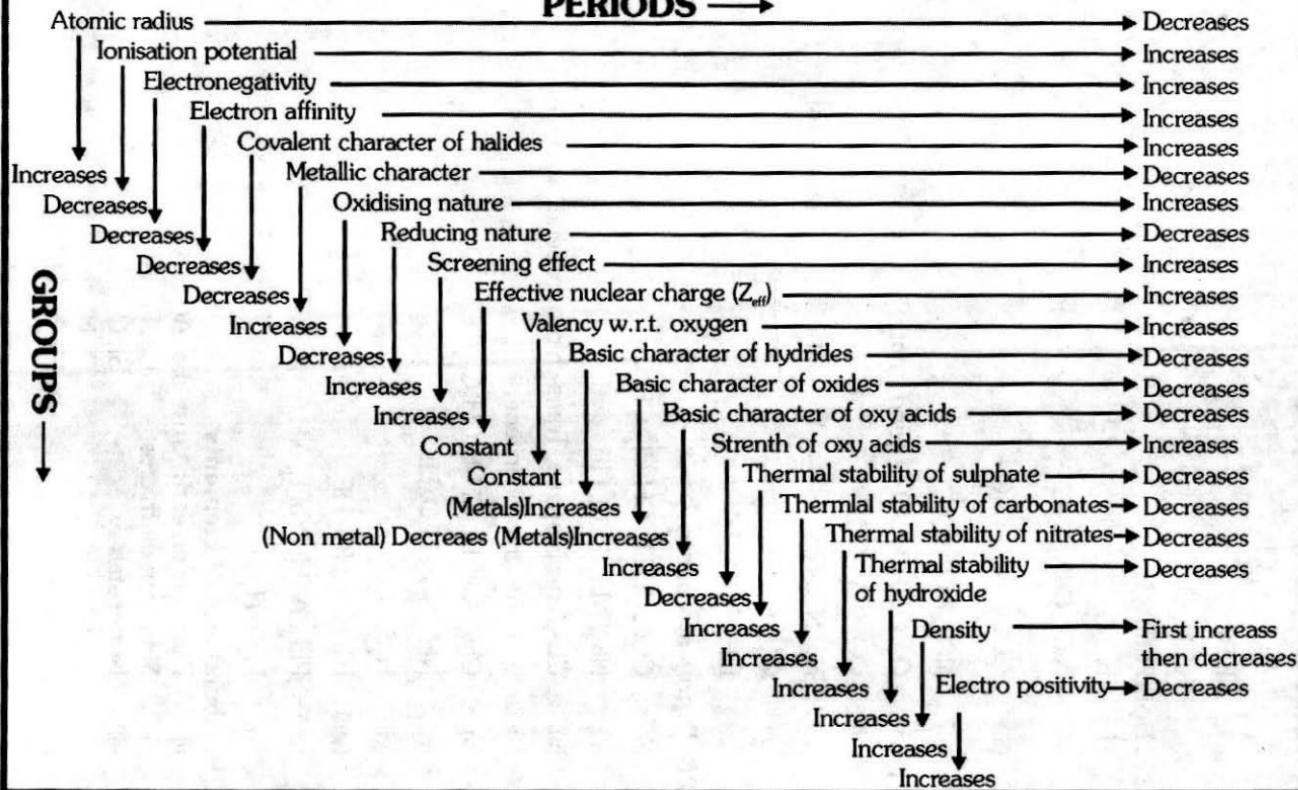


GENERAL TENDENCY OF DIFFERENT PROPERTIES IN THE PERIOD AND GROUPS

PERIODS →



PERIODIC TABLE

Arrangement of known element in horizontal rows and in vertical column in such a way that elements of similar properties are grouped together in one vertical column.

Development of periodic table :

(i) Prout concept:

All element made up of H-atom.

At. wt of an element : $n \times [\text{At wt of H}]$

Drawback : Could not explain fractional atomic mass.

(ii) Doberinier law of triads:

Triads : The atomic mass of middle element is the avg. of 1st & 3rd element.

$$\text{Li}^7 \qquad \frac{7+39}{2} = \frac{46}{2} = 23$$

Na^{23}

K^{39}

Triads : (Li, Na, K) (Be, Mg, Ca) (Ca, Sr, Ba) (K, Rb, Cs)
(P, As, Sb) (S, Se, Te) (Cl, Br, I)

Drawback : Not applicable for all element.

(iii) Newland law of octave:

Base : Increasing order of atomic mass.

Law : Properties of 1st and 8th elements are almost similar

							H
Li	Be	B	C	N	O	F	
Na	Ma	Al	Si	P	S	Cl	
K	Ca						

Chemistry Handbook**Drawback:**

- (i) Applicable only upto Ca.
- (ii) Discovery of inert gas gives death blow.

(iv) Lother meyer:

Curve between atomic mass and atomic volume.

Advantage : Elements of similar properties finds similar position e.g. alkali metals finds top position on curve alkaline earth metals on descending position, halogen are on ascending position.

(v) Mendeleef Periodic Law : Physical & chemical properties of elements are the periodic function of atomic mass.

Characteristics: Atomic mass = equivalent mass × valency

- (i) 8 group (I to VIII)
- (ii) I to VII group divides into A & B
- (iii) A sub group - Normal element
- (iv) B sub group & VIII – Transition element

Advantage:

- (i) Study of element became easy.
- (ii) Prediction of elements : Four elements named EKA.

EKA Boron → Scandium

EKA Al → Gallium

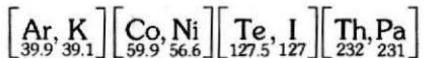
EKA Si → Germanium

EKA Mn → Technitium

- (iii) Correction of doubtful masses : Atomic mass of three elements (U, Be, In, Au, Pt) were corrected.

Drawback :

- (i) Position of hydrogen : Not fixed can be placed in IA & VIIA
- (ii) Position of Isotopes.
- (iii) **Anomalous pair** : Where increasing order of atomic mass not considered.



- (iv) Similar property elements find position in different group.
 - (v) Different property elements find position in same group.
 - (vi) Couldnot explain why the property of element repeated after a regular interval.
- (vi) Moseley Base** : Changed from atomic mass to atomic number.

Characteristics : (group zero) of inert gas included in the periodic table.

Advantage:

$$\sqrt{Y} = a(z - b) \quad a, b, = \underline{\text{constants}}$$

- (i) Position of isotopes resolved
- (ii) Short coming of anomalous pair resolved.

Drawbacks:

- (i) Position of hydrogen.
- (ii) Problem of periodic function. couldnot be solved.

Long form of periodic table

(Given by Bohr-Bury & Rang-Werner)

- Based on electronic configuration of outermost shell.

Achievement : Electronic configuration of outermost shell of elements repeats at regular interval i.e. why property repeats.

Characteristics : Having 18 group & 7 periods.

Chemistry Handbook**Description of periods:**

Period	n	Sub shell	No. of elements	Element	Name of Period
1.	1	1s	2	${}_1\text{H}$, ${}_2\text{He}$	Shortest
2.	2	2s, 2p	8	${}_3\text{Li}$ – ${}_{10}\text{Ne}$	Short
3.	3	3s, 3p	8	${}_{11}\text{Na}$ – ${}_{18}\text{Ar}$	Short
4.	4	4s, 3d, 4p	18	${}_{19}\text{K}$ – ${}_{36}\text{Kr}$	Long
5.	5	5s, 4d, 5p	18	${}_{37}\text{Rb}$ – ${}_{54}\text{Xe}$	Long
6.	6	6s, 4f, 5d, 6p	32	${}_{55}\text{Cs}$ – ${}_{86}\text{Rn}$	Longest
7.	7	7s, 5f, 6d,	26	${}_{87}\text{Fr}$ – ${}_{112}\text{Uub}$	Incomplete

IUPAC Nomenclature:

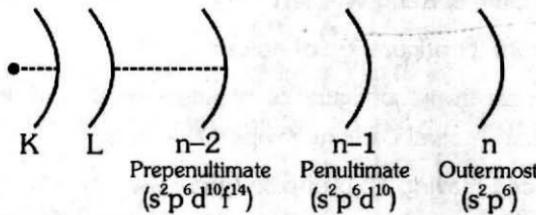
- (a) IUPAC gave names to elements above atomic No. 100 as follows –

0	1	2	3	4	5	6	7	8	9
nil	un	bi	tri	quad	pent	hex	sept	oct	enn

- (b) In all the elements suffix is – ium.

STUDY OF LONG FORM OF PERIODIC TABLE**Classification of elements:**

- (A) Bohr classification :** Based on electronic configuration.



Classify element into four type

(I) Noble gas:

- (a) Element in which outermost/ultimate shell is completely filled.
- (b) General configuration - ns^2np^6
- (c) Present in '0' group & from 1st to 6th period.
- (d) Total element 6(He, Ne, Ar, Kr, Xe, Rn)

(II) Normal or representative element

- (a) Element in which outermost/ ultimate shell is incomplete
- (b) General configuration $ns^{1-2} np^{0-5}$
- (c) Element of 'A' subgroup of mendeleef & from 1st, 2nd and 13th to 17th group in the long form of periodic table.

(III) Transition elements:

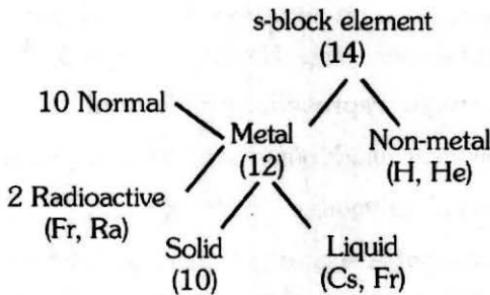
- (a) Element in which ultimate as well as penultimate shell are incomplete either in ground state as well as in ionic state.
- (b) 'B' subgroups & VIII group of Mendeleef & from 3rd to 11th group of long form of periodic table belongs to transition element.
- (c) According to this concept Zn, Cd, Hg, Uub are not transitional element.
- (d) General electronic configuration = $(n-1)s^2p^6\ d^{1-10}\ ns^{1-2}$

Inner transition elements:

- (a) Element in which ultimate (n), penultimate (n-1) & prepenultimate (n-2) all the three shells are incomplete.
- (b) Elements of IIB (except La, Ac) are known as. Inner transition element.
- (c) Total elements (28).

(B) Classification based on last electron entry :**(I) s-block elements :** last electron enters in s-subshell.

- Lies in two group 1st /IA and 2nd /IIA & period from 1st to 7th.
- General formula ns^{1-2} .

**(II) p-block elements :** in which last electron enters in p-subshell.

- Electronic configuration - $ns^2 np^{1-6}$
- IIIA to 'O' group or 13th to 18th group & from period 2nd to 6th.
- Total element - 30
- In this block metal, non-metal & metalloid are present.

(III) d-block elements in which last electron enters in d-subshell

- lies in between 3rd to 12th group.
- Period 4th to 7th.
- General configuration - $(n-1)d^{1-10} ns^2$

(IV) f-block elements last electron enters in f-subshell.

- lies in IIIB/3rd group & period 6th to 7th period.
- General configuration - $(n-2)f^{1-14} (n-1)d^{0-1}, ns^2$
- Total element 28

14 - Lanthanoids - found rarely on earth

14 - Actinoides - All are radioactive

Determination of period, block and group of an element

Period number : Maximum principal quantum number in the electronic configuration of an element denotes period number.

Block number : Can be decided by last e^- entrance.

Last e^- enters in

s-subshell - s-block

p-subshell - p-block

d-subshell - d-block

f-subshell - f-block

Group number:

(A) **s-block element :**

Group number = Number of electron in ns subshell.

(B) **p-block element:**

Group number = Number of electron in np subshell + 10

(C) **d-block element :**

Group No = number of electron in $(n-1)$ d sub shell + ns_{e^-} .

(D) **f-block element :** Group no. = IIB/3rd

Que. Predict the period, block & group number of element having atomic number 17.

$$17 = \underbrace{1s^2}_{n=2} \underbrace{2s^2}_{n=1} \underbrace{2p^6}_{n} \underbrace{3s^2}_{n} \underbrace{3p^5}_{n}$$

Period = 3rd; block = p ; group number = 12 + np_e

$$\therefore 12 + 5 = 17$$

Chemistry HandBook

Periodicity :

- ** Regular gradation in properties from top to bottom in a group and from left to right in a period.
 - ** **Cause of periodicity :** Due to repetition of same outermost shell configuration coming at regular intervals.

Periodic properties :

There are two type of periodic properties :

- (I) **Atomic properties** : Properties shown by individual atom. i.e. valency, I.P., E.A., E.N. and atomic radius.

(II) **Molecular property** : Properties shown by molecule i.e. density. M.P. & B.P.

(I) Atomic properties :

Valency : Combining capacity of an atom.

Two concept :

- (a) Old concept** (i) w.r.t. 'H' & 'Cl'
(ii) w.r.t. 'O'

- w.r.t. H & Cl valency of an element in a period initially increase from 1 to 4 & then decrease to 1.
 - w.r.t. 'O' along the period increases from 1 to 7.

- (b) New concept** (electronic concept) : The number of electrons required to gain or donate to achieve the nearest inert gas configuration.

For example : $\text{Na} = 1s^2, 2s^2 2p^6, 3s^1 \rightarrow$ one electron required to donate
 i.e. valency = 1

$\text{Cl} = 1s^2.2s^22p^63s^23p^5 \rightarrow$ One electron required to gain
i.e. valency = 1

Valency in a group remains same.

(II) Screening effect / Shielding effect (σ) :

Repulsive force created by inner electron on a last electron is known as screening effect. In single electron system σ is absent.

Slater : Rule of calculation of σ

- (a) ns, np e⁻ = 0.35
- (b) (n-1) s, p = 0.85, (n-1) d & f \rightarrow 1
- (c) (n-2) s, p, d, f = 1.0 \rightarrow After (n-1) every shell will be shielded by factor of 1
- (d) (n-3) & all innershell = 1.0

Calculation of σ

$[(\text{Number of electron in } n^{\text{th}} \text{ shell} - 1) \times 0.35 + \text{number of electron in } (n-1) \text{ shell} \times 0.85 + \text{number of electron in } (n-2) \text{ shell} & \text{ all inner shell} \times 1]$

Variation σ , along the period & down the group increases.

Order of σ s > p > d > f.

(III) Effective nuclear charge (Z_{eff})

Net nuclear attraction force exert by nuclei on a valence electron is known as Z_{eff}.

$$\boxed{Z_{\text{eff}} = Z - \sigma}$$

For single e⁻ species $\boxed{\sigma=0}$

$$\boxed{Z_{\text{eff}} = Z}$$

Variation:**(a) Along the period :****(i) Normal element :**

Z increases by 1

σ increases by 0.35

Z_{eff} increases by 0.65

(ii) d-block :

Z increases by 1

 σ increases by 0.85Z_{eff} increases by 0.15

(b) Down the group : Remains constant.
(IV) Atomic radii : Average distance between nucleus & valency electron cloud.

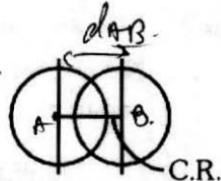
Accurate value of atomic radii cannot be measured due to

- (i) Isolation of atom is quite difficult .
- (ii) No. definite boundary of atom.

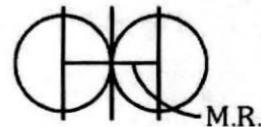
Type of Radii

- (a) Covalent radii (C.R.)
- (b) Metallic radii (M.R.)
- (c) Vanderwaal radii (VWR)
- (d) Ionic radii (I.R.) { Cationic radius }
Anionic radius }

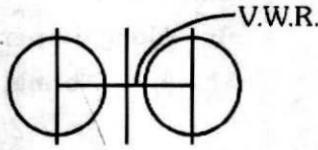
- ~~da - b = r_A + r_B~~
~~-(0.69) D_r~~ $D_r \rightarrow$ diff. in electro negativity.
- (a) Covalent radii :** Half of the internuclear distance when two homo atom bonded together with single bond.



- (b) Metallic radii :** Also called as crystal radii. Half of the inter nuclear distance when two adjacent atom (metal) bonded together with metallic bond.



- (c) Vanderwaal radii :** Half of the internuclear distance between two non-bonded atom of a inert gas.



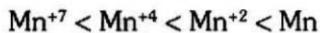
Vanderwaal radii is almost double of a covalent radii

$$VWR = 2 \times C.R.$$

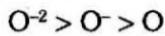
(d) Ionic radii :

(a) **Cationic radii :** Cation is always smaller than its parent atom due to

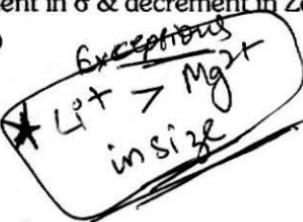
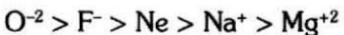
- (i) either outermost shell is removed.
- (ii) increased Z_{eff} to remaining electron.



(b) **Anionic radii :** Anion is always more than its parent atom due to increment in σ & decrement in Z_{eff} .

**Isoelectronic species :**

Anion > Neutral > Cation

**Variation :**

- (a) Along the period: Radius decreases.
- (b) Down the group : Radius increases.

Imp. In each period max. measured Atomic radii – Inert gas

In each period max. measured covalent radii - Alkali metal

In **d-block** along the period, Initially atomic size decreases then constant & then increases due to increment in σ .

Except : $B < \underset{\substack{\downarrow \\ \text{due to transition contraction}}}{\text{Al}} \approx \underset{\substack{\downarrow \\ \text{due to lanthanoid contraction}}}{\text{Ga}} < \text{In} \geq \underset{\substack{\downarrow \\ \text{due to lanthanide contraction}}}{\text{Tl}}$

Size of 4d \approx size of 5d due to lanthanide contraction.

Factors affecting atomic size

(i) Number of shells \propto Atomic size

$$(ii) Z_{\text{eff}} \propto \frac{1}{\text{atomic size}}$$

$$(iii) \text{Bond order} \propto \frac{1}{\text{atomic size}}$$

$$(iv) \text{Magnitude of +ve charge} \propto \frac{1}{\text{atomic size}}$$

$$(v) \text{Magnitude of -ve charge} \propto \text{atomic size}$$

IONISATION POTENTIAL

- Sufficient amount of energy required to remove most loosely bonded outermost shell electron from an isolated gaseous atom.
- $M_{(g)} + E \longrightarrow M^+ + e^-$
- Property of metal.
- Tendency to form cation.
- Always an endothermic process.
- **Successive I.P. :**

$IP_3 > IP_2 > IP_1$, due to increment in Z_{eff} .

Factors affecting I.P.

(i) I.P. \propto Z_{eff}

$$(ii) \text{I.P.} \propto \frac{1}{\text{Atomic size}}$$

(iii) I.P. \propto Magnitude of +ive charge

$$(iv) \text{I.P.} \propto \frac{1}{\text{Magnitude of -ive charge}}$$

- (v) Stability of Half-filled & fully filled orbital \rightarrow Half filled of p^3, d^5, f^7 or fully filled $s^2 p^6, d^{10}, f^{14}$ are more stable i.e. why more amt. of energy is required to remove electron so I.P. is more.

For ex. I.P. of 'N' $>$ I.P. of 'O'

Inert gas has maximum I.P. in respective period.

- (vi) **Penetration power :** $s > p > d > f$

IP of Mg $>$ IP of Al

IP of Be $>$ IP of B

Periodicity :-

- (i) Along the period I.P. generally increases.

Except : IIA $>$ IIIA, VA $>$ VIA

- (ii) Along the group I.P. generally decreases.

Except : Last two element due to Lanthanoid contraction.

Application of I.P. :

$$(i) \text{ Metallic character} \propto \frac{1}{\text{I.P.}}$$

$$(ii) \text{ Reactivity of metal} \propto \frac{1}{\text{I.P.}}$$

$$(iii) \text{ Basic character} \propto \frac{1}{\text{I.P.}}$$

- (iv) **Number of valence electron :** Number of valence electron can be predicted by counting lower value of successive I.P.

Number of valence electron = Number of lower I.P. value.

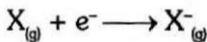
Chemistry Handbook

(v) Stability of oxidation state:

- (a) If $\Delta IP \leq 11$ eV then higher oxidation state is stable.
- (b) If $\Delta IP \geq 16$ eV then lower oxidation state is stable.

Electron Affinity/(Electron gain enthalpy)($\Delta eg.H$)

- Amt. of energy released or absorb when an electron is added to neutral gaseous atom.



EA_1 = exothermic generally (+ve E.A.)

EA_2 = endothermic

$$\begin{aligned} +\text{ve E.A.} &= -\Delta eg H \\ -\text{ve E.A.} &= +\Delta eg H \end{aligned}$$

- Inert gas has +ve value of $\Delta eg H$. due to stable configuration.
- Formation of polynegative ion is always an endothermic.

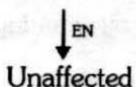
Factors:

(i) size $\propto \frac{1}{E.A.}$

(ii) $Z_{eff} \propto E.A.$

- (iii) **Stable configuration:** Be, N & inert gas have a very low value of EA due to stable configuration.

Max. \xleftarrow{IP} Stable configuration \xrightarrow{EA} min

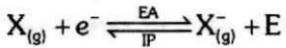


Variation :

- (a) - Along the period size \downarrow EA \uparrow
 - Along the period ΔegH becomes more -ve.
 - In each period halogen has a maximum E.A. due to more Zeff.
- (b) Down the group size \uparrow EA \downarrow

Exception : EA of 2nd period < EA of 3rd period.

Imp. : Max. E.A. \rightarrow Cl



$$\boxed{\text{EA of X} = \text{IP of } \text{X}^-}$$

Electronegativity

- Tendency of a bonded atom to attract shared pair of electron towards itself.
- Unit less property
- No energy released or absorbed

Factors :

- (i) EN \propto Zeff
- (ii) EN $\propto \frac{1}{\text{Atomic size}}$
- (iii) % s-character \propto EN
 $\text{sp} > \text{sp}^2 > \text{sp}^3$

Periodicity : Along the period Zeff \uparrow EN \uparrow

Down the group atomic size \uparrow EN \downarrow

- Max. EN – F
- Min. EN – Cs
- Inert gas has zero value of EN

Exception : EN Scale Zn < Cd < Hg

Chemistry HandBook

According to Mulliken scale :-

$$X_m = \frac{IP + EA}{2}$$

$$2X_m - IP - EA = 0$$

Relation between X_m & X_p :-

$$X_p = \frac{X_m}{2.8}$$

Application of electronegativity

(i) Nature of element

$$EN \propto \text{Non-metallic nature}$$

$$EN \propto \frac{1}{\text{Metallic nature}}$$

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

$$d_{A-B} = r_A + r_B - 0.09(\Delta EN)$$

Schoemaker & Stevenson law

(iii) Bond strength $\propto \Delta EN$

(iv) Bond energy $\propto \Delta EN$

(v) Acidic character of hydride in period (left to right) $\propto EN$

(vi) Nature of oxide

$$\text{Basic nature} \propto EN$$

$$\text{Acidic nature} \propto \frac{1}{EN}$$

(vii) % ionic character $\propto \Delta EN$

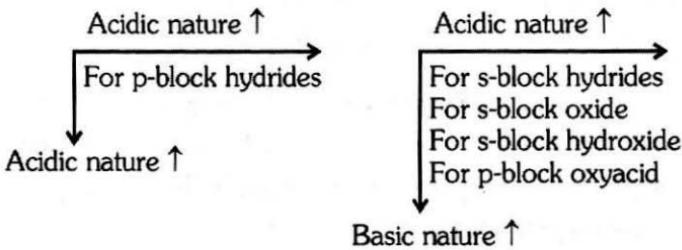
$$\% \text{ I.C.} = 16(\Delta EN) + 3.5(\Delta EN)^2$$

(viii) Acidic strength of oxy acid \propto EN of central atom.

(ix) Lewis base strength $\propto \frac{1}{EN}$

(x) Bond polarity $\propto \Delta EN$

In short :



CHEMICAL BONDING

Introduction : Force of attraction exist between various atom to hold them in a molecule.

Reason for chemical bonding : To attain the maximum stability (inert gas configuration) & minimum energy state.

Condition for chemical bonding:

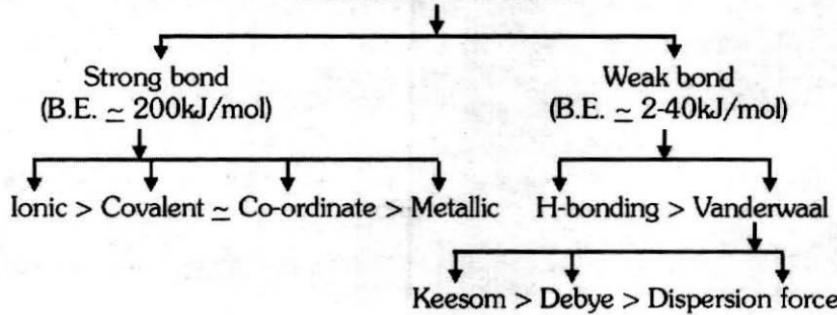
- (a) Force of attraction > Force of repulsion
- (b) Potential energy should be minimum

Lewis octet rule : Every atom try to attain $8e^-$ or nearest inert gas configuration by donating, by gaining or by sharing the electron.

Exception of lewis law :

1. **Electron deficient molecule :** Compound in which central atom has less than $8e^-$ in its valence shell.
For example BeI_2 , BH_3 , AlCl_3 , BF_3 , BCl_3 , BBr_3 , BeF_2 , BeCl_2 etc.
2. **Electron rich compound :** Compound in which central atom has more than $8e^-$ in the outermost shell.
For example IF_7 , SF_6 , PCl_5 , XeF_6 etc.
3. **Odd electron molecule :** The compound in which central atom has odd number of electron in their valence shell. e.g. NO , ClO_2 , NO_2 .
4. H, Li, never obeyed octet law.

Classification of bonds



Ionic bond :

- (a) Bond between cation & anion.
- (b) Bond between metal & non-metal.

Except : LiCl, MgCl₂, AlCl₃, BeO etc.

- (c) $\Delta EN > 1.7$

Condition for ionic bond formation :

- (a) Size of metal should be large
I.P. should be low
- (b) Size of non-metal should be small.
E.A. should be more.
- (c) Lattice energy should be high.

Energy involved in ionic bond formation (Born haber cycle)

$$\begin{aligned}\Delta H &= (\text{S.E.} + \text{I.E.} + D/2) - (\text{EA} + U) \\ &= (\text{Total energy absorbed}) - (\text{Total energy released})\end{aligned}$$

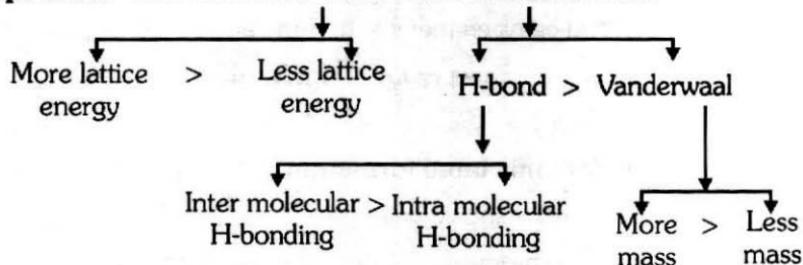
For bond formation $\Delta H = -\text{ive}$ (exothermic process)

Properties of ionic compound :

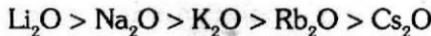
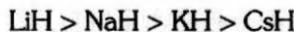
1. **Physical state :** Due to strong electrostatic force of attraction between cation & anion these compounds are hard, crystalline & brittle.
2. **Isomorphism :** Two compounds are said to isomorphs if they have similar number of electron i.e. similar configuration of cation & anion.
e.g. [NaF, MgO] [CaCl₂, K₂S]

Melting point & boiling point : High M.P. & B.P. due to presence of strong electrostatic force between ions.

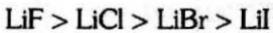
- Covalent solid like SiO₂, B₄C, have more m.p.t. due to 3-D giant network.
- Ionic solid like NaCl, Al₂O₃, have more m.p.t. due to high lattice energy.
- Molecular solid like CO₂ have least m.p.t. due to presence of weak vanderwaal force.

M.P. & B.P.**Imp. order** Covalent solid > Ionic solid > Molecular solid

If molecular mass of two covalent compound are same then ΔEN will be consider.

Imp. order

Among metal halide, flouride has maximum m.p.t.



Solubility : Ionic compounds are soluble in polar solvent like water.

Factor affecting solubility :

(i) Dielectric constant \propto solubility

(ii) Lattice energy $\propto \frac{1}{\text{solubility}}$

(iii) Hydration energy \propto solubility

For any compound to be soluble in water

Hydration energy > Lattice energy

Imp. order :

No compound is 100% ionic. Every compound contain some covalent character due to polarization

Polarization (covalent character in ionic compound)

Due to strong electrostatic force of attraction between cation & anion electron density of anion becomes more in between two ions & covalent character is developed.

$$\text{Covalent character} \propto \text{Polarization} \propto Z_{\text{eff}} \text{ of cation}$$

Polarization power (Ionic potential) : capacity of cation to polarize anion represented by (ϕ)

$$\phi = \frac{\text{Charge on cation}}{\text{Size of cation}}$$

Polarisability : Tendency of an anion to get polarized by cation.

Factor affecting polarization (Fajan's rule)

- (i) Charge on cation/anion \propto polarization \propto covalent character
- (ii) Size of cation $\propto \frac{1}{\text{Polarization}} \propto \frac{1}{\text{Covalent character}}$
- (iii) Size of anion \propto polarization \propto covalent character
- (iv) **Pseudo inert gas configuration :** Cation having pseudo inert gas configuration (i.e. 18 electron in outermost shell have more polarization power due to high Z_{eff}).

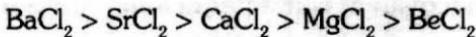
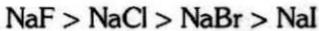


[due to poor Shielding effect of $d\ e^-$ in Cu^{+1}]

Some important facts :

- (i) Sulphides are less soluble in water than oxides of metal.
- (ii) Li salt are soluble in organic solvents.

Polarization increases Covalent character increases

M.P. decreases →

Covalent bond : Bond between two highly electronegative element

- Mutual sharing of electron takes place.

Orbital concept of covalent bond :

- An orbital can accommodate at the most 2 electron with opposite spin.
- Only those orbital will participate in bond formation which have unpaired electron.
- Empty orbital accepts two electrons to complete the orbital.
- Pairing of electron is an essential condition of covalent bond.
- 3rd, 4th, 5th period elements due to presence of vacant d-orbital can expand their octet in the presence of highly electronegative element like F, Cl, O, N etc.
- PCl_5 , SF_6 , IF_7 is possible but NCl_5 , OF_6 , are not possible.
- PF_5 , PCl_5 are possible but PH_5 is not.
- An element which have even valency will always show even valency in excited state.
- An element which have odd valency will always show odd valency in excited state.
- PCl_4 , SF_3 , SF_5 are not possible but PCl_3 , PCl_5 , SF_2 , SF_4 & SF_6 are possible.

- ⇒ **Short coming :** Couldnot provide information regarding shape of molecule & strength of bonds.

Wave Mechanical model

Two Model :

- (i) Valence bond theory (VBT)
- (ii) Molecular orbital theory (MOT)

(1) **Valence bond theory :**

Given by Heitler & London Extended by Pauling & Slater.

Strength of bond \propto Extent of overlapping.

Extent of overlapping depends on two factor.

(i) **Nature of orbital:**

- (a) directional orbital : p, d & f (more extent of overlapping)
- (b) non-directional orbital : s (less extent of overlapping)

Order of overlapping $p - p > s - p > s - s$

Exception $1s - 1s > 2p - 2p$

Nature of overlapping :

- (a) Co-axial overlapping (Along the internuclear axis)
Extent of overlapping is maximum, σ -bond is formed.
- (b) Co-lateral overlapping : Side wise overlapping.
Extent of overlapping is minimum, π -bond is formed.
 π -bond is formed after σ -bond.

For maximum bond strength :-

- (i) Lower value of principal quantum number.
- (ii) σ is stronger than π (when value of n is same)
- (iii) Directional nature (when type of overlapping is same)

Limitation :

- (i) Does not define the shape of the molecule.

Hybridisation (Pauling & Slater)

- Imaginary concept
- Mixing of different shape and approximate equal energy atomic orbital to give new orbital of same shape.
- Hybrid orbital always forms σ -bond. (Except - Benzyne)
- In hybridization all type of orbitals participate.
(Vacant, Half-filled or Fully filled)
- Number of hybrid orbital forms will be equal to the number of atomic orbitals taking part in hybridization.

Valence shell electron pair repulsion theory (VSEPR) :

- Given by Glessipie & Nyhom
- Defines the shape of molecule

Case-I Molecules in which central atom does not have any lone pair are called symmetric structure & their shape will be according to their hybridization.

Case-II Molecules in which central atom has lone pair are known as asymmetric structure. In that case lone pair should be kept at that position where lone pair exerts minimum repulsive force.

Order of repulsion : L.P. – L.P. > L.P. – B.P. > B.P. – B.P.

: M.B. – M.B. > M.B. – S.B. > S.B. – S.B.

TYPE OF HYBRIDIZATION & POSSIBLE STRUCTURE

Type of Hybridization	No. of B.P.	No. of L.P.	Shape	Examples
1. sp-hybridization	2	-	Linear	BeF_2 , CO_2 , CS_2 , BeCl_2
2. (a) sp^2 -hybridization	3	-	Trigonal planar	BF_3 , AlCl_3 , BeF_3^-
(b) sp^2 -hybridization	2	1	V-shape, Angular	NO_2^- , SO_2 , O_3
3. (a) sp^3 -hybridization	4	0	Tetrahedral	CH_4 , CCl_4 , PCl_4^+ , ClO_4^- , NH_4^+ , BF_4^- , SO_4^{2-} , AlCl_4^-
(b) sp^3 -hybridization	3	1	Pyramidal	NH_3 , PF_3 , ClO_3^- , H_3O^+ , PCl_3 , XeO_3 , $\text{N}(\text{CH}_3)_3$, CH_3^-
(c) sp^3 -hybridization	2	2	V-shape, Angular	H_2O , H_2S , NH_2^- , OF_2 , Cl_2O , SF_2 , I_3^+
4. (a) sp^3d -hybridization	5	-	Trigonal bipyramidal	PCl_5 , SOF_4 , AsF_5
(b) sp^3d -hybridization	4	1	See-Saw, folded square distorted tetrahedral	SF_4 , PF_4^- , AsF_4^- , SbF_4^- , XeO_2F_2
(c) sp^3d -hybridization	3	2	almost T-shape	ClF_3 , ICl_3
(d) sp^3d -hybridization	2	3	Linear	I_3^- , Br_3^- , ICl_2^- , ClF_2^- , XeF_2
5. (a) sp^3d^2 -hybridization	6	-	Square bipyramidal/ octahedral	PCl_6^- , SF_6

(b) sp^3d^2 -hybridization	5	1	Square pyramidal/ distorted octahedral	$XeOF_4$, ClF_5 , SF_5^- XeF_5^+
(c) sp^3d^2 -hybridization	4	2	Square planar	XeF_4
6. (a) sp^3d^3 -hybridization	7	-	Pentagonal bipyramidal	IF_7
(b) sp^3d^3 -hybridization	6	1	Pentagonal pyramidal/ distorted octahedral	XeF_6
(c) sp^3d^3 -hybridization	5	2	Pentagonal planar	XeF_5^-

Co-ordinate bond

This type of bond is formed by one side sharing of pair of electron between atoms. Electron pair of one atom is shared between two atom.

- Atom which provide lone pair for sharing is called donor.
- Atom which accepts electron pair is called acceptor.
- Shown by ' \rightarrow ' & direction is from donor to acceptor.

Necessary condition :

- Acceptor should have vacant orbital.
- Donor should have complete octet.

Example :

- (i) Protonation : $H_2O \rightarrow H_3O^+$, $NH_3 \rightarrow NH_4^+$, $N_2H_4 \rightarrow N_2H_5^+$
- (ii) Polymerization : $AlCl_3 \rightarrow Al_2Cl_6$, $BeCl_2 \rightarrow (BeCl_2)_n$

During the formation of coordinate bond, structure & shape of the molecule changed.

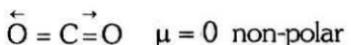
Dipole moment (μ)

- Measure the polarity in molecule $(\mu) = q \times d$
- Unit debye = esu-cm
- 1 Debye = 10^{-18} esu-cm.

Homonuclear diatomic $H_2, N_2, O_2, F_2 (\mu = 0)$ → non-polar

Heteronuclear diatomic ($\mu \propto \Delta EN$) $HF > HCl > HBr > HI$

Polyatomic molecule resultant dipole moment is a vector addition of bond moment of various bond.



Imp. order (a) $NH_3 > NI_3 > NBr_3 > NCl_3 > NF_3$

(b) $NH_3 > SbH_3 > AsH_3 > PH_3, \quad (c) HF > HCl > HBr > HI$

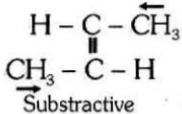
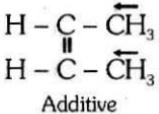
(d) $H_2O > H_2S, \quad (e) CH_3Cl > CH_3F > CH_3Br > CH_3I$

(f) $CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4 = CH_4$

Application :

- (i) Predict shape & polarity of molecule
- If central atom contain lone pair than $\mu \neq 0$ then molecule will be polar & unsymmetrical shape.
- If central atom surrounded with all identical atom then $\mu = 0$, molecule non-polar.
- (ii) Distinguish between cis & trans form

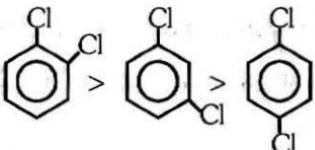
$$\mu_{cis} > \mu_{trans}$$



$$\mu \neq 0$$

$$\mu = 0$$

- (iii) To find out dipole moment of a substituent of benzene ring.



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

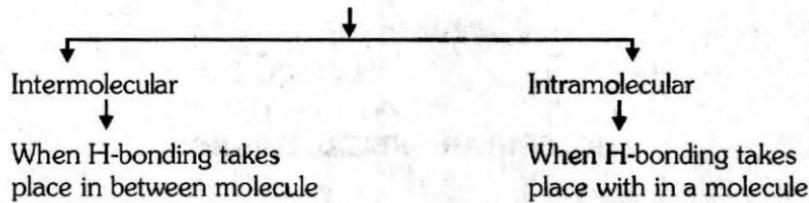
H-bonding

- Given by Latimer & Rodebush.
- Electrostatic force of attraction between H & highly electronegative atom.
- This is intermolecular force. i.e. why exist only in covalent molecule.
- Also known as dipole-dipole attraction.

Necessary conditions :

- (i) Hydrogen should be covalently bonded with highly electronegative element.
- (ii) Highly electronegative element should have EN ≥ 3 .
- (iii) Hydrogen bonding is possible only in those molecule in which H is directly attached with F,O,N,

Strength of H-bond \propto EN of highly electronegative element

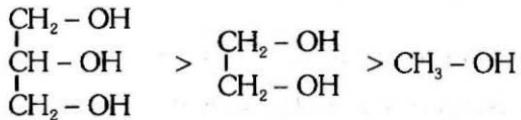
Type of hydrogen bonding

Strength of intermolecular H-bond > Intramolecular bond.

Imp. Intramolecular H-bonding taking place only in ortho-derivative of aromatic compound.

Application :

- (i) **Physical state :** H_2O is liquid H_2S gas.
 HF is liquid HCl gas.
- (ii) **M.P. & B.P. :** Due to presence of H-bonding M.P. & B.P. increases
 $\text{M.P. of alcohol} > \text{M.P. of thiol}$
- (iii) Volatility : M.P. & B.P. \uparrow volatility \downarrow
- (iv) Viscosity & Surface tension :
 $\text{Viscosity} \propto \text{Hydrogen bonding}$



- (v) **Solubility in H_2O :** Any organic compound which get dissolve in H_2O is due to H-bonding

Extent of solubility \propto H-bonding

- (vi) **Association of molecule :**

KHF_2 is possible but not KHCl_2 , $[\text{K}^+ \text{F}^- \cdots \cdots \text{H}-\text{F}]$
 ↓
 (H.Bond)

MOLECULAR ORBITAL THEORY

- Given to explain
 - Paramagnetic nature of O_2 molecule.
 - Existence of species like $\text{H}_2^+ \cdot \text{H}_2^-$ & species having fractional bond order.

Main point of M.O.T

- (a) Atomic orbital represented by ψ (wave function) participate to form molecular orbital.
- (b) Z-axis is considered as main axis so p_z combination form σ molecular orbital.
- (c) The number of orbital participating in combination must have almost same energy & same symmetry. Will produce same number of orbital.
- (d) Two type of molecular orbital formed.
 - (i) Bonding molecular
 - (ii) Anti-bonding molecular
- (e) Number of atomic orbital participate =

$$\frac{1}{2} \text{ number of B.M.O.} + \frac{1}{2} \text{ number of ABMO.}$$

- (f) BMO is formed by addition of two wave function ($\psi_A + \psi_B$) when they are in same phase, represented by σ, π
 - (g) ABMO is formed by subtraction of two wave function ($\psi_A - \psi_B$) when they are in opposite phase, represented by σ^*, π^* .
 - Energy of ABMO > Energy of A.O. > energy of BMO
- Imp. sequence order

for B_2, C_2, N_2 (Number of e^- 's ≤ 14) = $\sigma_{1s}, \sigma_{1s}^*, \sigma_{2s}, \sigma_{2s}^*$

$$\text{B.O. of } C_2 = \frac{8-4}{2} = 2 \quad (\pi_{2px} = \pi_{2py}), \sigma_{2pz}$$

(It contains two π bonds without σ bond
 \therefore last four e^- enters in π B.M.O.)

for O_2, F_2, Ne_2 (Number of e^- 's > 14) = $\sigma_{1s}, \sigma_{1s}^*, \sigma_{2s}, \sigma_{2s}^*, \sigma_{2px}$

$$(\pi_{2px} = \pi_{2py})$$

$$(\pi_{2px}^* = \pi_{2py}^*), \sigma_{2pz}^*$$

Significance of M.O.T. :

- (a) Concept of bond order :

$$\text{Bond order} = \frac{1}{2} [N_b - N_a]$$

N_a = number of antibonding \bar{e} 's

N_b = number of bonding \bar{e} 's

If $N_b > N_a$ B.O. = +ve molecule exist

$N_b < N_a$ B.O. = -ve molecule does not exist

- (b) Stability
- \propto
- B.O.
- \propto
- bond dissociation energy

$$(c) \text{B.O.} \propto \frac{1}{\text{Bond length}}$$

- Iso electronic species have same bond order & have same magnetic property.
- If species have fractional bond order it will always be paramagnetic.
- If in two species bond order is same the stability, will be decided by counting number of antibonding \bar{e} 's . If number of antibonding is more, than number of bonding \bar{e} 's then molecule will be unstable.

Bonding parameters**Imp. points :**

1. Bond length : Internuclear distance between two atom when they are bonded together.

Factor affecting bond length

- (i)
- ΔEN
- value

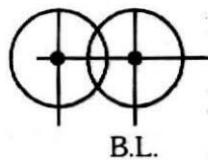
$$d_{A-B} = r_A + r_B - 0.09 (\Delta EN)$$

$\Delta EN \uparrow \quad B.L. \downarrow$



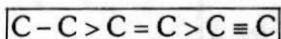
- (ii)
- Atomic size**

$$B.L. \propto \text{Atomic size}$$

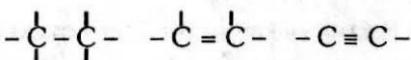
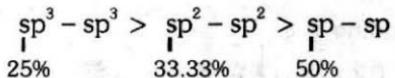


Chemistry Handbook

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



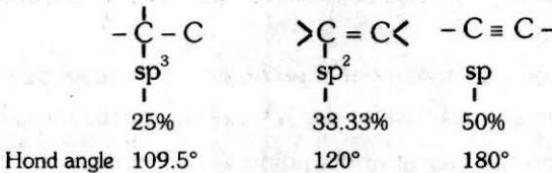
(iv) **Hybridisation :** $B.L. \propto \frac{1}{s\text{-character}}$



2. **Bond angle :** The angle between any two adjacent bond is known as bond angle.

Factor affecting bond angle

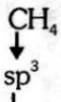
(a) **Hybridization :** On increasing % s-character bond angle also increases.



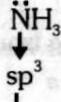
Case-I When hybridization is same, bonded atom are same but central atom & lone pair are different.

$$B.A. \propto \frac{1}{\text{Number of L.P.}}$$

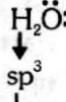
Example :



No L.P.



1 L.P.



2 L.P.

Case-II When hybridization is same, number of lone pair is same central atom is different & side atom are same then



$\ddot{\text{N}}\text{H}_3 > \ddot{\text{P}}\text{H}_3 > \ddot{\text{As}}\text{H}_3 > \ddot{\text{Sb}}\text{H}_3$

Example : Bond angle 107° 93° 91°

EN of central atom decrease
Bond angle decrease

$\text{H}_2\ddot{\text{O}}: > \text{H}_2\ddot{\text{S}}: > \text{H}_2\ddot{\text{Se}}: > \text{H}_2\ddot{\text{Te}}:$

Bond angle decrease

Case-III When hybridization is same, number of lone pair are same and central atom are same, but side atoms are different.

$$\text{B.A} \propto \frac{1}{\text{EN of side atom}}$$

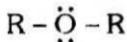


Note : Symmetrical mol. having no. l.p. and same hyb. B.A. are same.

- eg. (i) $\text{BF}_3 = \text{BCl}_3 = \text{BBr}_3 = \text{BI}_3$
 (ii) $\text{SO}_4^{2-} = \text{PO}_4^{3-} = \text{ClO}_4^-$

Imp. point :

In ethers oxygen has sp^3 hybridization having two L.P. but still bond angle is 110° because of larger size of alkyl group.



s-BLOCK ELEMENTS**Physical property of alkali metal & alkaline earth metal :**

1. Order of metallic or Ionic radii:

Cs > Rb > K > Ba > Sr > Ca > Na > Mg > Li > Be

2. Order of density :

Ist A Cs > Rb > Na > K > Li

IInd A Ba > Sr > Be > Mg > Ca

3. Order of MP & BP:

Ist A Li > Na > K > Rb > Cs

IInd A Be > Ca > Sr > Ba > Mg

4. Order of hydration in cation :

IA Li⁺ > Na⁺ > K⁺ > Rb⁺ > Cs⁺

IIA Be⁺² > Mg⁺² > Ca⁺² > Sr⁺² > Ba⁺²

5. Order of conductivity of cations in polar solvent

IA Cs⁺ > Rb⁺ > K⁺ > Na⁺ > Li⁺

IIA Ba⁺² > Sr⁺² > Ca⁺² > Mg⁺² > Be⁺²

6. Order of conductivity in non-polar solvent

IA Li⁺ > Na⁺ > K⁺ > Rb⁺ > Cs⁺

IIA Be⁺² > Mg⁺² > Ca⁺² > Sr⁺² > Ba⁺²

7. Colour of s-block metal in flame test

Li	Na	K	Rb	Cs
Crimson red	Golden yellow	Pale violet	Reddish violet	Sky blue

Be	Mg	Ca	Sr	Ba
X	X	Brick red	Crimson red	Apple green

Due to high IP

Chemical property of alkali metal & alkaline earth metal :

1. Reaction with air (N_2 & O_2)

All forms their normal oxide & nitrides.

Exception : Nitride of Na, K, Rb, Cs is not possible.

2. Reaction with O_2 & Excess of air

Li – normal oxide

Be – normal oxide

Na – peroxide

Mg – normal oxide

K – super oxide

Ca – peroxide

Rb – super oxide

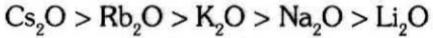
Sr – peroxide

Cs – super oxide

Ba – peroxide

3. Reaction with H_2O : All form their hydroxide & H_2 gas

Order of basic strength



Exception : Be does not react with H_2O :

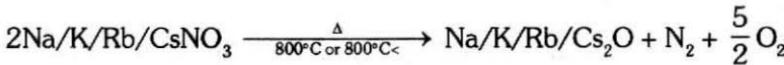
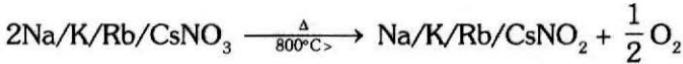
Order of reactivity with H_2O in IA and IIA group

$Cs > Rb > K > Na > Li$

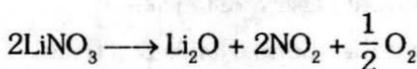
$Ba > Sr > Ca > Mg > Be$

4. CO_3^{2-} & SO_4^{2-} salt of Na, K, Rb and Cs only are not decomposed on heating due to large size and weak polarising power.

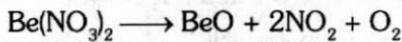
5. In nitrate salts



In other



and IIA nitrate



6. Types of hydride

Types of hydride

Ionic/salt like/saline
 * form ionic bond
 * gives H^- in H_2O
 eg. s, p-block metal
 BeH_2 and LiH are more covalent

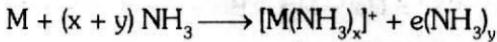
Covalent/molecular form covalent bond gives H^+ in H_2O
 p-block non-metal

Interstitial hydride
 do not form strong bond
 do not give H^+ and H^- in H_2O , d and f block metal

The higher oxides, peroxides and superoxides are strong oxidising agents. They react with water and dilute acids forming H_2O_2 and O_2 .

7. Sodium is obtained on large scale by Down's process.

8. The alkali metals dissolve in liquid ammonia without evolution of hydrogen. The colour of dilute solutions is blue. On heating colour changes to bronze. The colour is due to ammoniated electron.



These solutions are good conductors of electricity and have strong reducing properties. The solutions are paramagnetic in nature.

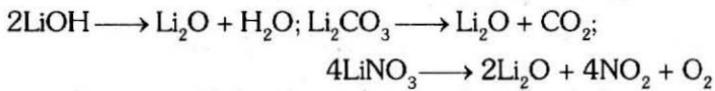
When dry ammonia is passed over hot metal, amides are formed.

9. Alkali metals have a very little tendency to form complexes. Lithium being small in size form certain complexes but this tendency decreases as the size increases.

10. Lithium shows abnormal properties due to its small size (atom and ion). Lithium ion on account of its small size exerts polarising effect on negative ions. Consequently, covalent character is developed in

Li-salts. Li has highest ionisation energy and electronegativity as compared to other alkali metals.

- (i) LiCl is more covalent than NaCl. LiCl is soluble in alcohol, pyridine, etc. Its melting point is lower than that of NaCl.
- (ii) LiOH, Li_2CO_3 , LiNO_3 behave differently than other alkali corresponding salts towards heating.



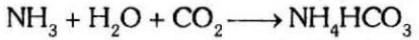
Hydroxides and carbonates of other alkali metals are stable. The nitrates of other metals decompose giving only oxygen.

- (iii) Lithium directly combines with nitrogen.



- (iv) LiHCO_3 is known only in solution but not in solid state.
- (v) Li_2SO_4 does not form double salt.
- (vi) LiF , Li_3PO_4 , $\text{Li}_2\text{C}_2\text{O}_4$, Li_2CO_3 are sparingly soluble in water.
- (vii) LiOH is weaker base in comparison to NaOH or KOH.
- (viii) Although Li has the highest ionisation potential, yet it is strongest reducing agent because of its high heat of hydration.

11. Table salt becomes wet in rainy season due to presence of impurities of MgCl_2 and CaCl_2 .
12. Sodium carbonate (washing soda), $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, is generally prepared by a process called ammonia-soda process or Slavay process.



Solvay process cannot be employed for the manufacture of K_2CO_3 because KHCO_3 is fairly soluble in water.

- 13.** Sodium hydroxide (caustic soda) is manufactured on a very large scale by the following processes :

Electrolytic process : The electrolysis of sodium chloride is carried out in an electrolytic cell. The following electrolytic cells are used :

(a) **Nelson cell :**

(b) **Castner-Kellner cell :**

- 14.** Sodium peroxide (oxone), Na_2O_2 , is formed by heating sodium at about 350°C in excess of air free from moisture . It is a pale yellow powder. It is used as an oxidising agent, for purification of air, for production of oxygen and for the preparation of H_2O_2 and benzoyl peroxide.

- 15.** Except Be, alkaline earth metals are easily tarnished in air as a layer of oxide is formed on their surface. The effect increases and barium in powdered form bursts into flame on exposure to air.

- 16.** Like alkali metals, alkaline earth metals react with acids and displace hydrogen.

However, Be dissolves in caustic/alkalies with liberation of H_2 .

- 17.** $\text{Be}(\text{OH})_2$ is amphoteric but rest are basic so is not alkaline earth metal.

- 18.** Alkaline earth metals directly combine with halogens, when heated with them. Be-halides are covalent. This is due to small size and high charge of Be^{2+} ion i.e., it has high polarising power. Halides of Be are known to have chains of $\text{---X}_2\text{BeX}_2\text{Be---}$. The halides of rest of the members are ionic. The halides are hygroscopic and readily form hydrates.

- 19.** Alkaline earth metals burn in nitrogen and form nitrides of the type, M_3N_2 . Be_3N_2 is volatile while rest are non-volatile being ionic crystalline solids . These are hydrolysed with water liberating NH_3 .

- 20.** With the exception of Be, other combine with carbon in an electric furnace to form carbides of the type, MC_2 . These are called acetylides as on hydrolysis evolve, C_2H_2 . Mg also forms Mg_2C_3 by heating, Mg_2C_3 on hydrolysis forms propyne. Beryllium oxide when heated with carbon forms Be_2C . This on hydrolysis gives methane.
- 21.** Like alkali metals, alkaline earth metals also dissolve in liquid ammonia to form coloured solutions. Dilute solutions are bright blue due to solvated ions.
- 22.** **Quick lime** (CaO) is obtained when limestone is heated at about $1000^{\circ}C$. On adding water, quick lime gives a hissing sound and forms calcium hydroxide, known as slaked lime. The paste of lime in water is called milk of lime while the filtered and clear solution is known as lime water. Chemically both are $Ca(OH)_2$.
- 23.** Quick lime is used for making caustic soda, bleaching powder, calcium carbide, mortar, cement, glass, dye stuffs and purification of sugar.
- Mortar :** It is a building material. It consists slaked lime and silica in the ratio of 1:3. The mixture made a paste with water. It is called mortar.
- 24.** Gypsum ($CaSO_4 \cdot 2H_2O$) found in nature, when heated, it first changes from monoclinic form to orthorhombic form without loss of water. At $120^{\circ}C$, it loses three-fourth of its water of crystallisation and forms hemihydrate ($CaSO_4 \cdot \frac{1}{2} H_2O$) known as plaster of Paris. It becomes anhydrous at $200^{\circ}C$ is known as dead burnt plaster and on strong heating it decomposes to give either calcium oxide and SO_3 or mixture of SO_2 and O_2 .

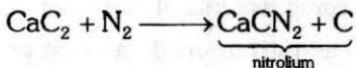
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- 25.** Plaster of Paris has the property of setting to a hard mass $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, slight expansion occurs during setting addition of alum to plaster of Paris makes the setting very hard. The mixture is known as **Keene cement**.

Plaster of Paris is used for setting broken or dislocated bones, castes for statues, toys and in dentistry.

When plaster of Paris is heated at 200°C , it forms anhydrous calcium sulphate which is known as dead plaster. It has no setting property.

- 26.** (a) Hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ is the main component of tooth enamel. Cavities are formed when acids decompose this enamel. This can be prevented by converting the hydroxyapatite to more resistant enamel-fluorapatite. $\text{Ca}_5(\text{PO}_4)_3\text{F}$.
- (b) Mg^{2+} and Ca^{2+} ions present in water are responsible for hardness of water.
- (c) CaC_2 is obtained by heating a mixture of CaO and carbon. It reacts with nitrogen forming nitrolium, used as a fertilizer.



- 27.** Cement is an important building material. The average composition of portland cement is : CaO 61.5%, SiO_2 22.5%, Al_2O_3 7.5%. Cement is a dirty greyish heavy powder containing calcium silicates and aluminates. Cement consists of :

Tricalcium silicate $3\text{CaO} \cdot \text{SiO}_2$

Dicalcium silicate $2\text{CaO} \cdot \text{SiO}_2$

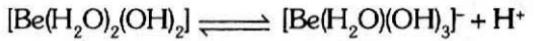
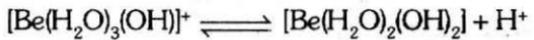
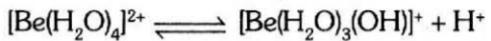
Tricalcium aluminate $3\text{CaO} \cdot \text{Al}_2\text{O}_3$

Tetracalcium alumino - ferrite $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$

For manufacture, limestone and clay are fused at 1400 - 1600°C in a rotary kiln. The product obtained is called clinker. It is mixed with 2–3% gypsum and powdered.

When cement is mixed with water, it sets to a hard mass, this is called setting. Setting is an exothermic process. During setting hydration occurs.

- 28.** Solutions of beryllium salts are acidic and dissolve appreciable quantities of $\text{Be}(\text{OH})_2$. In alkali solution $[\text{Be}(\text{OH})_4]^{2-}$ is formed.



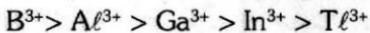
- 29.** BaSO_4 is used in medicine as a contrast medium for stomach and intestinal X-rays.

p-BLOCK ELEMENTS

GROUP 13 ELEMENTS

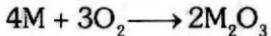
PHYSICAL PROPERTY

- Boron to Indium show +3 oxidation state in their compounds while thallium also show +1 oxidation state (due to inert pair effect) in their compounds. Relative stability of M^+ and M^{3+} ions may be given as :



CHEMICAL PROPERTIES

- Action of air :**



Reaction occurs at high temperature. With Al , a protective oxide layer is formed which makes it passive. Tl also forms Tl_2O . Ga and In are not affected by air.

- Action of water :**



Boron is not affected by water. It reacts with steam at red hot. Al decomposes cold water if it is not passive by oxide layer formation. Ga and In are not attacked by cold or hot water unless oxygen is present. Tl reacts with moist air to form $TlOH$.

- Action of nitrogen :** $2M + N_2 \longrightarrow 2MN$

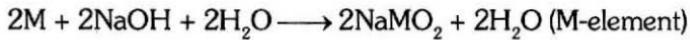
- Action of halogen :** $2M + 3X_2 \longrightarrow 2MX_3$

All the group 13 elements form trihalide except Tl . Tl form TlX . Tl reacts with I_2 and form TlI_3 ($Tl^+ I^-_3$).

- **Action of acids :** $2M + 6H^+ \longrightarrow 2M^{3+} + 3H_2$

Boron is not affected by non-oxidising acids like HCl and dilute H_2SO_4 while other elements dissolve to form trivalent salts.

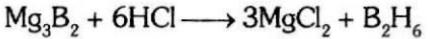
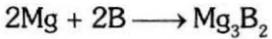
- **Action of alkalis :**



Only B, Al and Ga react with alkali.

- **Action of metals :**

Boron combines with metals on heating to form borides which are hard and refractory. Borides are decomposed by acids forming boranes.



The rest of the elements do not combine with metals. This shows that boron is a non-metal and rest of the elements are metal.

IMPORTANT COMPOUNDS OF GROUP 13 ELEMENTS

Boron is known to exist in two form (a) amorphous and (b) crystalline.

Amorphous boron is obtained by reduction of B_2O_3 with Na or K and Mg at high temperature in a covered crucible.

Crystalline form is obtained by the reduction of B_2O_3 with Al-powder. Crystalline boron is black and chemically inert in nature. It is very hard. Amorphous boron is brown and chemically active. Boron is used as a deoxidiser in the casting of copper and for making boron steel which are used as control rods in nuclear reactors.

Hydrides

- Boron forms a number of stable covalent hydrides called diboranes with general formula B_nH_{n+4} (called nido boranes) and B_nH_{n+6} (called arachno boranes, less stable).
- Aluminium forms a polymeric hydride called allane with general formula $(AlH_3)_n$. Ga forms Ga_2H_6 and In forms $(InH_3)_n$. Tl does not form hydrides.

Oxides and hydroxides

- The members of boron family form oxides and hydroxides of the general formula M_2O_3 and $M(OH)_3$ respectively.
- The acidic nature is represented as

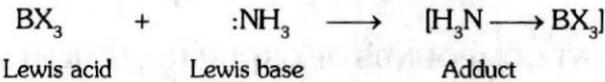
Oxides : $B_2O_3 > Al_2O_3 > Ga_2O_3 > In_2O_3 > Tl_2O_3$

Hydroxides : $B(OH)_3 > Al(OH)_3 > Ga(OH)_3 > In(OH)_3 > Tl(OH)_3$

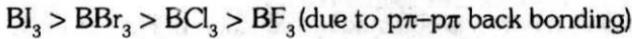
Nature : Acidic Amphoteric Amphoteric Basic Strongly basic

Halides :

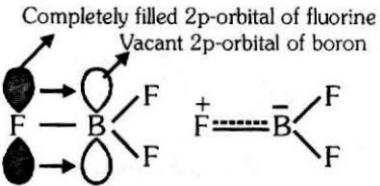
- BX_3 is electron deficient so behaves as a Lewis acid.



- Relative Lewis acid strength of boron halides are as follows :



In BF_3 , each F has completely filled unutilised 2p orbitals while B has a vacant 2p-orbital. Now since both of these orbitals belong to same energy level (2p) they can overlap effectively as a result of which electrons of B resulting in the formation of an additional $\pi\text{-}\pi$ bond. This type of bond formation of back as dative or back bonding. Formation of back bonding between B and F in BF_3 molecule as given below figure..



As a result of back donation of electrons from F to B, the electron deficiency of B is reduced and Lewis acid character is decreased. the tendency for the back bonding is maximum in BF_3 and decreases from BF_3 to BI_3 . Thus BI_3 , BBr_3 and BCl_3 are stronger Lewis acids than BF_3 .

□ **Anomalous behaviour of boron :**

Boron shows anomalous behaviour due to its small size, high nuclear charge, high electronegativity and non-availability of d-orbitals.

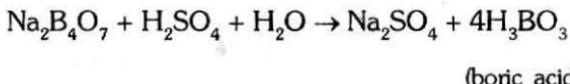
IMPORTANT COMPOUNDS OF BORON

□ **Boric acid (H_3BO_3)**

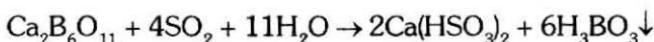
● **Preparation :**

(a) **From borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$):**

Boric acid can be prepared by adding a hot concentrated solution of borax to a calculated quantity of conc. H_2SO_4 . The solution on cooling gives crystals of boric acid, which can be separated by filtration.



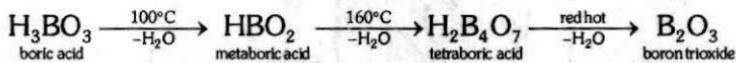
(b) **From Colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$):**



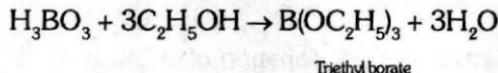
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● Properties :

(a) Action of heat :



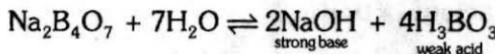
(b) Reaction with alcohol (test of boric acid) :



- Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) or $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$

❑ Properties :

- (i) Its solution is basic in nature due to hydrolysis.



- $$\text{(ii)} \quad \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \xrightarrow[-10\text{H}_2\text{O}]{\Delta} \text{Na}_2\text{B}_4\text{O}_7 \xrightarrow[740^\circ\text{C}]{\text{anhydrous}} 2\text{NaBO}_2 + \text{B}_2\text{O}_3 \quad (\text{transparent bead/glassy})$$

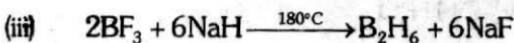
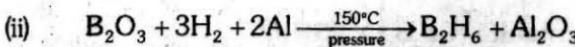
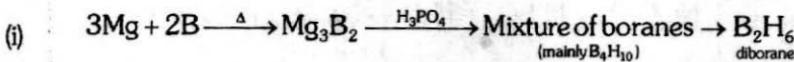
- (iii) Borax bead test : Borax on strong heating forms B_2O_3 which forms coloured glassy bead with coloured compounds of certain metals. It is called borax bead test.

Colour of beads	Cr	Mn	Fe	Co	Ni	Cu
	Green	Pink	Green	Blue	Brown	Blue

e.g. Cu(BO₂)₂
Blue bead

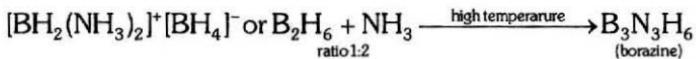
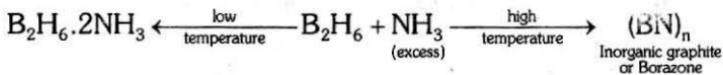
Diborane (B_2H_6)

● : Preparation :

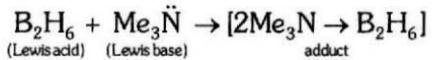


● Properties :

(i) Reaction with ammonia :

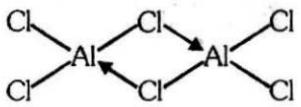


(ii) Reaction with amine :



- Borazine is known as inorganic benzene.

Anhydrous AlCl_3 is prepared by passing dry HCl or Cl_2 gas over heated aluminium turnings in absence of air. It is also obtained by passing Cl_2 gas over heated mixture of Al_2O_3 and coke. It is used as a catalyst in Friedel - Craft's reaction. The molecule is an autoclomer and is represented as :



Anhydrous AlCl_3 is a Lewis acid. Anhydrous form is covalent while hydrated $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ is ionic.

ALUMS

- Alums are the double sulphates of the type $\text{M}_2\text{SO}_4 \cdot \text{M}'(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ where M is a univalent cation like Na^+ , K^+ and NH_4^+ and M' is a trivalent cation like Al^{3+} , Fe^{3+} and Cr^{3+} .

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Potash alum	$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
Sodium alum	$Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
Ferric alum	$(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$
Ammonium alum	$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
Chrome alum	$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$

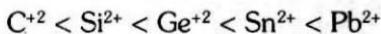
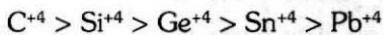
Ultramarine is an artificial Lapis-Lazuli, a rare mineral $(Na_3Al_3Si_3S_3O_{12})$ which has fine blue colour. It is used in making blue paint.

Precious stones such as sapphire, ruby, topaz, etc., are Al_2O_3 containing oxides of transition metals.

(GROUP 14 ELEMENTS)

PHYSICAL PROPERTIES

Stability order

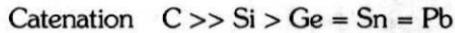


(due to inert pair effect)

I.P. order

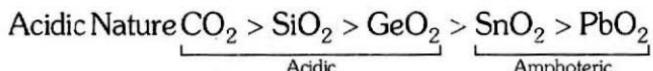
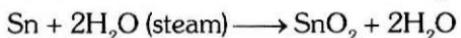


(due to lanthanoid contraction)



Except lead, all other elements of this group show allotropy.

Diamond, fullerene and graphite are allotropes of carbon.

CHEMICAL PROPERTIES**□ Action of air :****(i) Monoxides :** $2M + O_2 \longrightarrow 2MO$ **(ii) Dioxides :** $M + O_2 \longrightarrow MO_2$ **□ Action of water :**C, S, Ge and Pb are unaffected by H_2O .

□ Action of acids : Non-oxidising acids do not attack C and Si, Ge is not attacked by dilute HCl. When Ge is heated in a steam of HCl gas, germanium chloroform is formed.

Sn dissolves slowly in dilute HCl but readily in concentrated HCl.

Pb dissolves in conc. HCl forming chloroplumbous acid, but the reaction stops after sometime due to deposition of PbCl_2 .

□ Action of alkali : C is unaffected by cold alkali. Si reacts slowly with cold aqueous NaOH and readily with hot NaOH forming silicate.

Sn and Pb form stannate and plumbate respectively on reaction with hot alkali.

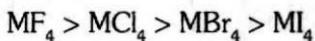
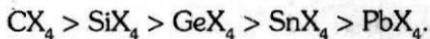
IMPORTANT COMPOUNDS OF GROUP 14 ELEMENTS :**□ Hydrides :** MH_4 (General formula) CH_4 Methane

on moving top to bottom

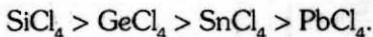
 SiH_4 Silane \rightarrow B.L. \uparrow GeH_4 Germane \rightarrow T. Stability \downarrow SnH_4 Stanane \rightarrow Acidic nature \uparrow PbH_4 Plumbane \rightarrow Reducing nature \uparrow

Halides :

All the element forms covalent halides, MX_4 (except PbBr_4 and PbI_4).
the thermal stability of halides decreases as :



The halides are readily hydrolysed by water (except CX_4 , due to absence of d-orbital). The order of ease of hydrolysis is



Degree of hydrolysis \propto covalent chr.

 Carbides :

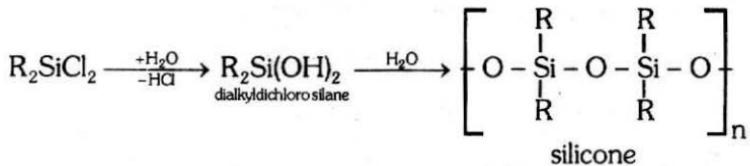
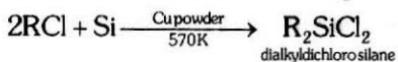
- The binary compounds of carbon with elements other than hydrogen are called carbides.
- Ionic carbides are formed by the most electropositive metals such as alkali and alkaline earth metals and Al.

Both Be_2C and Al_4C_3 are called methanides because they react with H_2O yielding methane.

- Covalent carbides are formed by metalloids like Si and B.
- SiC (carborundum) has a diamond like structure, hence it is called artificial diamond. B_4C (Norbide) is hardest known artificial substance.
- Interstitial carbides are formed by transition elements in which C-atoms occupy tetrahedral holes in the close-packed arrays of metal atoms. W, Zr, Ti, Ta and Mo can form ideal interstitial carbides.

 Silicones :

- Silicones are polymeric organo-silicon compounds containing Si—O—Si linkages. The name silicone has been given from similarity of their empirical formula (R_2SiO) with ketones (R_2CO)
- Silicones are formed by the hydrolysis of alkyl or aryl substituted chlorosilanes and their subsequent polymerisation.



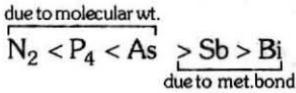
- Silicones have good thermal, oxidative stability. These are excellent water repellants and chemically inert substances. Liquid silicones are used as excellent lubricants.
- Silicates** : Silicates are metal derivatives of silicic acid $[\text{H}_4\text{SiO}_4]$ or $\text{Si}(\text{OH})_4$. Silicates are made up of SiO_4^{4-} tetrahedral units in which Si is sp^3 hybridised and is surrounded by four oxygen atoms.
- All these elements combine with halogens forming corresponding halides.

Note : Boron and aluminium combine with nitrogen and carbon on heating to form nitrides and carbides respectively.

(GROUP 15 ELEMENTS)

PHYSICAL PROPERTIES

- Melting and boiling points



- Oxidation state** : These elements can show negative as well as positive oxidation states.

As we go down the group, the stability of +3 oxidation state increases while that of +5 oxidation state decreases due to inert effect.

- **Non-metallic and metallic character :** Down the group, metallic character increases.
- **Allotropy :** All the elements except bismuth show allotropy. Phosphorus exists in three allotropic forms such as white or yellow, red or violet and black phosphorus.

Property	White phosphorus	Red phosphorus	Black phosphorus
Colour	White, but turns yellow on exposure	Dark red	Black
State	Waxy solid, can be cut with knife	Brittle powder	Crystalline with greasy touch
Smell	Garlic smell	Odourless	—
Ignition temperature	307 K	543 K	673 K

CHEMICAL PROPERTIES

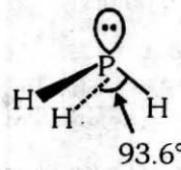
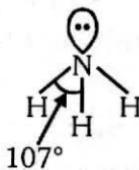
□ Hydrides :

General formula for hydrides is MH_3 .

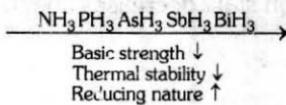
e.g. NH_3 , PH_3 , AsH_3 , SbH_3 , BiH_3 .

All these hydrides are covalent in nature and have pyramidal structure (sp^3 hybridised).

e.g.



As we go down the group, the bond angle decreases. This is due to the increase in size and decrease in electronegativity of central metal ion.



Halides :

Elements of group 15 form two types of halides viz. (i) trihalides and (ii) pentahalides. The trihalides are predominantly basic (Lewis bases in nature) and have pair of electrons (central atom is sp^3 hybridised). The pentahalides are thermally less stable than the trihalides.

Property	Gradation	Reason
Stability of trihalides of nitrogen	$NF_3 > NCl_3 > NBr_3$	Large size difference between N and the halogens
Lewis base strength	$NF_3 < NCl_3 < NBr_3 < NI_3$	Decreasing electron density
Bond angle among the halides of phosphorus	$PF_3 < PCl_3 < PBr_3 < PI_3$	Due to increases in size of X, Steric repulsing \uparrow due to which bond angle increases.

 Formation of oxides :

All the elements of this group form two types of oxides, i.e. M_2O_3 and M_2O_5 and are called trioxides and pentoxides.

Property	Gradation	Reason
Acidic strength of trioxides	$N_2O_3 > P_2O_3 > As_2O_3$	Electronegativity of central atom decreases
Acidic strength of pentoxide	$N_2O_5 > P_2O_5 > As_2O_5 > Bi_2O_5$	Electronegativity of central atom decreases
Acidic strength of oxides of nitrogen	$N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$	Oxidation state of central atom increases
The stability of pentoxide	$P_2O_5 > As_2O_5 > Sb_2O_5 > N_2O_5 > Bi_2O_5$	Stability of oxides of a higher oxidation state i.e., M_2O_5 decreases with increasing atomic number

Uses :**□ Nitrogen (N_2)**

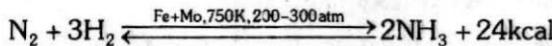
- Manufacture of HNO_3 , NH_3 , $CaCN_2$, etc.
- Provides inert atmosphere in many metallurgical processes.

□ Phosphorus (P_4)

- Uses in manufacture of matches, in rat poison, in the manufacture of tracer bullets, etc.

IMPORTANT COMPOUNDS OF GROUP 15 ELEMENTS**1. Ammonia (NH_3)****□ Preparation :**

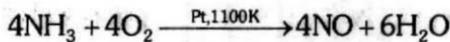
- (i) $2NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} CaCl_2 + 2NH_3 + 2H_2O$
- (ii) $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$

□ Manufacture (Haber's process) :**□ Physical properties :**

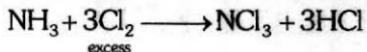
- Colourless, pungent smell, basic in nature.
- Liquefies on cooling under pressure.
- On heating it causes cooling.

□ Chemical properties :

- $4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$



- $8NH_3 + 3Cl_2 \xrightarrow[\text{excess}]{} 6NH_4Cl + N_2$



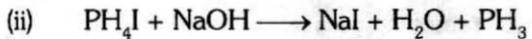
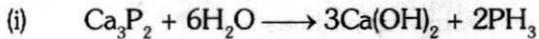
**Uses :**

- It is used as refrigerant.
- In the manufacture of fertilizers and HNO_3 .
- It is used for removing grease.
- Used as a solvent.

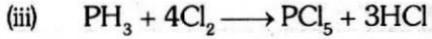
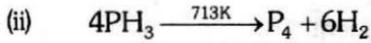
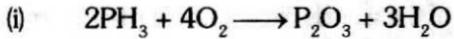
2. HNO_3 , nitric acid was earlier called as aqua fortis (meaning strong water). It usually acquires yellow colour due to its decomposition by sunlight into NO_2 .

It acts as a strong oxidising agent. Non-metals converted into highest oxyacids by hot and conc. HNO_3 . NO_2 gas is evolved (S to H_2SO_4 ; P to H_3PO_4 ; C to H_2CO_3 ; I₂ to HIO_3 ; As to H_3AsO_4 ; Sb to H_3SbO_4 and Sn to H_2SnO_3). Most of the metals except noble metals are attacked by HNO_3 . It plays double role in action on metals, i.e., it acts as an acids as well as an oxidising agent.

Concentration of nitric acid	Metal	Main products
Very Dilute HNO_3	Mg, Mn	H_2 + metal nitrate
	Fe, Zn, Sn	NH_4NO_3 + metal nitrate
	Cu, Ag, Hg	No reaction
Dilute HNO_3	Fe, Zn	N_2O + metal nitrate
	Zn, Fe, Pb, Cu, Ag	NO + metal nitrate
Conc. HNO_3	Sn	NO_2 + H_2SnO_3 (Metastannic acid)
Conc. HNO_3	Fe, Co, Ni, Cr, Al	rendered passive

3. Phosphine (PH_3) **Preparation :** **Laboratory preparation :** **Physical properties :**

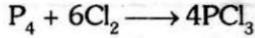
- Colourless gas having smell of garlic or rotten fish, slightly soluble in water and slightly heavier than air.

 Chemical properties : **Uses :**

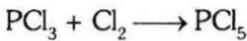
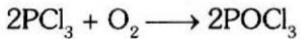
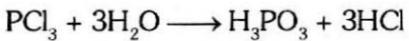
- As Holme's signals in deep seas and oceans.
- For the production of smoke screens.

4. Phosphorus halides :

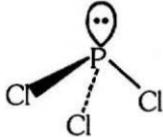
Phosphorus form two types of halides, phosphorus trihalides, PX_3 and phosphorus pentahalides, PX_5 ($\text{X} = \text{F, Cl, Br}$).

(i) PCl_3 : **Preparation :**

Properties :

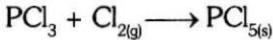
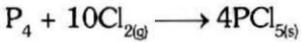


Structure :



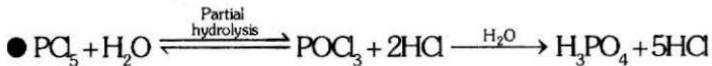
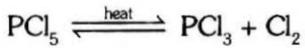
(ii) PCl_5 :

Preparation :

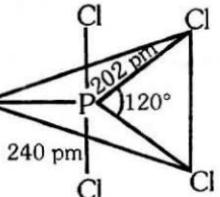


Properties :

- Pale yellow crystalline solid.
- In solid state it exists as $[\text{PCl}_4]^+ [\text{PCl}_6]^-$.
- It sublimes on heating.



Structure :



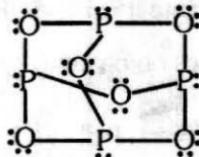
Structure of oxides of nitrogen and phosphorus

Nitrogen

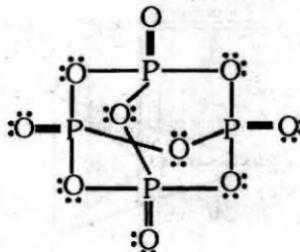
Oxide of N	Oxid. state	Physical appearance	Structure
N_2O nitrous oxide	+1	Colourless gas	$N \equiv N \rightarrow O$
NO Nitric oxide	+2	Colourless gas	$N = O$
N_2O_3 Dinitrogen trioxide	+3	Blue colour solid	
N_2O_4 Dinitrogen tetraoxide	+4	Colourless solid	
NO_2 Nitrogen dioxide	+4	Brown gas	
N_2O_5 Dinitrogen pentoxide	+5	Colourless solid	

Phosphorus

- Structure of phosphorus trioxide (P_4O_6) :



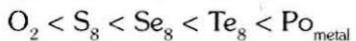
- Structure of phosphorus pentaoxide (P_4O_{10}) :



(GROUP 16 ELEMENTS)

PHYSICAL PROPERTIES

- **Melting and boiling points :**



- **Metallic and non-metallic character :**



- **Elemental state :** Oxygen exists as diatomic gaseous molecule. Sulphur and selenium exist as octa-atomic molecules. Both have puckered ring structure.
- **Allotropy :** All the elements of this group show allotropy. Oxygen exists in two non-metallic forms i.e., O_2 and O_3 . Sulphur provides a very good example of an element that exhibits allotropy.

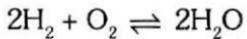
Allotropic forms of sulphur :

- **Rhombic sulphur or octahedral or α -sulphur :** This is the common and stable form of sulphur. It is a pale yellow crystalline solid consisting of S_8 structural units and packed in octahedral shape.
- **Monoclinic or prismatic or β -sulphur :** This form is stable above 95.6°C. It exists as amber yellow, needle shaped crystals soluble in carbon disulphide.
- **Plastic sulphur :** It is an amber brown, soft rubber like mass which hardens on standing.

CHEMICAL PROPERTIES :

- **Hydrides :**

All these elements form stable hydrides of the type H_2M



- H_2O is a liquid due to hydrogen bonding. Others are colourless gases with unpleasant smell.

- Compound : $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$

Bond angle : 105.5° 92.5° 91° 90°

(all sp^3 hybridised)

- The weakening of M-H bond with the increase in the size of M (not the electronegativity) explains the increasing acid character of hydrides down the group.

□ Halides :

All these elements form a number of halides. The halides of oxygen are not very stable. Selenium does not form dihalides.

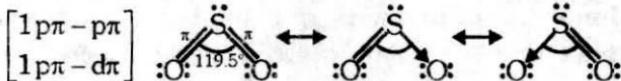
e.g. OF_2 , Cl_2O_6 , I_2O_5 , etc.

□ Oxides :

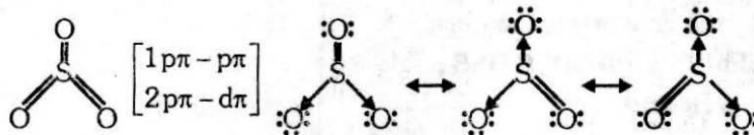
Oxides of other elements are as follows :

Element	Monoxide	Dioxide	Trioxide
S	SO	SO_2	SO_3
Se	-	SeO_2	SeO_3
Te	TeO	TeO_2	TeO_3
Po	PoO	PoO_2	-

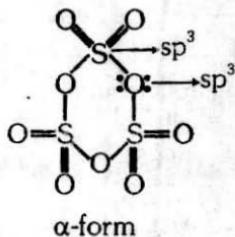
- SO_2 is a gas having sp^2 hybridisation and V-shape



- SO_3 is a gas, sp^2 hybridised and planar in nature.



- In solid state it exists as a cyclic trimer (SO_3)₃, α -form or as linear cross-linked sheets, β -form.

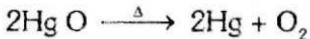


$$\begin{aligned} \text{S} = \text{O} \text{ bond} &\Rightarrow 6 \\ \text{S} - \text{O} - \text{S} \text{ bond} &\Rightarrow 3 \end{aligned}$$

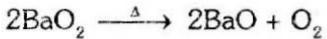
IMPORTANT COMPOUNDS OF GROUP 16 ELEMENTS**1. Oxygen (O_2) :**

- Preparation :** By action of heat on oxygen rich compounds :

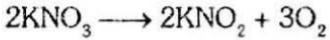
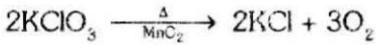
- From oxides :



- From peroxides :

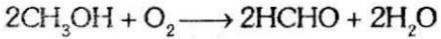
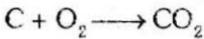


- From decomposition of certain compounds :



- Properties :** It is colourless, odourless, tasteless, slightly heavier than air, sparingly soluble in water but soluble in pyrogallol.

- Chemical properties :** On heating it combines directly with metals and non-metals.

**Uses :**

- When mixed with He or CO_2 , it is used for artificial respiration.

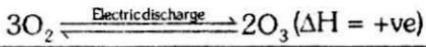
- In welding and cutting.

- As a fuel in rockets.

2. Ozone (O_3) :

- Preparation :**

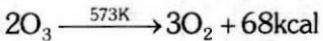
- **Lab method :**



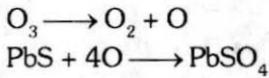
Chemistry Handbook

- Properties :** Pale blue gas with characteristic strong smell, slightly soluble in water but more soluble in turpentine oil or glacial acetic acid.

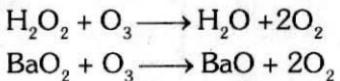
- Decomposition:



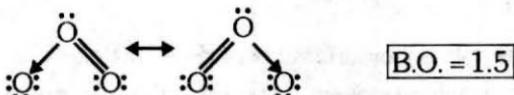
- Oxidising action:



- Reducing action:



- Structure :**



Oxidation state of O is +1 and -1.

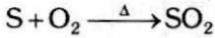
- Uses :**

- Bleaching ivory, flower, delicate fabrics, etc.
- As germicide and disinfectant, for sterilising water.
- Manufacture of KMnO_4 and artificial silk.

3. Sulphur dioxide (SO_2)

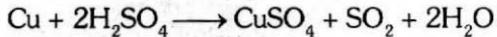
- Preparation :**

- By heating sulphur in air.



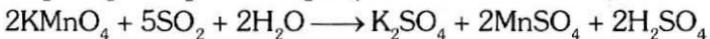
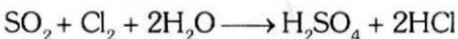
- Lab method :

By heating Cu with conc. H_2SO_4 .



Properties :

- As reducing agent :

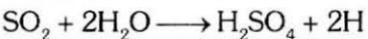


- As oxidising agent :



- Bleaching action :

Its bleaching action is due to reduction.



Coloured matter + H → Colourless matter.

(Nascent hydrogen)

 Uses :

- In the manufacture of sulphuric acid, sulphites and hydrogen sulphide.
- As a disinfectant and fumigant.
- For bleaching delicate articles.

4. Sulphuric acid (H_2SO_4) :

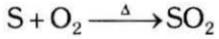
It is also known as oil of vitriol and king of chemicals.

 Manufacture of sulphuric acid :

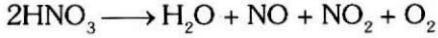
- Lead chamber process :

The various steps involved are :

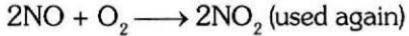
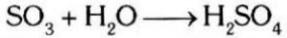
- (a) Production of SO_2 : By burning S or iron pyrites.



- (b) Production of catalyst : Oxides of nitrogen.



- (c) Reaction in lead chamber

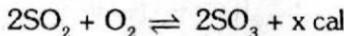


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- **Contact process :**

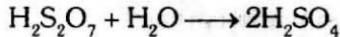
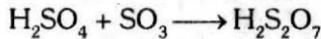
The steps involved are :

- (a) **Production of SO₂** : It is produced by burning sulphur or iron pyrites and purified by treating with steam to remove dust particles.
- (b) **Conversion of SO₂ to SO₃** : It is done in container or catalyst chamber after being pre-heated to 450°C.



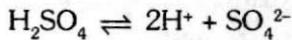
Catalyst : Formerly, platinised asbestos was used which is costly and easily poisoned. These days V₂O₅ is used.

- (c) SO₃ is absorbed by conc. H₂SO₄ and then water is added to produce the acid of desired concentration.

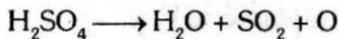


□ **Properties :** Its specific gravity is 1.8 and it is 98% by weight.

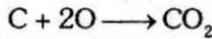
- It is strong dibasic acid.



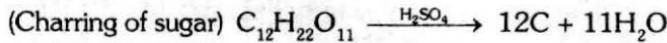
- It acts as an oxidising agent.



- Non metals are oxidised to their oxides and metals to the corresponding sulphates.



- Dehydrating agent : It is strongly dehydrating in nature.



□ **Uses :**

- In lead storage batteries.
- In manufacture of paints and pigments.
- In metallurgy for electrolytic refining of metals.

(GROUP 17 ELEMENTS)**PHYSICAL PROPERTIES**

- Oxidation state :** All the halogens show an oxidation state of -1. Except fluorine, all halogens show positive oxidation states also.

- Metallic character :**

$$\text{F} < \text{Cl} < \text{Br} < \text{I} < \text{At}$$

- Bond dissociation energy :** Bond dissociation energy of fluorine is lower than those of chlorine ($\text{Cl}-\text{Cl}$) and bromine ($\text{Br}-\text{Br}$) because inter-electronic repulsions present in the small atom of fluorine. Hence bond energy decreases in the order.

$$\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$$

- Bond length :**

$$\text{F}_2 < \text{Cl}_2 < \text{Br}_2 < \text{I}_2$$

- Melting point and boiling point :**

$$\text{F}_2 < \text{Cl}_2 < \text{Br}_2 < \text{I}_2$$
CHEMICAL PROPERTIES

- Reactivity :** All halogens are chemically very reactive elements. This is due to their low dissociation energy and high EN. Fluorine is the most reactive and iodine is the least reactive halogen.

- Oxidising power :** F is the most oxidising element due to high hydration enthalpy.

$$\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$$

- Hydrogen halides :**

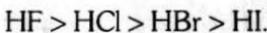
- Bond strength, bond length and thermal stability :

- Since size of halogen atom increases from F to I down the group, bond length of H-X bond increases down the group.

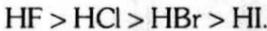
∴ reactivity and acidic character ↑.

$$\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$$

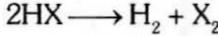
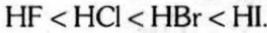
- Bond strength is inversely proportional to bond length i.e., larger the bond length, lower the bond strength is



- Higher the bond dissociation energy, greater will be thermal stability. Thus, thermal stability follows the order.

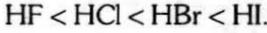


- Reducing character : The reducing character of hydrogen halides increases down the group as



A less thermally stable compound has more tendency to release hydrogen easily and show greater reducing property.

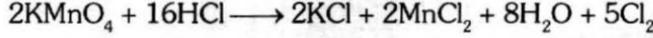
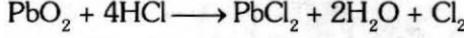
- **Acidic strength :** The acidic strength of these acids increases down the group and hence follows the order.



Since H-I bond is weakest, it can be easily dissociated into H^+ and I^- ions while HF with greater bond dissociation energy can be dissociated with maximum difficulty.

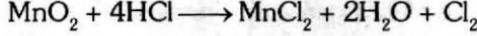
CHLORINE (Cl_2)

- **Preparation :** By oxidation of conc. HCl.



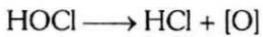
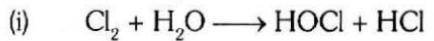
- **Manufacture :**

Weldon's process : By heating pyrolusite with conc. HCl.



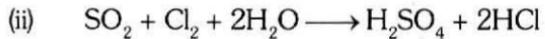
- **Properties :** It is a yellowish green gas, poisonous in nature, soluble in water. Its aqueous solution is known as chlorine water which on careful cooling gives chlorine hydrate $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$.

- Bleaching action and oxidising property

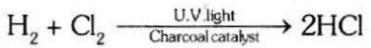


Coloured matter + nascent [O] \longrightarrow Colourless matter

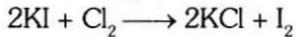
The bleaching action of chlorine is permanent and is due to its oxidising nature.



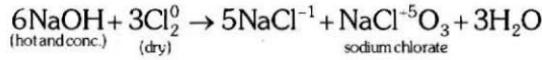
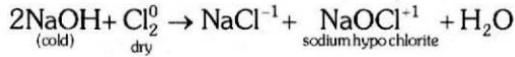
- Action of hydrogen :



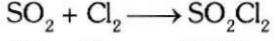
- Displacement reactions :



- Action of NaOH :



- Addition reactions :



□ Uses :

- It is used as a

(i) bleaching agent

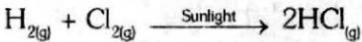
(ii) disinfectant

(iii) in the manufacture of CHCl_3 , CCl_4 , DDT, bleaching powder, poisonous gas phosgene (COCl_2), tear gas (CCl_3NO_2) and mustard gas ($\text{ClC}_2\text{H}_4\text{SC}_2\text{H}_4\text{Cl}$).

Chemistry HandBook
HYDROCHLORIC ACID, (HCl)

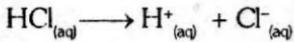
- **Preparation :** By dissolving hydrogen chloride gas in water. Hydrogen chloride gas required in turn can be prepared by the following methods:

- By the direct combination of hydrogen and chlorine.



- Hydrogen chloride gas can also be obtained by burning hydrogen in chlorine.

- **Properties :** Hydrogen chloride is a covalent compound but when dissolved in water it ionizes to form hydrogen ions and chloride ions.

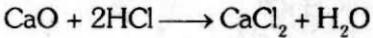


Thus anhydrous HCl does not show acidic properties. Only aqueous HCl or in presence of moisture, HCl behaves as an acid.

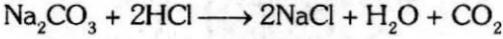
- Metal + Hydrochloric acid \longrightarrow Metal chloride + Hydrogen



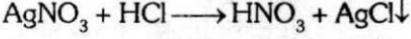
- It reacts with bases and basic oxides or hydroxides to form their respective chlorides and water.



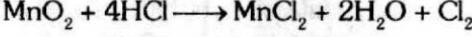
- It reacts with metal carbonates, bicarbonates, sulphides, sulphites, thiosulphates and nitrites, etc, to form their respective chlorides.



- It reacts with silver nitrate and lead nitrate solution to form their white precipitates.



- Reducing property : HCl is a strong reducing agent.



- **Uses :**

- In the production of dyes, paints, photographic chemicals, etc.
- Used in the preparation of chlorides, chlorine, aqua-regia, etc.
- Used as a laboratory reagent.

INTERHALOGEN COMPOUNDS :

- These compounds are regarded as halides of more electropositive (i.e. less electronegative) halogens.
- Types of interhalogen compound :

AB type : ClF, BrF, BrCl, ICl, IBr

AB₃ type : ClF₃, BrF₃, ICl₃

AB₅ type : BrF₅, IF₅

AB₇ type : IF₇

Variation of the general properties of oxyacids of halogens

Halogen	Hypohalous acids (X = +1)	Halous acids (X = +3)	Halic acids (X = +5)	Perhalic acid (X = +7)
Cl	HClO	HClO ₂	HClO ₃	HClO ₄
Br	HBrO	-	HBrO ₃	-
I	HIO	-	HIO ₃	HIO ₄

- Oxidation number of the central atom increases

(X = +1, +3, +5, +7) →

- Thermal stability increases →

- Covalent character of X – O bond increases →

- Oxidising power decreases →

- Basicity of decreases →

← Electronegativity of the central atom decreases -

← Thermal stability decreases -

← Oxidising power decreases -

← Acidic strength decreases -



COORDINATION CHEMISTRY

Complex formation : Due to high polarising power and partially filled 'd' subshell, transition elements form complex.

Terminology :

Ligand : The species which donate the e^- pair is called as ligand. On the basis of the number of e^- pairs available for donation; ligands are classified as :

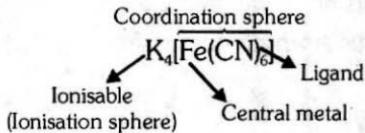
- Monodentate (One pair of e^-)
- Bidentate (Two pair of e^-)

Ambidentate ligand : It is the monodentate ligand having more than one (e^- pair) to donate, but always acts as unidentate due to inactivation of the second e^- pair for donation. For example, $-CN^-$, and $-NC^-$, $-SCN^-$ and $-NCS^-$, NO_2^- and ONO^- , $-OCN^-$ and NCO^- . These ligands are responsible for linkage isomerism.

Flexidentate ligands : Exhibit variable denticity eg. SO_4^{2-} , CO_3^{2-} , EDTA $^{4-}$.

Chelating ligand : These are the polydentate ligands which bind to the central metal to form a puckered ring structure. Chelation always, leads to extra stability, for example, EDTA (ethylene diamine tetra acetate).

Coordinate complex :



Ionisation sphere constitutes of the ions which may satisfy the primary valency. **Coordination sphere** constitute the metal coordinates with ligands, which cannot be ionised after dissolution and exist as stable identities – either neutral or charged.

Coordination number : It is the number of ligands by which central metal is surrounded in coordination sphere or it is the number of coordinate bonds around central metal ion in a complex entity.

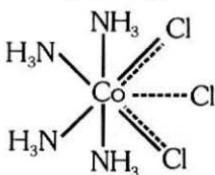
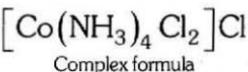
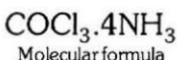
Charged ligands can satisfy primary valency beside being the part of coordination sphere hence, satisfy both primary and secondary valencies but still remain unionisable.

Werner's theory :

Metal in a complex shows two type of valences - Primary & secondary.

Primary valency	Secondary Valency
It is oxidation no. of metal.	It is coordination no.
It is variable	It is non variable.
Satisfied by anions (present in coordination or ionisable sphere).	Satisfied by ligands (present in coordination sphere)
Ionisable	Nonionisable
Ionic ∴ nondirectional	Directional ∴ decide geometry of complex ion.
Represented by dotted line in Werner structure.	Represented by solid lines in Werner structure.

eg.



{3 dotted line shows – Primary Valence
{6 solid line shows – Secondary Valence

Werner structure

EAN rule : (According to sidgwick and Lowrry)

Primary valence – loss of electrons.

Secondary valence – gain of electrons.

∴ Total number of electron associated with metal ion in a complex entity is called EAN.

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Central metal ion have tendency to achieve atomic number of nearest inert gas element during formation of complex. Called EAN rule.

EAN = Atomic number of Central metal ion – Oxidation state + (2 × Coordination number)

$$\text{K}_4[\text{Fe}(\text{CN})_6] \quad \text{EAN of Fe} = 26 - 2 + (2 \times 6)$$

$$\begin{aligned} \text{Stable according to EAN rule} &= 24 + 12 \\ &= 36 \end{aligned}$$

(equals to atomic number of Kr₃₆)

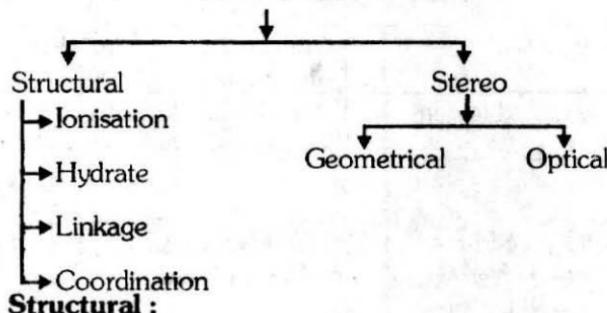
$$\text{K}_3[\text{Fe}(\text{CN})_6] \quad \text{EAN} = 26 - 3 + 12$$

$$(\text{Less stable}) \quad = 35$$

∴ act as oxidising agent.

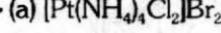
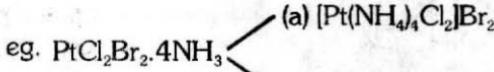
Isomerism :

Isomerism



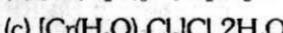
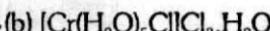
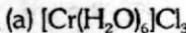
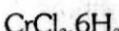
Structural :

- (a) **Ionisation isomerism** : Same molecular formula but gives different ionisable species. (Only anionic)

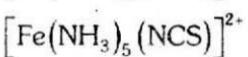
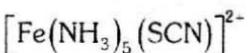


- (b) **Hydrate isomerism** : Same molecular formula but different number of water molecules associated with central metal.

eg.:

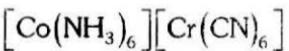


(c) **Linkage isomerism** : Structural isomerism shown by ambidentate ligands (NO_2^- , CSN^- , CN^- , CNO^- etc)



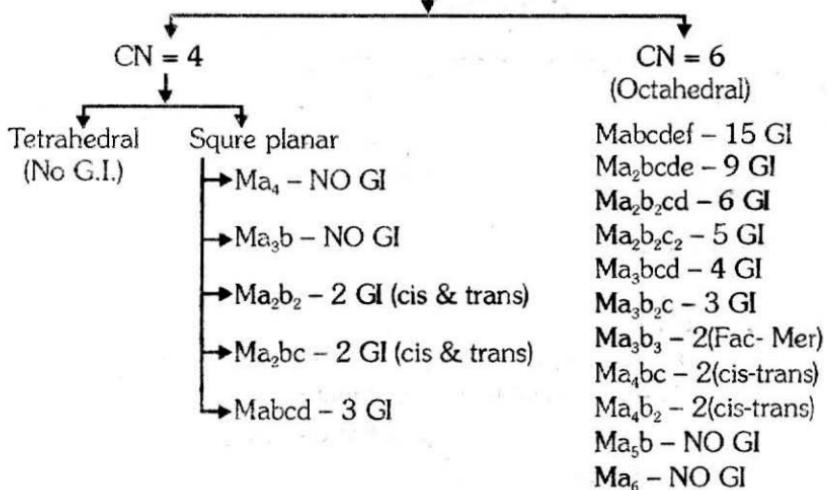
(d) **Coordination isomerism** : Isomers having both anion and cation as complex entity.

Can inter change position of ligands as well as metal.



10. Stereoisomerism :

(a) Geometrical Isomerism (GI)

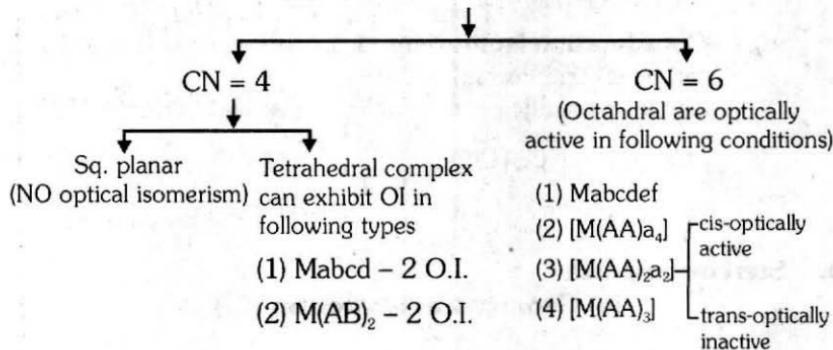


- Sq. planar complex with symmetrical bidentate ligand – No. GI
- Sq. planar complex can exhibit GI only in two types $\begin{bmatrix} \text{M}(\text{AB})_2 \\ \text{M}(\text{AB})\text{ab} \end{bmatrix}$

* On increasing number of one type of ligand total number of geometrical isomers decreases.


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- Octahedral $[M(AA)_4]$ and $[M(AA)_3]$ type of complex can not exhibit G.I.
- $[M(AA)_2a_2]$ type of complex have two GI (cis & trans)

(b) Optical Isomerism (OI)


* $[M(AA)_2a_2]$ type of complex gives three stereoisomer :

- (1) cis
- (2) trans
- (3) mirror image of cis

Crystal field theory (CFT) :

- If the complex is formed by the use of inner d-orbitals for hybridisation (d^2sp^3), it is called inner orbital complex.
- If the complex is formed by the use of outer d-orbitals for hybridisation (sp^3d^2), it is called an outer orbital complex. Such a complex is also called as high spin complex e.g. $[CoF_6]^{3-}$.
- **Crystal field splitting -**
- The splitting of five degenerate d-orbitals of the metal into different sets of orbitals having different energies in the presence of electrostatic field of ligands is called crystal field splitting.

$$eg \text{ set} - dx^2-y^2, dz^2$$

$$t_2g \text{ set} - dxy, dyz, dxz$$

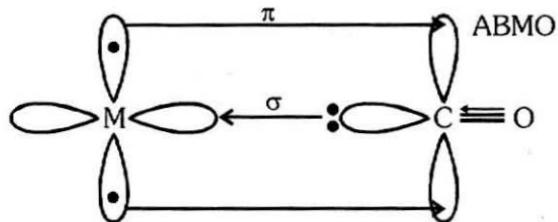
- Crystal field splitting energy, (Δ_o for octahedral structure and Δ_t for tetrahedral structure) is the difference between the various sets of energy levels formed by crystal field splitting.
- Weak field ligands are those ligands which cause a small degree of crystal field splitting e.g. I^- , Br^- , Cl^- , NO_3^- , F^- , OH^- , $C_2O_4^{2-}$, H_2O , etc.
- Strong field ligands are those ligands which cause a high degree of splitting e.g. CO , CN^- , NO_2^- , etc.
- Spectrochemical series
 $I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- < ox^{2-} < H_2O < py \sim en < dipy < o\text{-phen} < NO_2^- < CN^- < CO$.
(C and N donor act as a SFL except N_3^-)

12. Organometallic compounds :

Compounds in which the central metal atoms are bonded directly to carbon atoms of hydrocarbon molecules are called organometallic compounds.

- **σ -bonded compounds** formed by nontransition elements.
 $R-Mg-X$, $(CH_3-CH_2)_2Zn$, Ziegler natta catalyst, etc.
- **π -bonded organometallic compounds** are generally formed by transition elements e.g. Zeise's salt, ferrocene, dibenzene chromium, etc.
- **σ -and π -bonded organometallic compounds** : Metal carbonyls, compounds formed between metal and carbon monoxide belong to this class. $Ni(CO)_4$, $Fe(CO)_5$ etc.

Synergic bonding :



IUPAC nomenclature of complex compounds :

- (A) For anionic complex (like $K_4[Fe(CN)_6]$)

Common name of normal cation (without numeral prefix) + name of ligands (with numeral prefix) + latin name of CMI along with suffix ate + Ox. St (in roman number).

eg. : Potassium hexacyanoferrate (II)

- (B) For cationic complex (like $[Cu(NH_3)_4]SO_4$)

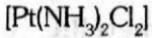
Name of ligands (with numeral prefix) + Common name of CMI + Ox. St (In roman number) + Name of anion (without numeral prefix)

eg. : Tetraammine copper (II) sulphate.

- (C) For neutral complex (like $[Fe(CO)_5]$)

Name of ligands (with numeral prefix) + Common name of CMI + Ox. St. (In roman number)

eg. : Pentacarbonyl iron (O)



Diamminedichloroplatinum (II)

Some important rules :

- Ligands are to be written in alphabetical order
- Repetition of organic ligands and ligands having numeral prefix in their name is to be done by using prefix – bis, tris, tetrakis etc.

d-BLOCK (TRANSITION ELEMENTS)

Definition:

Incomplete n and n-1 shell in atomic or in ionic state. Zn, Cd & Hg – are d-block nontransition elements.

General electronic configuration : $ns^{0-2}(n-1)d^{1-10}$

Exceptions $\begin{cases} \text{Cr } 4s^1 3d^5 \\ \text{Cu } 4s^1 3d^{10} \end{cases}$

Transition series :

1 st	3d series	Sc ₂₁ — Zn ₃₀	9 + 1 = 10
2 nd	4d series	Y ₃₉ — Cd ₄₈	9 + 1 = 10
3 rd	5d series	La ₅₇ , Hf ₇₂ — Hg ₈₀	9 + 1 = 10
4 th	6d series	Ac ₈₉ , Unq — Uub	9 + 1 = 10

Atomic radius :

3d series Sc > Ti > V > Cr > Mn ≥ Fe ≈ CO ≈ Ni ≤ Cu < Zn

In a group 3d to 4d series increases but 4d and 5d series nearly same due to poor shielding of f e⁻ (Lanthanide contraction)

$$\boxed{3d < 4d = 5d}$$

e.g.: Ti < Zr ≈ Hf $\begin{cases} \text{Smallest radius - Ni} \\ \text{Largest radius - La} \end{cases}$

Melting point : s-block metals < d-block metals

In a series on increasing number of unpaired e⁻ mpt increases upto Cr then decreases.

Sc < Ti < V < Cr > Mn < Fe > Co > Ni > Cu > Zn

↓
Half filled d⁵
∴ weak metallic bond

↓
Fully filled d¹⁰
∴ weak metallic bond

Melting point $\begin{cases} \text{Zn} > \text{Cd} > \text{Hg} \\ \text{Cu} > \text{Ag} \leq \text{Au} \end{cases}$

E.N. Exception Zn < Cd < Hg

Density :

s-block metals < d-block metals

3d series Sc < Ti < V < Cr < Mn < Fe < Co ≤ Ni < Cu > Zn

Density in a Group 3d < 4d << 5d

Metallic character : They are solid, hard, ductile, malleable, good conductor of heat and electricity and exhibit metallic lusture, high tensile strength. Hg is liquid

Elect. cond. Ag > Cu > Au > $\underbrace{\text{Al}}_{\text{d-block}}$ $\underbrace{\text{Al}}_{\text{p-block}}$

Oxidation state : Transition elements exhibit variable oxidation state due to small energy difference of ns and (n-1)d electrons.

- Sc(+3) and Zn(+2) exhibit only one oxidation state
- Common oxidation state is +2
- 3d series highest oxidation state is +7 (Mn)
- In d-block series highest oxidation state is +8 (Os)
- In carbonyl compound oxidation state of metals is zero due to synergic effects.
- Their higher oxidation states are more stable in fluoride and oxides.
- Higher oxidation states in oxides are normally more stable than fluorides due to capability of oxygen to form multiple bonds.

e.g. stable fluoride in higher ox. st. of Mn is MnF_4 while oxide is Mn_2O_7

Some more stable oxidation states of d-block elements :

Cu +2	Mn +2	Pt +4
Ag +1	Cr +3	Sc +3
Au +3	Ni +2	

Common oxidation states :

Ti(+4), V(+5), Cr(+3, +6), Mn(+2, +4, +7),
 Fe(+2, +3), Co(+2, +3), Ni (+2), Pt (+2 + 4)

In p-block lower oxidation states of heavier elements are more stable while in d-block heavier element, higher oxidation state are more stable.

eg. In VIB gp Mo(+6) & W(+6) are more stable than Cr(+6)

Magnetic property :

All transition elements are paramagnetic due to presence of unpaired electrons. They attract when magnetic field is applied. Magnetic moment of unpaired electron is due to spin and orbital angular momentum.

"Spin only" magnetic moment can be calculated by using formula

$$\mu = \sqrt{n(n+2)} \text{ Bohr magneton. } (n \text{ is number of unpaired } e^-.)$$

If n is 1 $\mu = 1.73 \text{ BM}$

n is 2 $\mu = 2.84 \text{ BM}$

n is 3 $\mu = 3.87 \text{ BM}$

n is 4 $\mu = 4.90 \text{ BM}$

n is 5 $\mu = 5.92 \text{ BM}$

Substances that are not attracted by applied magnetic field are diamagnetic. They have all the electrons paired. d-block element and ions having d^0 and d^{10} configuration are diamagnetic.

Colour :

Colour in transition metal ions is associated with d-d transition of unpaired electron from t_{2g} to e_g set of energies.

This is achieved by absorption of light in the visible spectrum, rest of the light is no longer white.