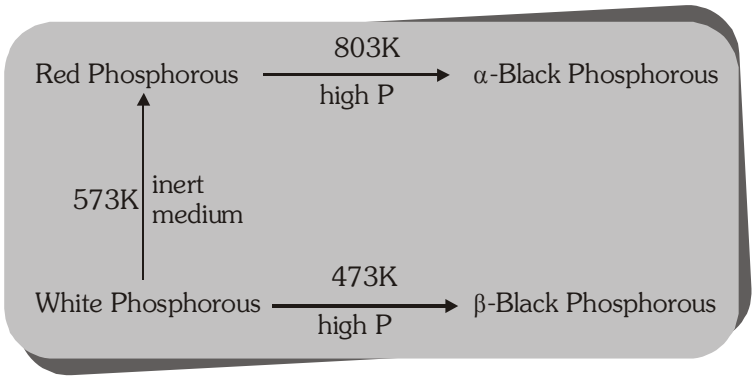
Latest discovered allotrope of carbon it is found in chimney sooty particle.
It contain C_{60}-C_{320}, C : sp^2 hybrid
Contain pentagon & hexagonal structure
C_{60}: Buckminster fullerene soccer ball (football) or bucky ball.
C_{60} : 20 hexagon rings
12 pentagon rings
Purest form of carbon
No dangling 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 or MP or density → white < red < black



ALLOTROPES OF SULPHUR

S

Crystalline

Rhombic sulphur (α-S)
most stable form

Monoclinic sulphur (β-S)

$\alpha\text{-S} \underset{<95^\circ,6^\circ C}{\overset{>95.6^\circ C}{\rightleftharpoons}} \beta\text{-S}$

95.6°C = transition Temp.
both are soluble in CS_2
but insoluble in water

Amorphous

Milk of sulphur
Plastic sulphur (γ-S)

Colloidal sulphur

$\underset{RA}{H_2S} + \underset{OA}{2HNO_3} \xrightarrow[Redox]{} S + 2NO_2 + 2H_2O$

(a)density of αS > βS (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

$S_{8(\alpha)} \xrightarrow{95.5^\circ C} S_{8(\beta)} \xrightarrow{119^\circ C} S_{(liq)} \xrightarrow{130\text{-}200^\circ C}$ Viscosity of liquid increase $\xrightarrow{> 200^\circ C}$ 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) $lnCl_3$, $GaCl_3$, $AlCl_3$
(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, MgF_2, NaF
(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

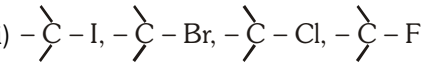
12. Extent of Hydrolysis

(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) 

(iii) N – N, N = N, N ≡ 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

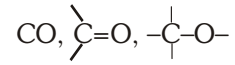
18. Reactivity Towards Air

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) 

(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 examples, 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

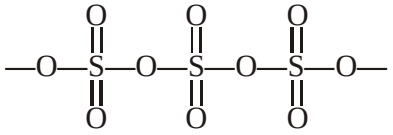
(3) SF_6, PF_5, XeF_6, XeF_4 & XeF_2 exist while SH_6, PH_5, XeH_6, XeH_4, XeH_2 do not exist

ALLOTROPIC FORM OF SO_3

SO_3 have three allotropic forms α-SO_3 , β-SO_3 and γ-SO_3

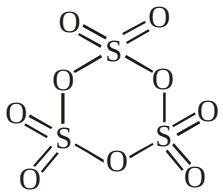
α-SO_3 ,

Cross linked solid



Polymeric chain structure

β-SO_3



γ-SO_3

(S_3O_9)

cylic trimer

IMPORTANT NOTES