100 JM
30–40 IOC
Poori

IOC Mega Revision

● Live at 8:00 PM

1st March - 13th March

मंत

I Love Chemistry


Samjho, dekho & yaad karo

Development of Periodic Table

7, 8 → repeat

1. Lavoisier Classification
2. Dobereiner triads
3. NewLand's Octaves
4. Lothar Meyer Curves

Ga - EkaAl

Group

Mendeleev → Atomic Weight

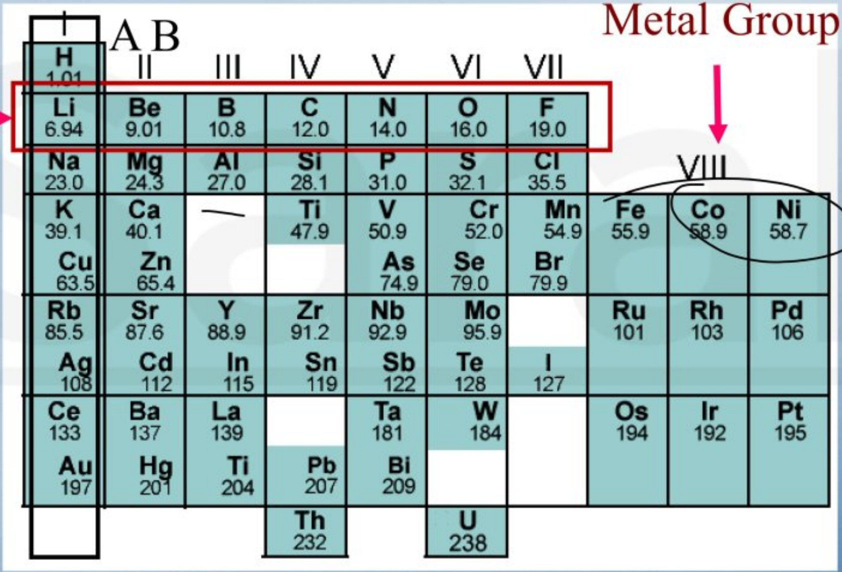
Ga

Transition Metal Group

Period

A = normal

B = transition



A B

I	II	III	IV	V	VI	VII	VIII		
H 1.01									
Li 6.94	Be 9.01	B 10.8	C 12.0	N 14.0	O 16.0	F 19.0			
Na 23.0	Mg 24.3	Al 27.0	Si 28.1	P 31.0	S 32.1	Cl 35.5			
K 39.1	Ca 40.1	—	Ti 47.9	V 50.9	Cr 52.0	Mn 54.9	Fe 55.9	Co 58.9	Ni 58.7
Cu 63.5	Zn 65.4			As 74.9	Se 79.0	Br 79.9			
Rb 85.5	Sr 87.6	Y 88.9	Zr 91.2	Nb 92.9	Mo 95.9		Ru 101	Rh 103	Pd 106
Ag 108	Cd 112	In 115	Sn 119	Sb 122	Te 128	I 127			
Ce 133	Ba 137	La 139		Ta 181	W 184		Os 194	Ir 192	Pt 195
Au 197	Hg 201	Ti 204	Pb 207	Bi 209					
			Th 232		U 238				

Moseley

$$\sqrt{\nu} \propto Z$$ At. No

no of e^- → valence

↓

Chemical

This is also known as 'Modern Periodic Law'.

Nomenclature of elements

0	**Nil**
1	**Un**
2	**Bi**
3	**Tri**
4	**Quad**
5	**Pent**
6	**Hex**
7	**Sept**
8	**Oct**
9	**Enn**

Imp

Learn

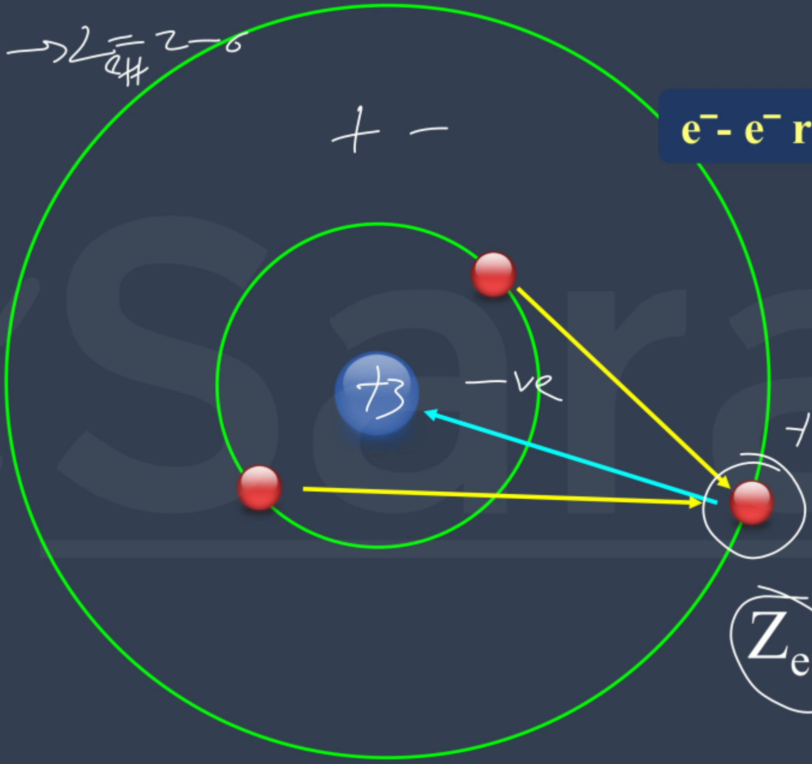
116

ununhexium

101	unnilunium	Unu
102	unnilbium	Unb
103	unniltrium	Unt

Slaters rule → $Z_{eff} = Z - \sigma$

AR
IE
EGE
EN



e⁻- e⁻ repulsion

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

Trends

order of shielding is

s > p > d > f

Period L $\rightarrow$ R $Z_{eff}\uparrow$

d, f poor shielding

Group $\downarrow$ Z_{eff} ~

$$\boxed{Z_{eff} \propto \frac{\text{positive charge}}{\text{negative charge}}}$$

+ve e$^-$ $\downarrow$

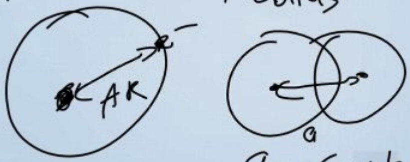
$Fe^{+3} > Fe^{+2}$

$O^{2-} < O^{-}$

Element	Li	Be	B	C	N	O	F	Ne
Z_{eff}	1.30	1.95	2.6	3.25	3.90	4.55	5.20	5.85

Element	Li	Na	K	Rb	Cs	Fr
Zeff	1.30	2.20	2.20	2.20	2.20	2.20

Atomic Radius



$\frac{a}{2}$ = Covalent radius

(a) Z_{eff} increases, atomic radius decreases

(b) Number of shell (n) increases, atomic radius increases generally

Li < Na < K < Rb < Cs

Increase in n > Z_{eff}

$O < O^{-} < O^{-2}$ — -ve ↑ AR ↑

$Mn > Mn^{+2} > Mn^{+3} > Mn^{+4}$ — +ve ↑ AR ↓

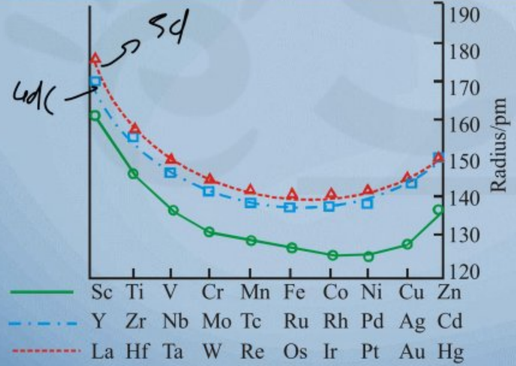
Li > Be > B > C > N > O > F ⟶ AR ↓ Z_{eff} ↑

3d

Nuclear > shielding 9mp **Nuclear ≈ shielding** **Nuclear < shielding**

↓ ~ ↑

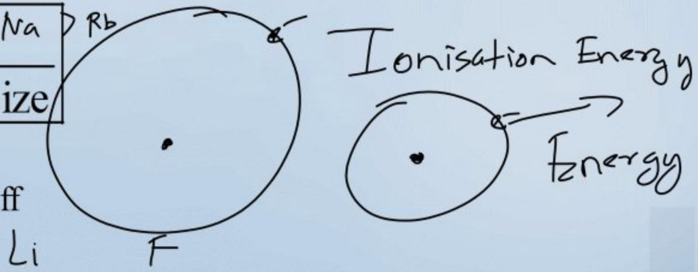
Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radius (pm)	162	147	134	127	126	126	124	124	124	138



Trends in atomic radii of transition elements

$$\boxed{\text{Ionisation Energy} \propto \frac{1}{\text{atomic size}}}$$

Na > Rb



Ionisation Energy $\propto Z_{eff}$

$Fe^{+3} > Fe^{+2} > Fe$ +ve ↑ IE ↑

$$\boxed{s > p > d > f}$$

Penetration

$$\boxed{\text{Reactivity of metals} \propto \frac{1}{\text{IE}}}$$

IE_1 N > O

$1s^2, 2s^2\ 2p^3$ $1s^2, 2s^2\ 2p^4$

half filled, fully filled Be > B

$2s^2$

Ionisation Energy Ga > Al (due to poor shielding of 3d)

Ionisation Energy of 5d > 4d (due to lanthanide contraction)

Ex. Hf > Zr

Q) The IP_1, IP_2, IP_3, IP_4 and IP_5 of an element are 7.1, 14.3, 34.5, 46.8, 5 162.2 eV respectively. The element is likely to be:-

Noble gas e^- [illegible]

(1) Na $1e^-$

(2) Si $4e^-$

(3) F $7e^-$

(4) Ca $2e^-$

Ans 2

Atomic Size $\propto \frac{1}{EA}$

EGE of N, Be, Ne are positive → half / fully filled $EA = 0$

(a) In period – EGE becomes more negative generally as we go from left to right in a period. → $EA \uparrow$

$EA = -EGE$

1st EGE $(-ve)$
2nd " $(+ve)$

(b) In Group

In a group, the electron affinity decreases on moving from top to bottom. ↓

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Electron affinity of 3rd period element is greater than electron affinity of 2nd period elements of the respective group.

F < Cl

[He] $2s^2 2p^5$ [Ne] $3s^2 3p^5$

2nd P Size

E.N. of $Fe^{+3} > Fe^{+2} > Fe$ +ve ↑ EN ↑

Electronegativity

$N^{3-} < N^{-} < N$ -ve ↑ EN ↓

EN

$$\boxed{\text{Electronegativity} \propto \frac{1}{\text{Atomic size}}}$$

$$\boxed{\text{Electronegativity} \propto Z_{eff} \propto \frac{\text{positive charge}}{\text{negative charge}}}$$

(a) Electronegativity decreases down the group.

(b) In period on moving from left to right electronegativity increases.

Nature of oxides

→ $H_2O > Li_2O$

1. Along a period acidic nature increases.
2. Down the group basic nature increases

Amp

Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl

Basic ⟷ Amphoteric ⟷ Acidic

Acidic Nature $\propto$ Oxidation state

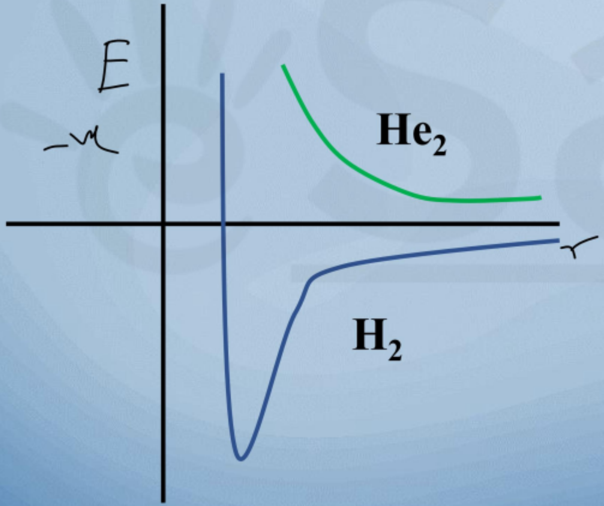
$\overset{+6}{SO_3} > \overset{+4}{SO_2}$

$N_2O_5 > N_2O_3$

Chemical Bonding

$$\text{Stability} \propto \frac{1}{Energy}$$

Q) H-forms H_2 but He doesn't form He_2?



Conditions for formation of covalent bonds

↳ sharing

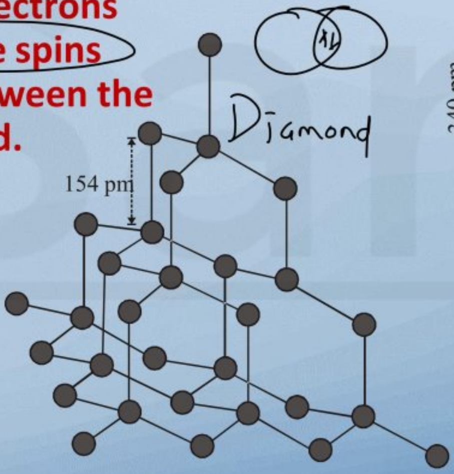
(1) Similar Electronegativity

Na F → Ionic

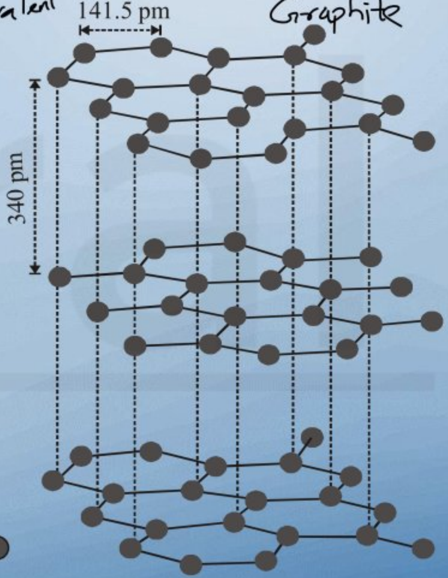
F, O Covalent

(2) The shared pair of electrons should have opposite spins and are localized between the two atoms concerned.

Diamond



Graphite



Formal Charge

$\bar{O}H$

$6-3-\frac{8}{2}$

$6-3-4=-1$

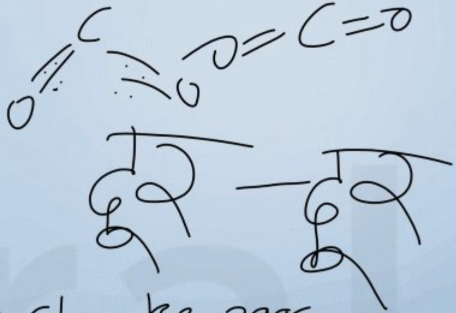
Formal Charge (F.C.) on an atom in Lewis Structure = **Total number of valence electrons in the free atom** – **Total number of non bonding (lone pair) electrons** – **½[Total number of bonding (shared) electrons]**

VSEPR

Valence Shell Electron Pair Repulsion Theory

lp – lp > lp – bp > bp – bp

maha imp



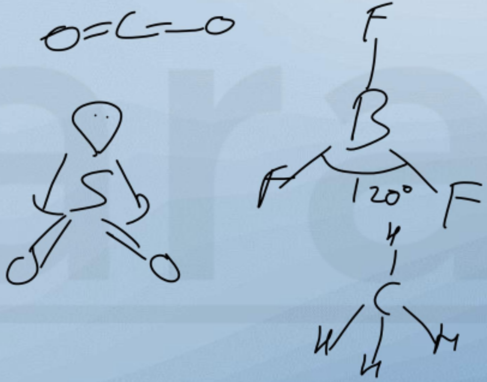
lp → atom ke paas

Space

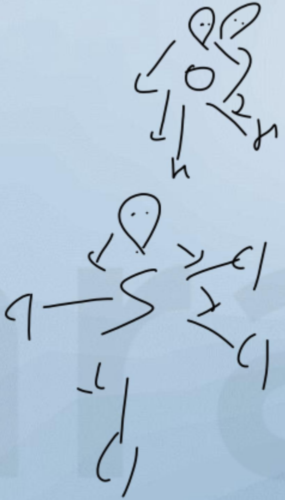
Number of bond pairs	Number of Lone pairs	Molecular Geometry	Bond Angle
2	0	Linear	180^0 Ex : CO_2
3	0	Trigonal Planar	120^0 Ex : BF_3
2	1	Bent, Angular or V-shape	$<120^0$ Ex : SO_2
4	0	Tetrahedral	109.5^0 Ex : CH_4

4-8 number

CB → shape



Number of bond pairs	Number of Lone pairs	Molecular Geometry	Bond Angle
3	1	Tetrahedral	<109.5° Ex : NH_3 107°
2	2	Bent	104.5° Ex : H_2O
5	0	Trigonal Bipyramidal	90°- 6 120° - 3 180°- 1 Ex : PCl_5
4	1	See-Saw	<120° <90° Ex : SF_4



Number of bond pairs	Number of Lone pairs	Molecular Geometry	Bond Angle
3	2	T shape	$<90^0$ Ex : ClF_3
2	3	Linear	180^0 Ex : XeF_2
6	0	Octahedral	90^0- 12 Ex : SF_6
5	1	Square Pyramidal	$<90^0$ Ex : BrF_5

$Xe \longrightarrow$ Compounds

Number of bond pairs	Number of Lone pairs	Molecular Geometry	Bond Angle
4	2	Square Planar	90° Ex : XeF_4
7	0	Pentagonal Bi Pyramidal	90°-10 72°- 5 180°- 1 Ex : IF_7
6	1	Pentagonal Pyramidal or distorted octahedron	<90° <72° Ex : XeF_6
5	2	Pentagonal Planar	72° Ex : $[XeF_5]^-$

6, 1

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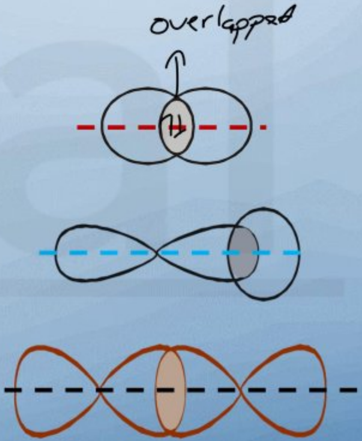
ICl_6^-

VBT

→ overlapping

axial overlapping

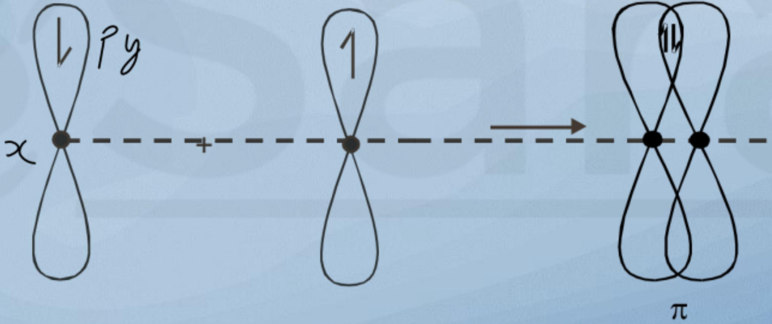
σ overlapping



1. **s-s overlapping**
2. **s-p overlapping**
3. **p-p overlapping**

Pi (π) bond

Sideways



Here we can see that bonding happens perpendicular to the inter-nuclear axis.

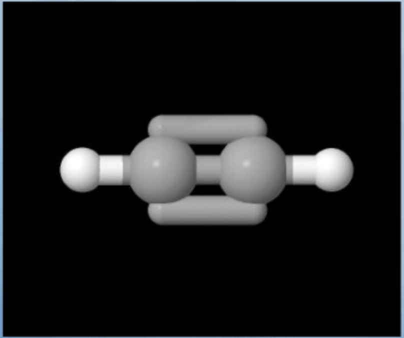
Q) Count the number of σ & π bond in acetylene (C_2H_2)

$3\sigma, 2\pi$

$H\overset{\sigma}{-}C\underset{2\pi}{\overset{\sigma}{\equiv}}C\overset{\sigma}{-}H$

1 σ, 2 π C-C

2 σ C-H



Bond Strength

2p-2p

1s-1s

$$BS \propto \frac{1}{size}$$

1s - 2p > 2s - 2p > 3s - 3p

2nd period

2p-2p > 2p-2s > 2s-2s

BS ∝ directional nature

p - p > s - p > s – s

Sigma > Pi

Size is the dominant factor

Bond Energy → todne

$BE \propto BS$

$$BE \propto \frac{1}{size}$$

$$BE \propto \frac{1}{repulsions}$$

In the two, size is the dominant factor. When size is similar compare on the basis of lp-lp repulsion.

Hybridisation

$1s$ $3p$ sp^3

Definition : Mixing of different shapes and approximate equal energy atomic orbitals, and redistribution of energy to form new orbitals, of same shape & same energy. These new orbitals are called hybrid orbitals and the phenomenon is called hybridisation.

Nmber of hybrid orbitals required =
Number of σ-bond around that atom + Number of lone pair on that atom.

	lp	σ	
$BeCl_2$	0	2	sp
BF_3	0	3	sp^2
H_2O	2	2	sp^3
XeO_2	2	2	sp^3
PCl_5	0	5	sp^3d
$Xe\overset{4}{O}_2\overset{4}{F}_4$	0	6	sp^3d^2
IF_7		7	sp^3d^3

π-pure

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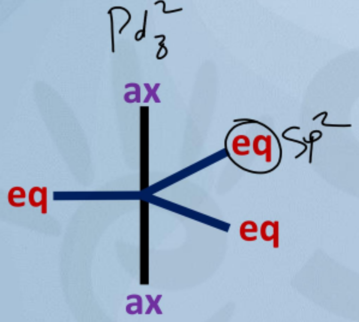
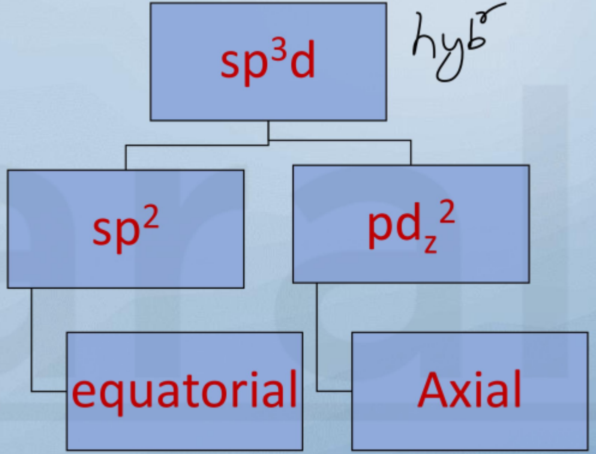
Hyb^{r} in solid state

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

Bent's Rule





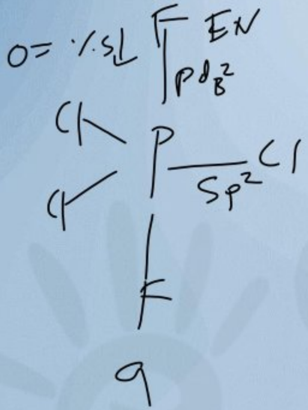
sp^3d hyb^r

sp^2 — equatorial

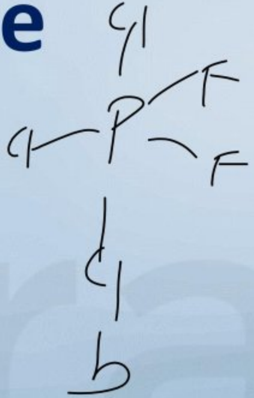
$pd_{z}{}^{2}$ — Axial

$$PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$$

Bent's Rule



$\frac{1}{3}$ = 33% PCl_3F_2



According to Bent when all the surrounding atoms are attached to the central atom by single bond than more electronegative surrounding atom prefers hybrid orbital with less s-character.

DB, LP → % s character

Lp > DB, TB

Seasaw

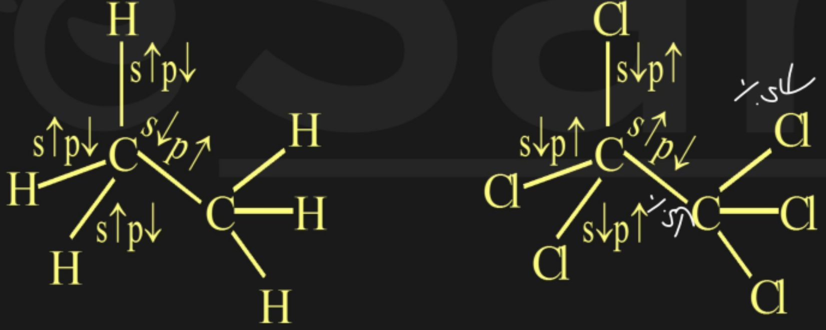
Q) Compare C–C bond length in C_2H_6 and C_2Cl_6

Cl > H

BS $s > p > d > f$ %s↑

BS↑ BL↓

$C–C(C_2H_6) > C–C(C_2Cl_6)$



Drago's Generalisation

Element of 3rd period (p-Block) and lower than 3rd period do not allow hybridisation in molecule when they form compound with less electronegative elements such as hydrogen

eg : PH_3, SiH_4, AsH_3 , H_2S do not undergo hybridisation

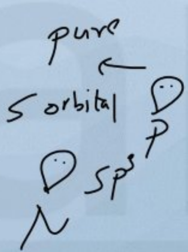
Basic Character $NH_3 > PH_3$

Lone pair of N is in sp^3

Lone pair of P is in almost pure s orbital (94%)

$PH_3 \rightarrow hyb^r$ ✗

$PF_3 \rightarrow hyb^r$ ✓

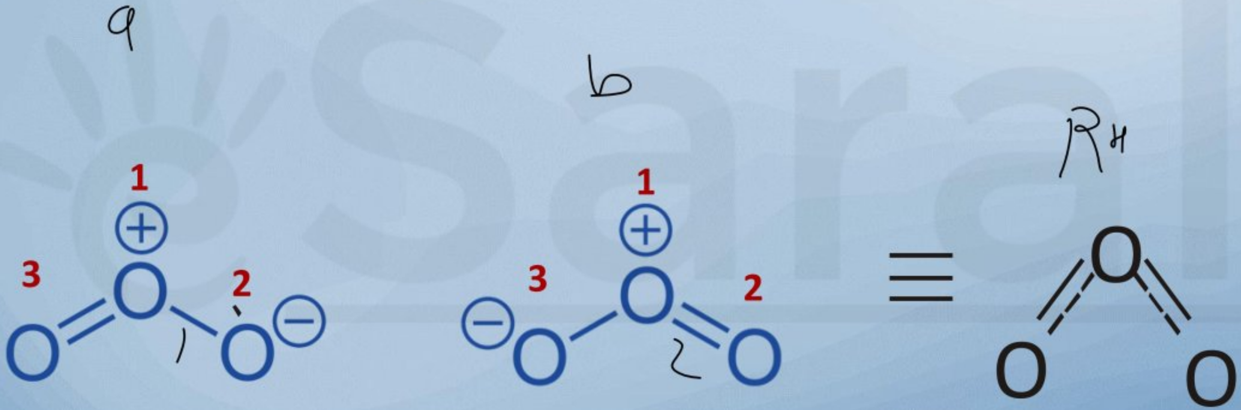


30%

$$\text{Bond order} = \frac{\text{Total number of bonds in all canonical forms}}{\text{Total canonical Structures}}$$

$\frac{3}{2}$

Resonance



O— O Bond order = 3/2 = 1.5

Back Bonding

2nd }
3rd }

B—F BL

single bond

Back bonding generally takes place when

1) Out of two bonded atoms one of the atom has vacant orbitals (generally this atom is from second or third period)

2) The other bonded atom is having some non-bonded electron pair(generally this atom is from the second period)

Both the conditions must be satisfied simultaneously

Q) Order of Lewis acid of following? → lp accepting

BF_3, BCl_3, BBr_3, BI_3

Ans.

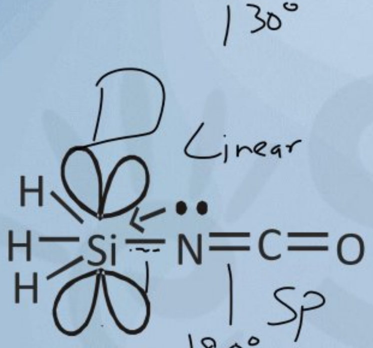
Best Moder No No

$BF_3 < BCl_3 < BBr_3 < BI_3$

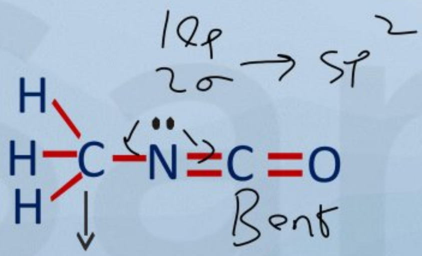
BB D D

Q) Silyl isocyanate (SiH_3NCO) is linear but methyl isocyanate (CH_3NCO) is bent explain.

Common



vacant
d-orbitals



No vacant
orbitals

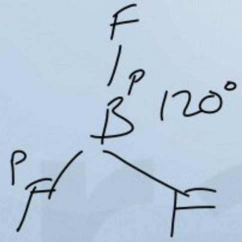
pπ–dπ back bonding

Type of bonding

So back bonding can be of two types.

1. $p\pi-p\pi$ (as in BF_3)
2. $p\pi-d\pi$ (as in silyl isocyanate)

$Si \rightarrow d$
p

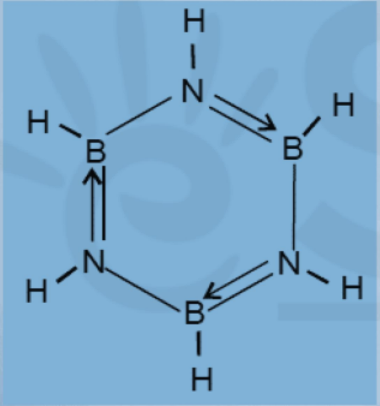


Effect of Back Bonding

1. Bond length decreases (BF_3)
2. Bond angle may increase (same in BF_3. Increases in silyl isocyanate)

3) Hybridisation of central atom may change (same in BF_3, for Nitrogen in silyl isocyanate it becomes sp from sp^2)

Inorganic Benzene



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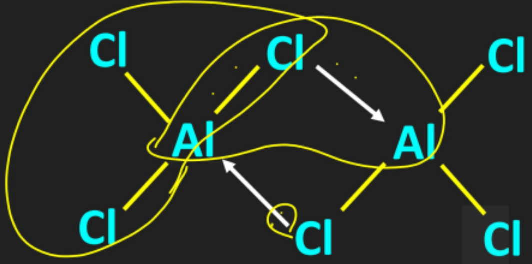
Bridge Bond

3 centered-4 electron

When lone pair involved.

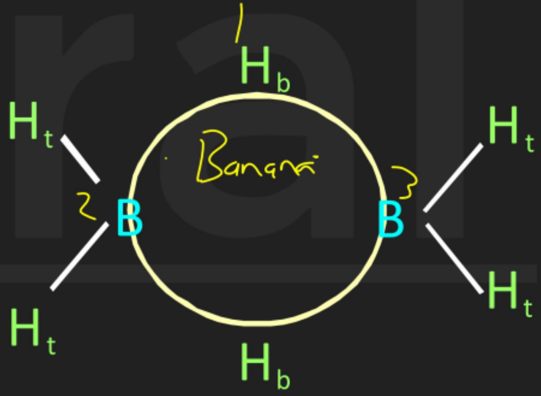
Example Al_2Cl_6



3 centered- 2 electron

When lone pair not involved.

Example B_2H_6



B_2H_6

Odd electron molecule

⊙

NO_2

7 16 23

ClO_2

ClO_3

BA ∝ % s-character

C :

$CH_4 \rightarrow 109.5°$

BA ∝ 1/presence of lp

107

BA ∝ EN of Central Atom

$$BA \propto \frac{1}{\text{EN of surrounding atom}}$$

rep↓ BA↓

BA ∝ size of surrounding atom

BL ∝ 1/% s-character

BL ∝ size

BL ∝ 1/BO

Q) Compare the bond energy in the following
F_2, Cl_2, Br_2 and I_2

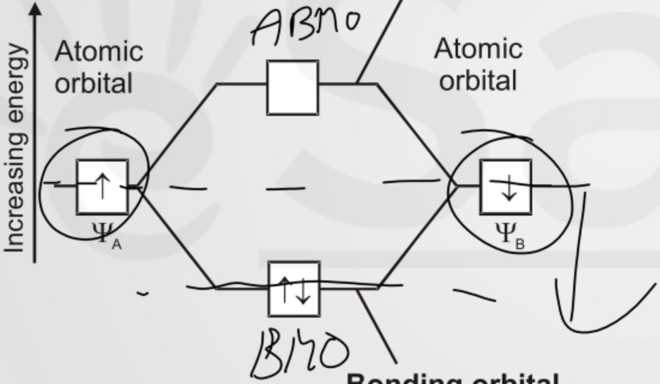
Bond Energy

Ans. $Cl_2 > Br_2 > F_2 > I_2$
Bond energy order (Experimental facts)

Molecular Orbital Theory

Molecular orbitals

Antibonding orbital
higher enrgy than
that of atomic orbitals



Bonding orbital
lower energy than
that of atomic orbital

Gerade and Ungerade

↳ symmetrical   un sym

Type	BMO	ABMO
σ	g, np=0	U, np=1
π	u, np=1	g, np=2

Energy Level Order For Molecular Orbitals

jyada to σ peeche

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2_{pz} < (\pi 2_{px} = \pi\ 2_{py}) < \pi^* 2_{px} = \pi^* 2_{pz} < \sigma^* 2_{pz}$

For elctrons > 14

Example: O_2, F_2

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2_{px} = \pi\ 2_{py}) < \sigma 2_{pz} < \pi^* 2_{px} = \pi^* 2_{py} < \sigma^* 2_{pz}$

For electrons ≤ 14

Example: C_2, N_2

Electronic configuration and molecular behaviour

$BO \leq 0$ unstable

$BO > 0$ stable

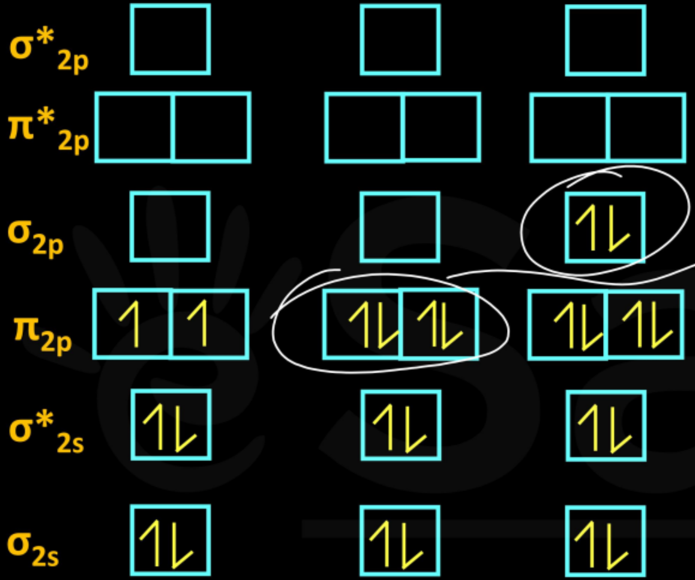
N_b-number of e^- in BMO

N_a-number of e^- in ABMO

(i) The molecule is stable if N_b is greater than N_a

(ii) The molecule is unstable if N_b is less than N_a

$$\boxed{\text{Bond order (B.O.)} = \tfrac{1}{2}(N_b - N_a)}$$



N_2 का σ

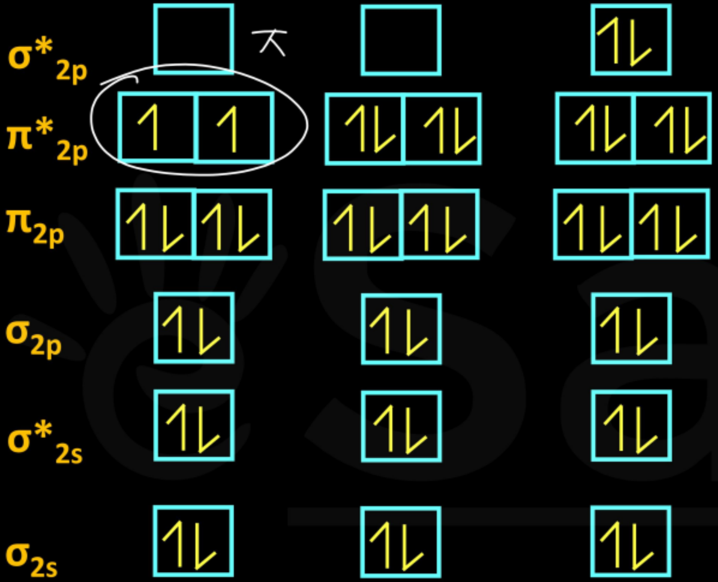
→ 2 pi bonds

no σ bond

BO $B_2 = 1$ $C_2 = 2$ $N_2 = 3$

$\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < (\pi_{2px} = \pi_{2py}) < \sigma_{2pz} < \pi^*_{2px} = \pi^*2_{py} < \sigma^*2_{pz}$

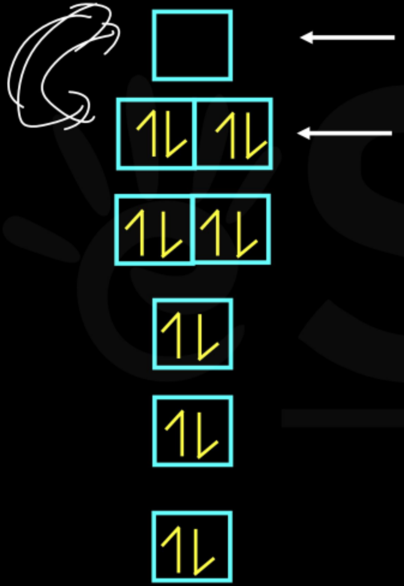
For electrons ≤14



$O_2 = 2$ $F_2 = 1$ $Ne_2 = 0$

O_2 ka π^*
↳ paramagnetic

$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2pz} < (\pi_{2px} = \pi_{2py}) <$
$\pi^*_{2px} = \pi^*_{2py} < \sigma^*_{2pz}$ For elctrons > 14

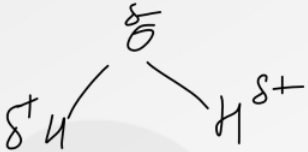


LUMO

HOMO

F_2	Pale Yellow
Cl_2	Greenish
Br_2	Red-Brown
I_2	Violet

Dipole Moment

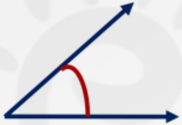


$$\boxed{\mu = q \times d}$$

q = magnitude of charge on any one of the atom of the bond.

d = distance between two atoms of the bond.

Resultant DM



$$\mu_{\text{resultant}} = \sqrt{\mu_1{}^2 + \mu_2{}^2 + 2\mu_1\mu_2\cos\theta}$$

Q) What is the order of Dipole Moment in HF, HCl, HBr, HI?

EN diff

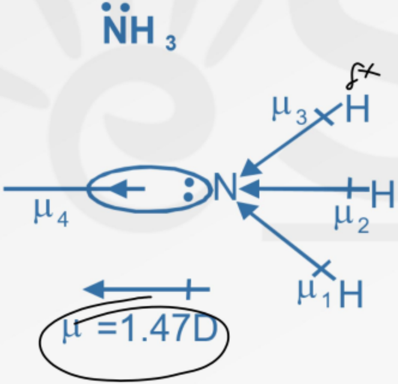
δ+↑

HF > HCl > HBr > HI

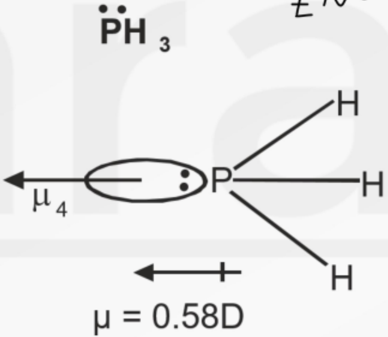
1.92D, 1.03D, 0.78D, 0.38D

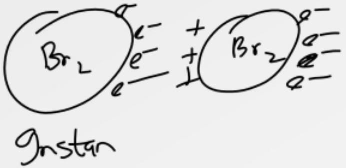
EN↑ Dipole MT↑

Chem +ve → -ve

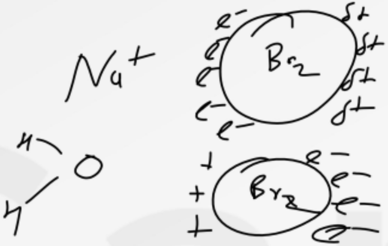


EN↓





Weak Bonds



(a) Ion-dipole attraction

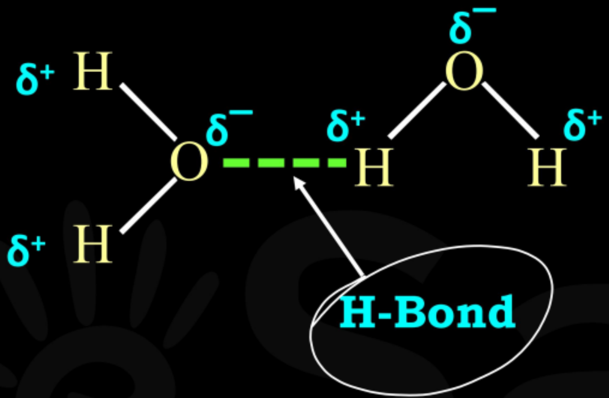
(b) Dipole-dipole attraction

(c) Ion-induced dipole attraction

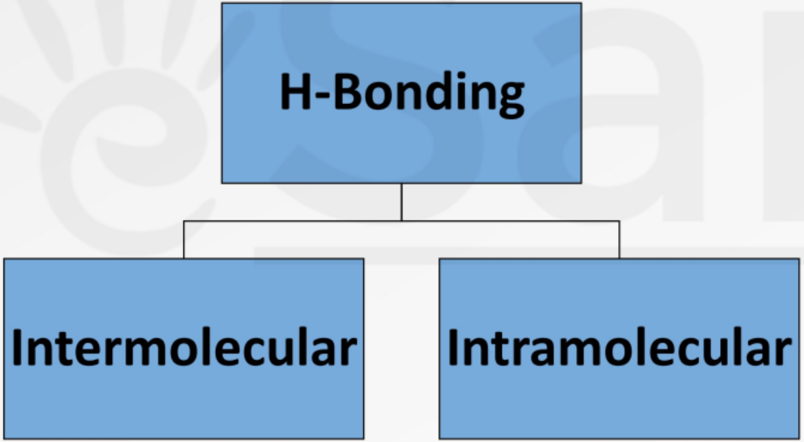
(d) Dipole-induced dipole attraction

(e) Instantaneous dipole-Induced dipole (Dispersion force or London forces)

strength of Weak bonds a > b > c > d > e

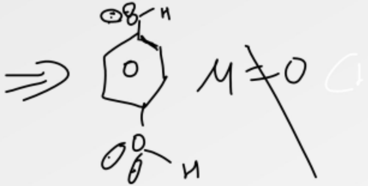


1) Happens in the case of high EN elements.
Such as F, O and N.



H-Bonding

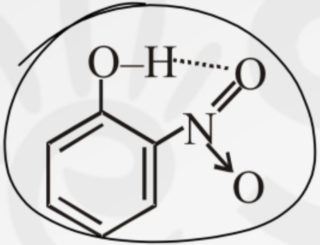
- Intermolecular
- Intramolecular



H-bonding

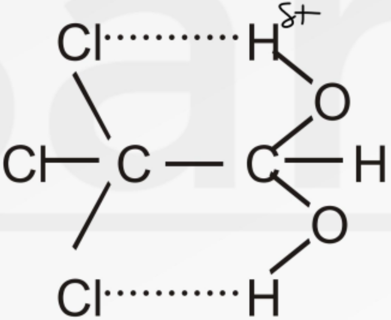
CH_3COOH — monomer

— Dimer → Intermol H-bonding



o-nitrophenol
less soluble in water

Butterfly shape



Chloral hydrate

Electrovalent or Ionic bond

NaCl → Lattice Energy released

Low I.E. ✓✓

High EA ✓✓

High LE

p-block electrovalency

→ Variable

Pb^{+2} Pb^{+4}

NO

N_2O_5

N_2O_3

Variable Electrovalency

Inert pair effect

Tendency of the s subshell electrons of p block to become inert to bonding in the elements at the bottom of the groups.

Increased effective nuclear charge at the bottom of the groups.

$Pb^{+2} > Pb^{+4}$
$Tl^{+1} > Tl^{+3}$

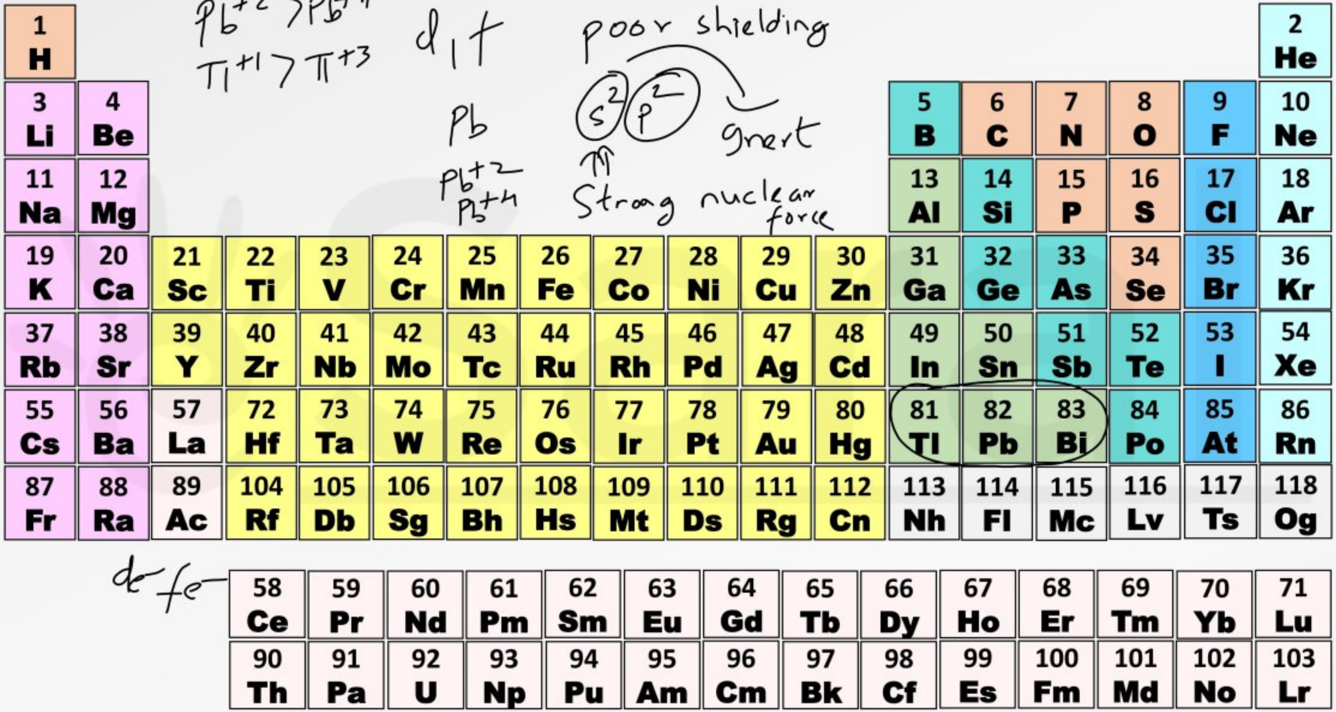
d, f

poor shielding

s^2 p^2 inert

Pb
Pb^{+2}
Pb^{+4}

↑↑ Strong nuclear force



1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
		d- f-	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
			90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Fajan’s Rules

$BeCl_2 \rightarrow$ Ionic comp

Charge ↑ ϕ ↑

Size ↓ ϕ ↑

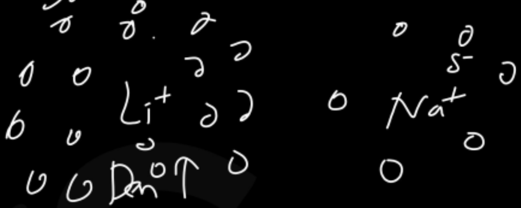
$$\text{Ionic Potential } \phi \text{ (phi)} \propto \frac{\text{Charge on cation}}{\text{Size of Cation}}$$

No comp is 100%

gonic

Summary

Φ ↑



Φ ↑	Color ↑ cov ↑
Φ ↑	Solubility in polar solvent ↓ cov ↑
Φ ↑	Thermal Stability of polyatomic anion ↓
Φ ↑	Melting point ↓
Φ ↑	Ionic Mobility ↓

$$MCO_3 \xrightarrow{\Delta} MO + CO_2$$

$Na_2CO_3 \xrightarrow{\Delta} CO_2 \times$

$Li_2CO_3 \xrightarrow{\Delta} CO_2 \uparrow$

Carbonates of alkali metals other than Li_2CO_3 do not decompose on heating, they melt on heating.

Thermal Stability of Metal Sulphates

$MSO_4 \xrightarrow{\Delta} MO + SO_3$ (T> 800^0 C then $SO_3 \longrightarrow SO_2 + \frac{1}{2}O_2$)

Thermal Stability of Metal Nitrates

$$2MNO_3 \xrightarrow{\Delta} M_2O + 2NO_2 + \frac{1}{2}O_2$$

MP Exception

Covalent

$NaCl > KCl > RbCl > CsCl > LiCL$

Condition for Solvation

NaCl

$O^{\delta-}$

O^{δ} Na^+

O O O

NaCl Na^+ Cl^-

Lattice Energy

$$\Delta H_{\text{hydration}} > \Delta H_{\text{Lattice energy}}$$

SO_4^{2-}

Generally solubility increases down the group, but in case of polyatomic anion it decreases down the group when number of anion is ≥ number of cations.

Exceptions

CB samapt

1) $BaF_2 > BeF_2 > SrF_2 > CaF_2 > MgF_2$

Learn

Above happens because BeX_2 forms a soluble complex in water, leading to increased solubility.

2) NaCl > KCl > RbCl > CsCl > LiCl

3) NaF > KF > LiF > RbF > CsF

4) $MgC_2O_4 < CaC_2O_4 < SrC_2O_4 < BaC_2O_4 < BeC_2O_4$

(A) Double Salts

Break down into simpler ions.

$A\{BCD\}$

$A^+ \, [BCD]^-$

$M \leftarrow L$

(B) Coordination Compounds

Retain their identity in solution.

(I) Perfect Complexes

(II) Imperfect Complexes

Classification of Ligands

(A) Based on charge

(i) Neutral ligands

H_2O, NO, CO, C_6H_6 etc.

(ii) Positive ligands NO^+, $N_2H^+{}_5$

(iii) Negative ligands

Cl^- , $NO^-{}_2$, CN^- , OH^-

~~(b) Bidentate ligands~~

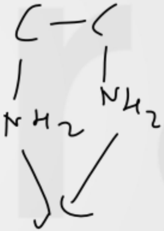
denticity

(a) Unidentate/monodentate ligands

1 lp

X^-, CN^-, NO_2^-, NH_3, Pyridine, OH^-, NO_3^-, H_2O, SO_3^{-2}, CO, NO, OH^-, O^{-2}, $(C_6H_5)_3P$, CH_3CO^- etc.

(b) Based on denticity



2 lp

en, bn, pn, ox, DMG, gly, Dipy.

(c) Tridentate ligands

Dien, imda, Terpy.

(d) Hexadentate ligands

EDTA

(h) Ambidentate ligands

$\left[\begin{array}{l} CN^- \\ NC^- \end{array}\right.$ $\left[\begin{array}{l} NO_2^- \\ ONO^- \end{array}\right.$ $\left[\begin{array}{l} SCN^- \\ NCS^- \end{array}\right.$ $\left[\begin{array}{l} CNO^- \\ NCO^- \end{array}\right.$ $\left[\begin{array}{l} S_2O_3^{2-} \\ OSO_2S^{2-} \end{array}\right.$

1lp

(C) Based upon bonding interaction between the ligand and the central atom.

(i) Classical or simple ligand dene waale

(ii) Non classical or π-acid or π -acceptor ligand len-den waale

(a) σ donor π acceptor Ex. CO, CN^-, NO^+, PF_3, PR_3 etc.

(b) π donor π acceptor Ex. C_2H_4, C_6H_6, $C_5H_5^-$ etc.

Sidgwick Theory or Effective Atomic Number Concept (EAN)

↳ Octet

EAN = (atomic number of the metal – oxidation state of central metal) + number of electrons gained from the donor atoms of the ligands.

$[Co(NH_3)_6]Cl_3$ +3

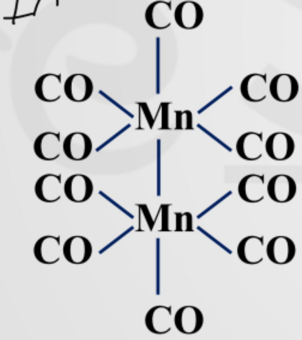
6

EAN = 36

$(27 - 3) + (6 \times 2)$

24

= 36 (kr) → noble gas



$Mn_2(CO)_{10}$

Werner's Co-ordination Theory

Father

Q) Old	New	No. of Cl^- Ions precipitate	Total No. of ions
(i) $\overset{+3}{Co}\overset{-3}{Cl_3}\cdot \overset{\leftarrow}{6}NH_3$	$\overset{\text{secondary}}{[Co(NH_3)_6]}\overset{\text{Primary}}{Cl_3}$	3	4
(ii) $CoCl_3\cdot \overset{\leftarrow}{5}NH_3$	$[Co(NH_3)_5Cl]Cl_2$	2	3
(iii) $CoCl_3\cdot \overset{\leftarrow}{4}NH_3$	$[Co(NH_3)_4Cl_2]Cl$	1	2

Sol. Order of electrical conductivity of $\propto$ no of ions
aq. solution. (i) > (ii) > (iii)

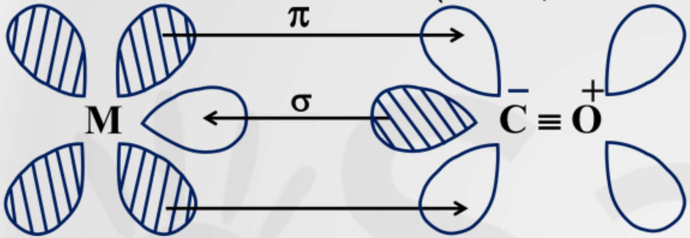
Synergic Bonding

BO↑

ABMO ↑ BO↓

π → acceptor

$\frac{1}{2}(N_b - N_a)$



non-classical

σ - donor , π - acceptor

Synergic Bonding

M — C — O

B.O. ↑ ↓

B.L. ↓ ↑

IUPAC nomenclature of coordination compounds

(a) Like simple salts, the positive part of the coordination compound is named first.

(b) Naming of coordination sphere

The names of ligands along with their numerical prefixes (to represent their no.) are written first, followed by the name of central metal.

(c) The ligands can be neutral, anionic or cationic.

(i) The neutral ligands are named as the molecule

C_5H_5N [pyridine]

$(C_6H_5)_3P$ [Triphenyl phosphine]

$H_2N-CH_2-CH_2-NH_2$ [ethylene diamine]

CH_3NH_2 [methyl amine]

Me_2O [diemthyl ether]

The neutral ligands which are not named as the molecule are

CO [carbonyl]

CS [thiocarbonyl]

NO [nitrosyl]

H_2O [aqua]

NH_3 [ammine]

Symbol	Name as ligand	Symbol	Name as ligand
Cl^-	Chloro/Chlorido	N^{3-}	Nitrido
Br^-	Bromo/Bromido	O_2^{2-}	Peroxo/Peroxido
CN^-	Cyano/Cyanido	O_2H^-	Perhydroxo/Perhydroxido
O^{2-}	Oxo/Oxido	S^{2-}	Sulphido
OH^-	Hydroxo/Hydroxido	NH^{2-}	Imido
H^-	Hydrido	NH_2^-	Amido

Symbol	Name as ligand	Symbol	Name as ligand
CO_3^{2-}	Carbonato	SO_3^{2-}	Sulphito
$C_2O_4^{2-}$	Oxalato	CH_3COO^-	Acetato
SO_4^{2-}	Sulphato	ClO_3^-	Chlorate
NO_3^-	Nitrato		
$S_2O_3^{-2}$	Thiousulphate		

(iii) Positive ligand naming ends in 'ium'

$NH_2 - NH_3^+$ [Hydrazinium]

NO_2^+ [nitronium]

NO^+ [nitrosonium/nitrosylium]

(iv) Ambidentate ligands

NO_2^- [nitro, nitrito-N]

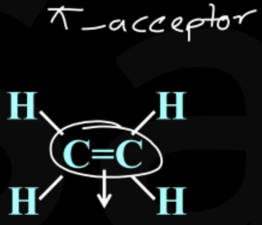
ONO^- [nitrito-O]

CN^- [cyano/cynido]

(v) π-donor and π-acceptor ligands

Prefix of Greek letter η^x (ita) is repeated before the name of each different kind of π- donar, π- acceptor ligand.

Where x is the number of carbon atoms to which donated electron cloud is bounded. x is known as heptacity of ligand.

				no. of donated e^-
(i)	π-C_2H_4		η^2-ethylene	2
(ii)	π-$C_5H_5^-$		η^5-cyclopentadienyl	6

(d) If ligands are present more than once, then their number is indicated by prefixes like di, tri, tetra etc.

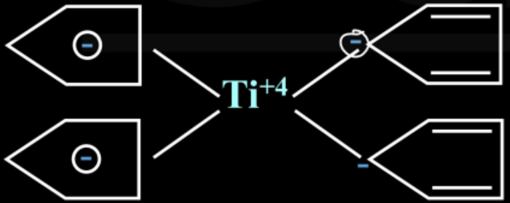
Ex: $[Cr(H_2O)_4Cl_2]^{+}Cl$

Tetraaquadichlorochromium(III)Chloride

(e) If words like di, tri, tetra are already used in the naming of ligand, or if it is polydented ligand or organic ligand, the prefixes bis–, tris– tetrakis–, pentakis– etc. are used to specify their number.

Example

$Ti(\sigma\text{-}C_5H_5)_2(\pi\text{-}C_5H_5)_2$ Bis(η^1-cyclopentadienyl)bis(η^5-cyclopentadienyl) titanium(IV)



If the complex is the part of anion then
some of center metal atom/ion is named as

Al – aluminate

Pt – Platinate

Mo – Molybdate

Ni – Nickelate

Fe – Ferrate

Mn – Manganate

Q) The naming of some of the complexes is done as follows (as per IUPAC)

Complex Compounds	IUPAC Name
Anionic (i) $K_4[Fe(CN)_6]$ (anionic complex) so suffix 'ate' is added with metal name	Potassium hexacyanoferrate(II)
(ii) $K_2[Pt\,Cl_6]$	Potassium hexachloroplatinate(IV)
(iii) $[Co(NH_3)_6]\,Cl_3$ (Cationic complex) so metal is without any suffix	Hexamminecobalt (III) Chloride

(i) If a complex ion has two metal atoms then it is termed polynuclear.

The ligand which connects the two metal ions is called as Bridging ligand or Bridge group.

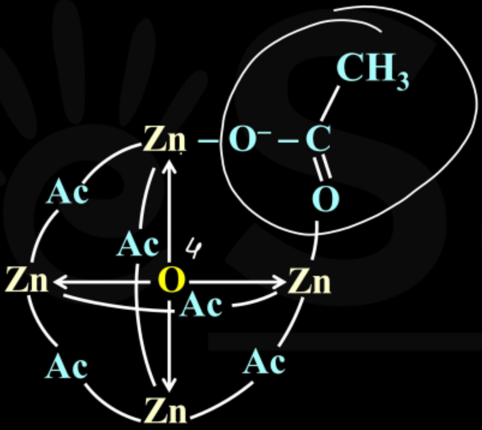
A prefix of Greek letter μ^x is repeated before the name of each different kind of bridging group.

Where x is number of center metal atom/ion joined by one bridge ligand.The value of x is only mentioned when it is more than two.

Q) $[Zn_4O(CH_3COO)_6]$

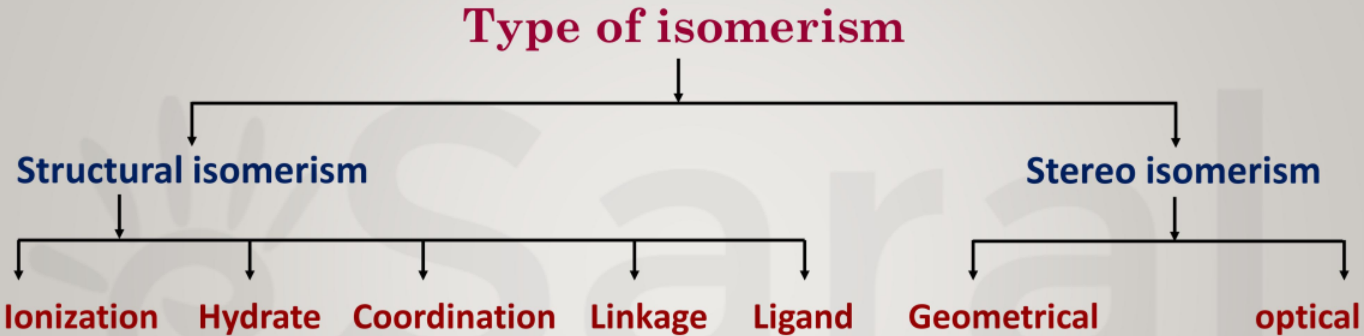
2 donation μ^x × $x > 2$

Sol. Hexa-μ–acetato – μ⁴– oxido –tetrazinc(II)



Ac : CH_3COO^-

Classification of Isomerism



Type of isomerism

- Structural isomerism
  - Ionization
  - Hydrate
  - Coordination
  - Linkage
  - Ligand
- Stereo isomerism
  - Geometrical
  - optical

(a) Ionisation isomerism

Q) Find the ionisation isomers of the following

(1) $Co(NH_3)_4Br_2SO_4$

Sol. $[Co(NH_3)_4Br_2]SO_4$ (red violet)
and $[Co(NH_3)_4SO_4]Br_2$ (red)

(b) Hydrate isomerism

Q) Find the hydrate/solvate isomers of $Cr(H_2O)_6Cl_3$ Compound.

Sol. $Cr(H_2O)_6Cl_3$ has four possible structures

(i) $[Cr(H_2O)_6]Cl_3$ violet 0

(ii) $[Cr(H_2O)_5Cl]\ Cl_2 .H_2O$ green 1

(iii) $[Cr(H_2O)_4Cl_2]Cl\ .\ 2H_2O$ dark green 2

(iv) $[Cr(H_2O)_3Cl_3].3H_2O$ dark green 7

(c) Linkage isomerism

(i) This type of isomerism arises due to presence of ambidentate ligands like NO_2^-, CN^- and SCN^-

(d) Coordination isomerism

(i) This type of isomerism is exhibited when the complex has two complex ions in it - 'Cationic and anionic'.

$[Cu(NH_3)Cl][Pt(NH_3)(Cl)_3]$

$[\overset{+2}{Cu}(NH_3)_2Cl_2^{-2}]$ $(Pt(Cl_2)(NH_3)_2)$

×

neutral

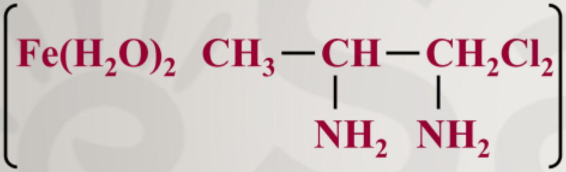
(a) $[Cu(NH_3)_4][PtCl_4]$

Ans. 4

(e) Ligand isomerism

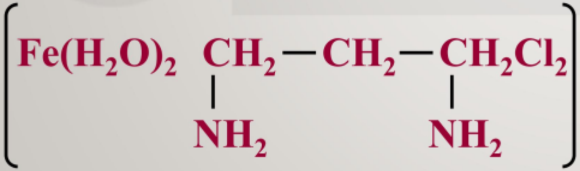
Q) Find the ligand isomers of $[Fe(H_2O)_2\,C_3H_6(NH_2)_2Cl_2]$

Sol. It has two different ligand structures



$$\left[Fe(H_2O)_2\ \ CH_3-\underset{NH_2}{\underset{|}{CH}}-\underset{NH_2}{\underset{|}{CH_2}}Cl_2\right]$$

and



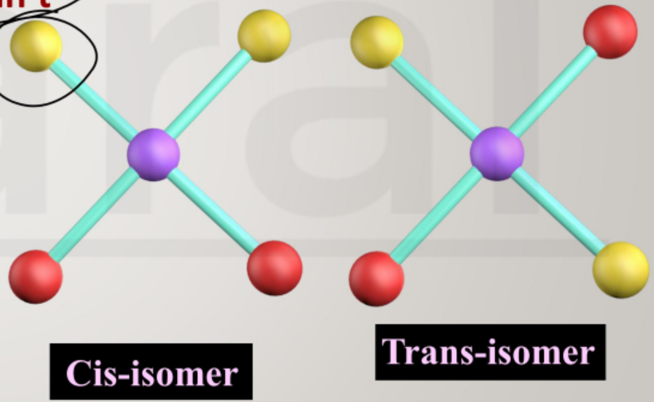
$$\left[Fe(H_2O)_2\ \ \underset{NH_2}{\underset{|}{CH_2}}-CH_2-\underset{NH_2}{\underset{|}{CH_2}}Cl_2\right]$$

(B) Stereo Isomerism

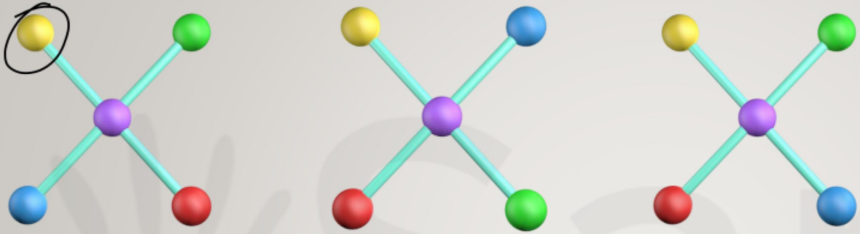
(a) Geometrical Isomerism

(i) Ma_4, Ma_3b, $M(AA)_2$, $M(AA)a_2$, $M(AA)ab$, $M(AB)a_2$, $M(AA)(AB)$, $M(AA)(BB)$ can't show GI.

(i) Complexes with general formula, Ma_2b_2 (where both a and b are monodentate) can have Cis-and trans isomers.



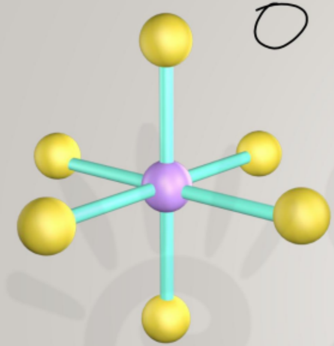
Complex Mabcd



Stereoisomerism In Octahedral Complexes

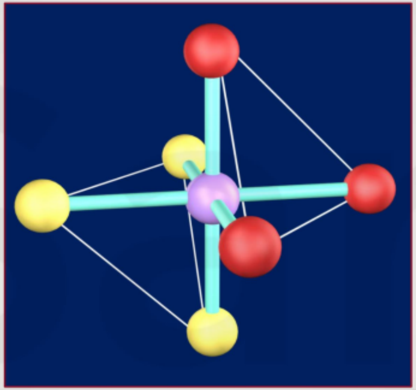
Ma_6

0



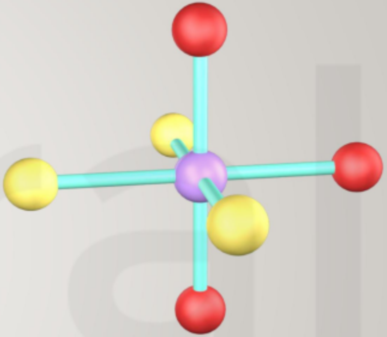
Learn **Ma_3b_3**

fac



Special

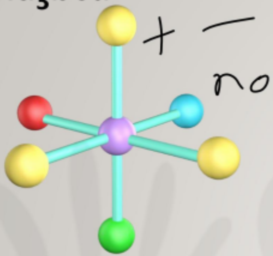
mer



Ma_3bcd

mahamantra

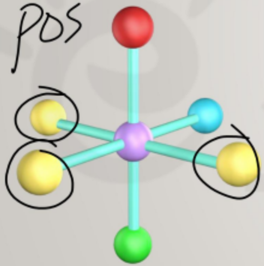
OA

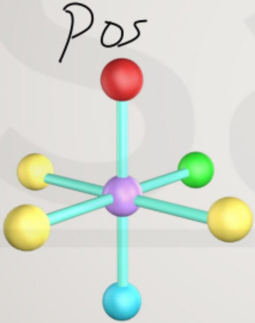


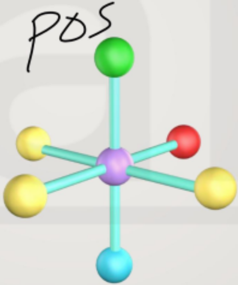
Octahedral

2 same species in trans

Optically Inactive



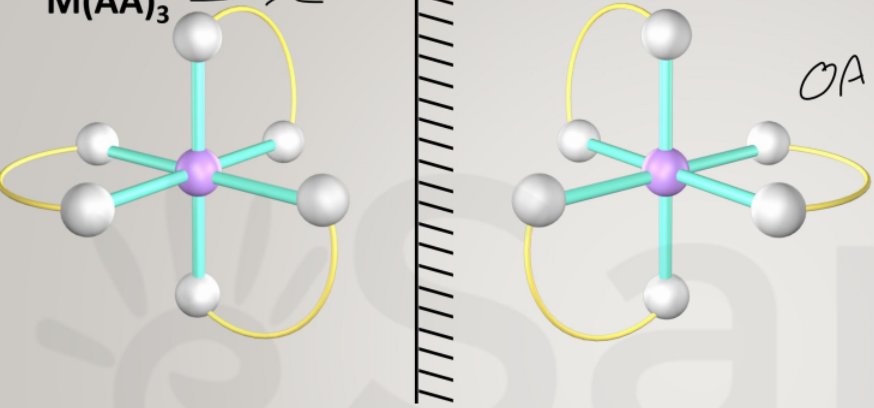




General formula	GI	Pairs of Enantiomers	Total
Ma_6	1	0	1
Ma_5b	1	0	1
Ma_4b_2	2	0	2
Ma_4bc	2	0	2
Ma_3b_3	2	0	2
Ma_3b_2c	3	0	3
Ma_3bcd	4	1	5
$Ma_2b_2c_2$	5	1	6
Ma_2b_2cd	6	2	8
Ma_2bcde	9	6	15
$Mabcdef$	15	15	30

mono dentate

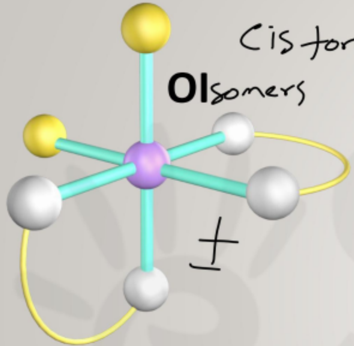
$M(AA)_3 \longrightarrow 2$



OA ± 2

M(AA)$_2$a$_2$

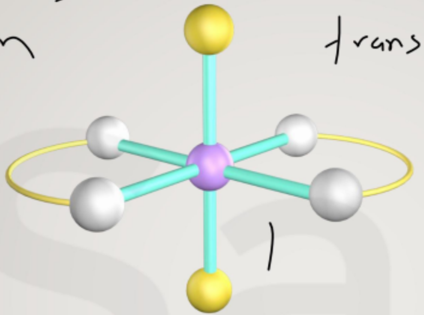
3



Cis form

OIsomers

±



trans

1

Valence Bond Theory

(i) In octahedral complexes with CM having d^0, d^1, d^2, d^3 configuration, pairing of e^- don't take place, no matter what the ligand is.

And all such complexes are inner orbital complexes with $\mu = 0, \sqrt{3}, \sqrt{8}, \sqrt{15}$ respectively (d^2sp^3 configuration)

d^0 **Diamagnetic**

d^1, d^2, d^3 **Paramagnetic**

(ii) In octahedral complexes with CM having d^8, d^9, d^{10} configuration pairing of e^- doesn't take place, whatever be the ligand, and all such complexes are **outer orbital complex** (sp^3d^2) with $\mu = \sqrt{8}, \sqrt{3}, 0$ BM respectively.

$K_4[\overset{II}{Fe}(CN)_5(O_2)]$ → paramagnetism

is parameganetic due to parameganetic nature of O_2^- (superoxido)

3d

4d, 5d

d φ

Irres of Ligands
↓
pairing

(vi) In all the octahedral complexes of 4d and 5d series metal ions with configuration d^4, d^5, d^6 and d^7, pairing of e^- takes place whatever may be the ligand.

Q) For $[Fe(H_2O)_{\underset{5}{5}}\underset{+1}{NO}]SO_4$ (Brown ring complex), $\mu = \sqrt{15}\ \mathrm{B.M.}$ Select the correct statement(s)

(A) oxidation state of Fe is +1

(B) geometry is octahedral

(C) hybirdisation of Fe is sp^3d^2

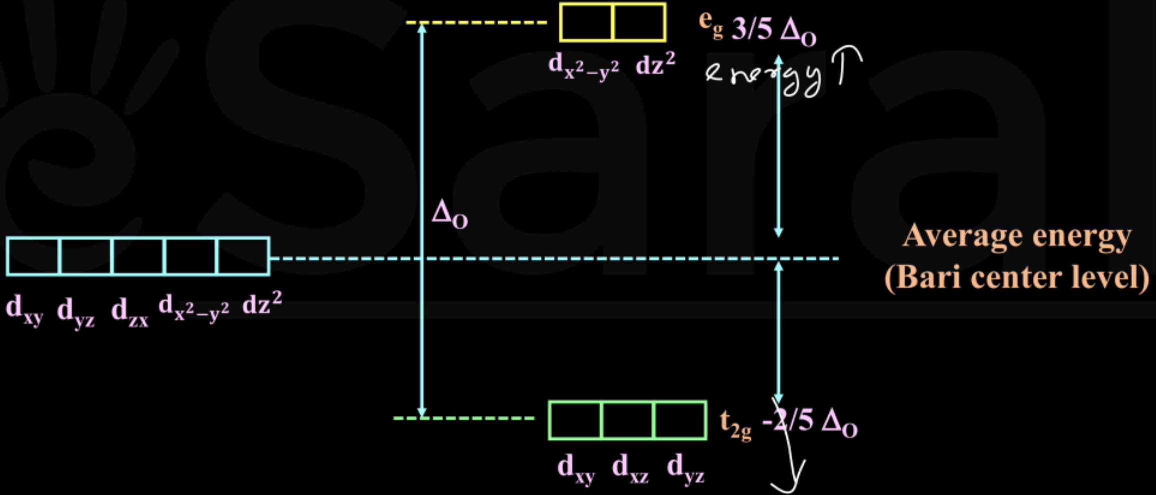
(D) NO is neutral ligand

Ans. A, B, C

Crystal Field Theory

Ligand → axis

Crystal field splitting for octahedral complex



CFSE depends upon the following factors

1. Higher the charge on the metal ion higher will be CFSE.
2. It depends upon the nature of metal ion, that is the metal ion is of which transition series.

4d, 5d CFSE super high

3. It depends upon the nature of ligand.

WFL ←

→ SFL

Spectrochemical series

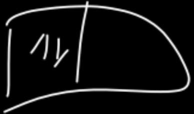
$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O \,|\, < NCS^- < EDTA^{4-}$
$< NH_3 < en < NO_2^- < CN^- < CO$

3. It depends upon geometry.

$\Delta_{sp} > \Delta_O > \Delta_t$

$\Delta_{sp} > 1.3\Delta_O$

$\Delta_t > 4/9\Delta_O$



d^2sp^3

sp^3d^2

Mean pairing energy (P)

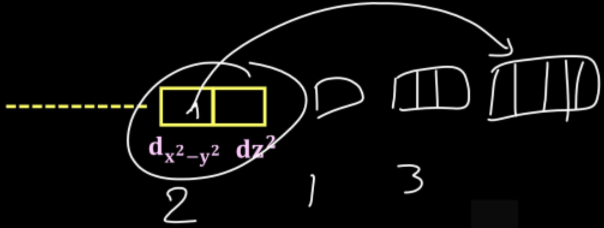
It is the energy required for electron pairing in a single orbital. And it is defined per pair. d^4

(i) If $\Delta_O < P$, $t^3_{2g}e_g^1$

(ii) If $\Delta_O > P$, $t_{2g}^4 e_g^0$.

$d^0 \rightarrow d^3$ × d^2sp^3

$d^8 - d^{10}$ × sp^3d^2



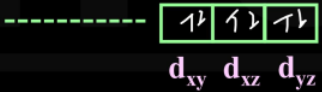
d^2sp^3

d^4, d^5, d^6, d^7

WFL → sp^3d^2

SFL → d^2sp^3

d^7 will shift its 7th e- to the higher energy level



WFL + SFL → Can't be predicted unless the relationship b/w Δ_O & P is directly or indirectly given.

high spin

magnetic moment

hybr

WFL

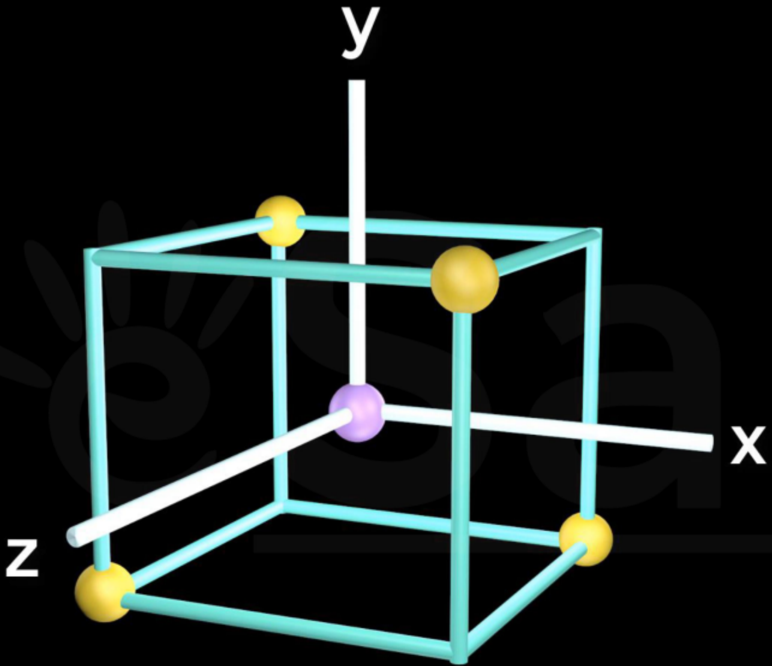
	No. of upe
d^4	4
d^5	5
d^6	4
d^7	3

high spin

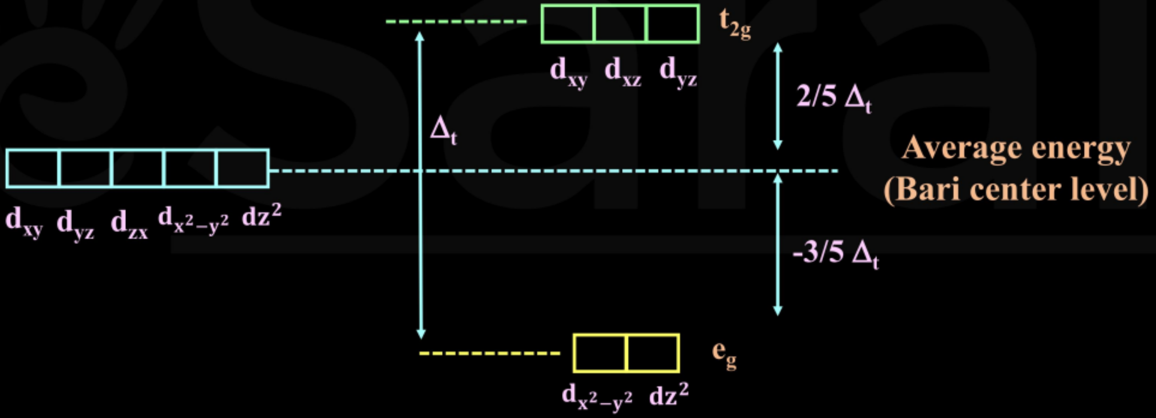
SFL

	No. of upe
d^4	2
d^5	1
d^6	0
d^7	1

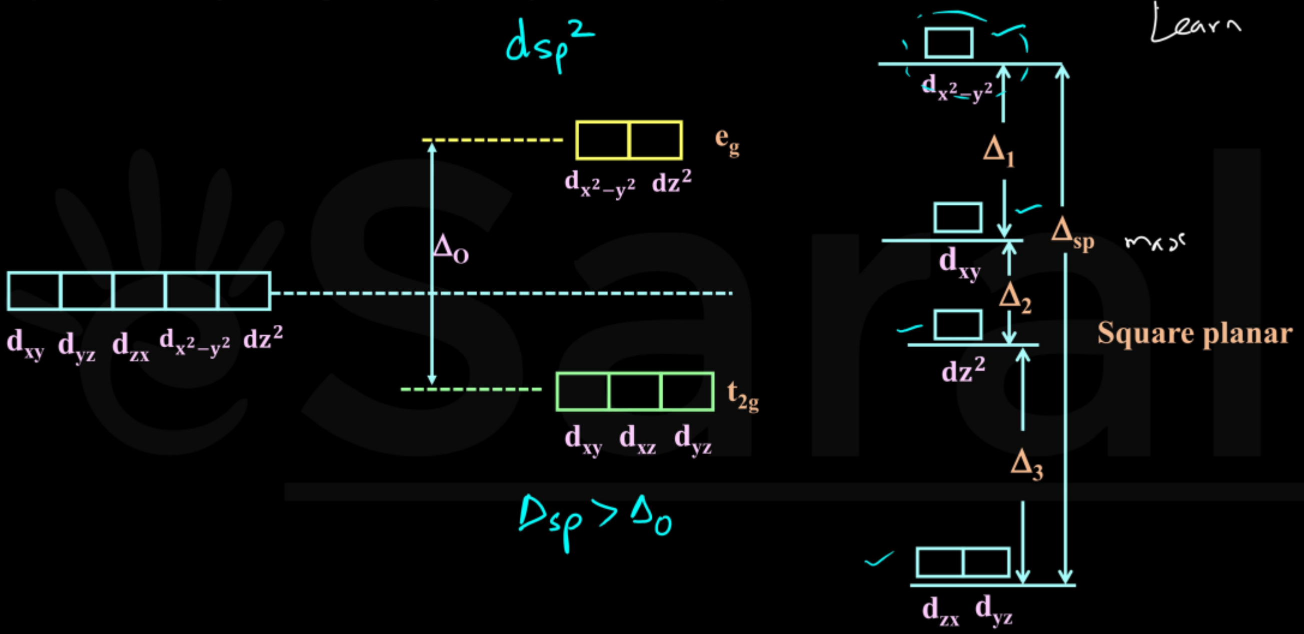
Low Spin


y
x
z

Crystal field splitting for tetrahedral complex



Crystal field splitting for square planar complex



$\Delta_{sp} > \Delta_o$

CN = 4

WFL → sp^3 (outer orbital complex)

tetrahedral

SFL → dsp^2 (inner orbital complex)

Not valid for d^{10} Sq planar

Q) Which of the following are expected to have non sp^3 hybridisation but tetrahedral geometry?

d^3s CN 4 d^0, d^1 Learn

6 $4s^1$ $3d^5$

(A) $[Ni(CO)_4]$ (B) $[PtCl_4]^{2+}$ ✓ (C) $[CrO_4^{2-}]$ Cr (D) NH_3

+6 d^0

d^1

Sol. Since this is a d^0 system.

Ans. (C)

WFL

* $[Mn(NH_3)_6]^{2+}$

Learnt

WFL

* $[Fe(NH_3)_6]^{2+}$

SFL

* $[Co(H_2O)_6]^{3+}$

SFL

* $[NiF_6]^{2-}$

(F) Factors Influencing the Magnitude of CFSE

× $[Co(NH_3)_6]^{3+}$ rings > $[Co(en)_3]^{3+}$

5d > 4d > 3d (CFSE

1. Higher the CFSE value higher will be the stability of complex

   a) $[Fe(H_2O)_6]^{3+} > [Fe(H_2O)_6]^{2+}$

   b) $[CoCl_6]^{3-} < [Co(C_2O_4)_3]^{3-} < [Co(CN)_6]^{3-}$

   c) $[ML_4]^{n\pm} > [ML_6]^{n\pm} > [ML_4]^{n\pm}$

   d) $\overset{3d}{[Co(NH_3)_6]^{3+}} < \overset{4d}{[Rh(NH_3)_6]^{3+}} < \overset{5d}{[Ir(NH_3)_6]^{3+}}$

2. Chelated complexes are more stable than non-chelated complexes given the donor atoms are same

(ii) $[Pd(en)_2]Cl_2$ < $[Pd(trien)]Cl_2$

2 rings 3 rings

3. Same charges on the cation but the number of d-electrons is different

d electrons ↑ stability ↑

The magnitude of CFSE increases with the increase of the number of d-electrons.

de^- ↑

e.g., $[Co(H_2O)_6]^{2+} < [Ni(H_2O)_6]^{2+}$

Colour In Coordination Compounds

According to the crystal field theory the colour of coordination compound is due to d-d transition of electron

Colour wheel

VIBGYOR

$\lambda \uparrow$

Q) The correct order for the wavelength of absorption in the visible resion is

Energy$\uparrow$ $\lambda\downarrow$

Energy$\uparrow$ $\lambda\downarrow$ E$\downarrow$ $\lambda\uparrow$

(A) $[Ni(NO_2)_6]^{4-} < [Ni(NH_3)_6]^{2+} < [Ni(H_2O)_6]^{2+}$

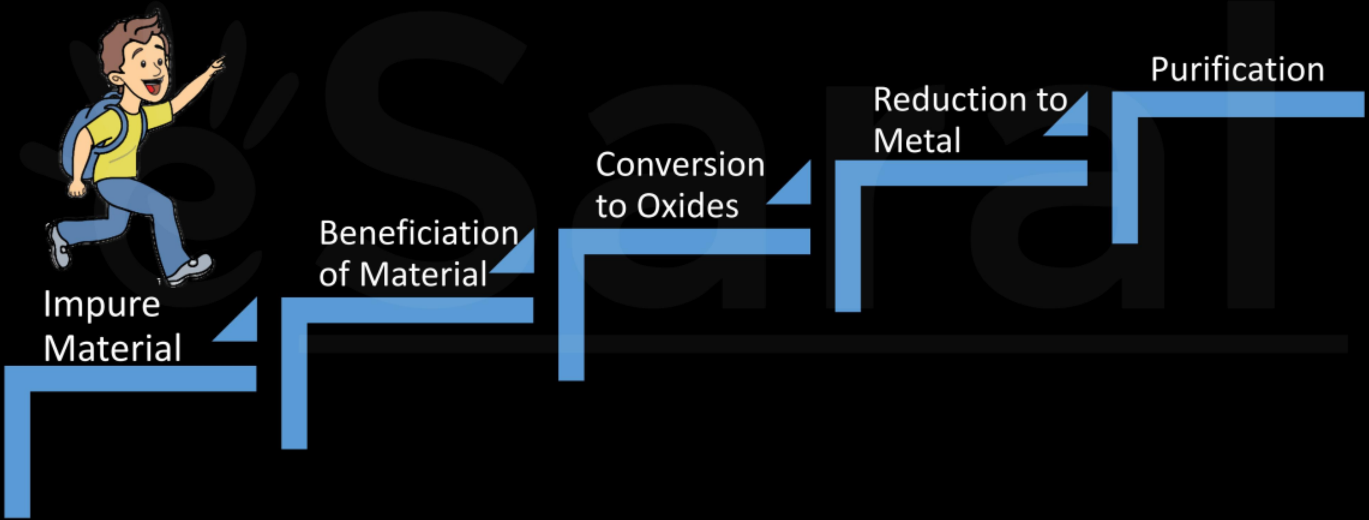
(B) $[Ni(NO_2)_6]^{4-} < [Ni(H_2O)_6]^{2+} < [Ni(NH_3)_6]^{2+}$

(C) $[Ni(H_2O)_6]^{2+} < [Ni(NH_3)_6]^{2+} < [Ni(NO_2)_6]^{4-}$

(D) $[Ni(NH_3)_6]^{2+} < [Ni(H_2O)_6]^{2+} < [Ni(NO_2)_6]^{4-}$

Ans. (A)

Metallurgy



Impure Material

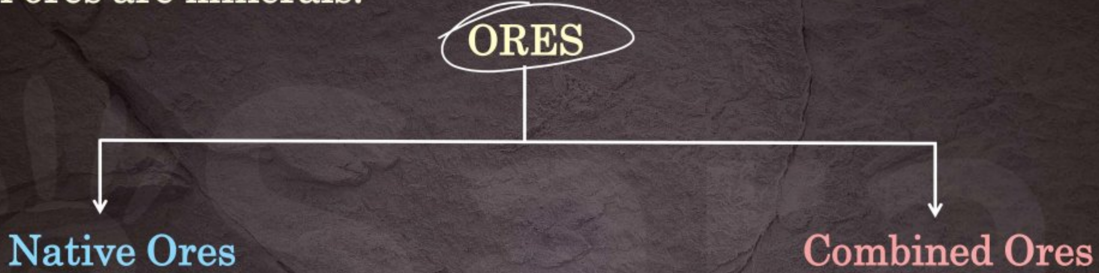
Beneficiation of Material

Conversion to Oxides

Reduction to Metal

Purification

All minerals are not ores
but all ores are minerals.



ORES

Native Ores

Combined Ores

Silver, gold, platinum etc, occur as native ores.

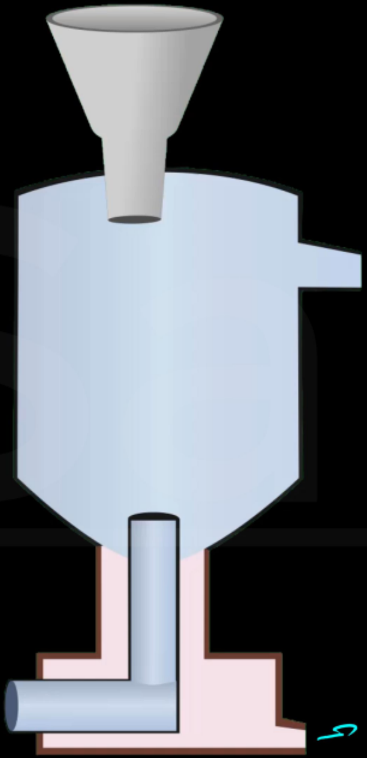
They contain the metal in combined form.

An ore is usually contaminated with earthy or undesired materials known as gangue.

Physical Separation Method

Hydraulic washing or Gravity separation or Levigation method

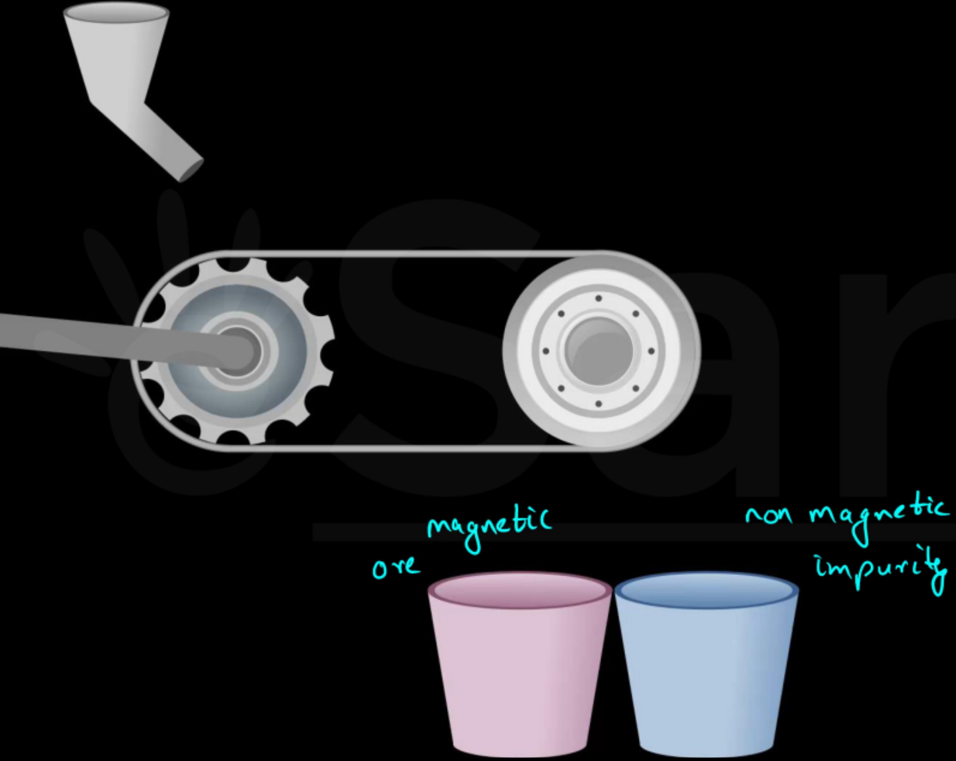
This method is generally used for the concentration of oxide and native ores.


→ lighter particles

Magnetic Separation

It is used when either the ore or the impurities associated with it are magnetic in nature.

Chromite ore($FeO.Cr_2O_3$) is separated from non–magnetic silicious impurities and cassiterite ore(SnO_2) is separated from magnetic Wolframite ($FeWO_4 + MnWO_4$) impurities.


magnetic
ore
non magnetic
impurity

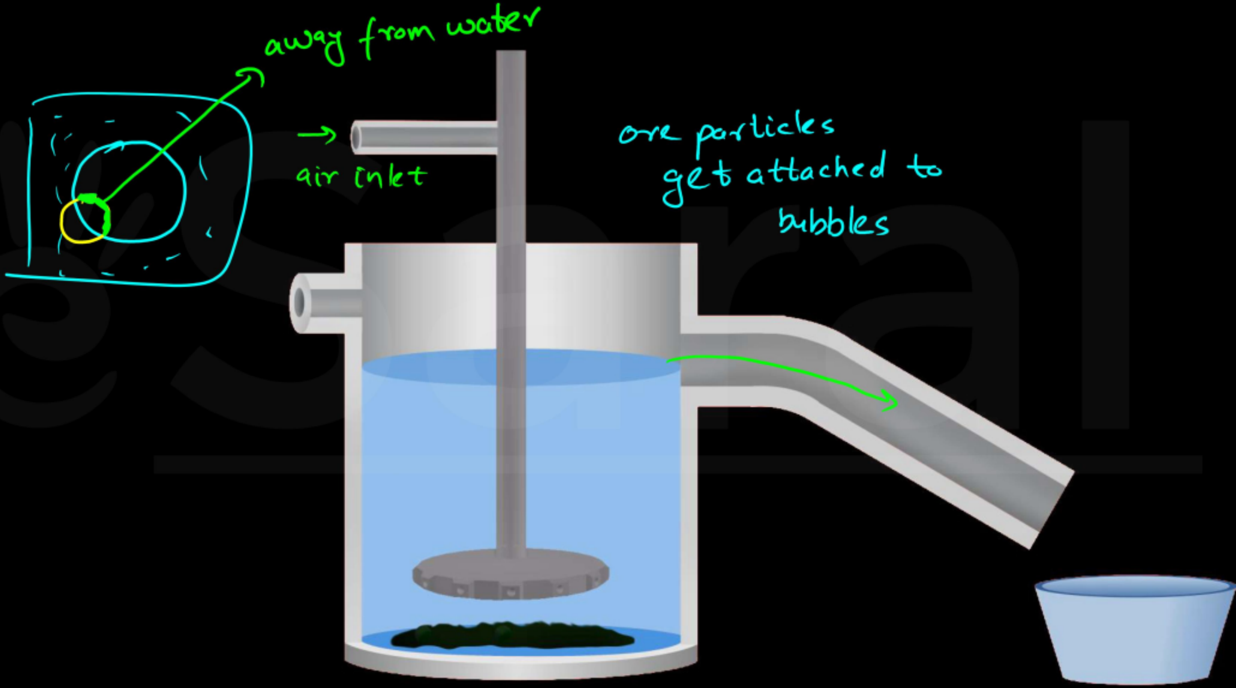
Froth Flotation Process

(sulphide)

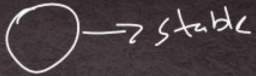
This method is commonly used for the concentration of the low grade sulphide ores like galena, PbS (ore of Pb) ; copper pyrites $Cu_2S.Fe_2S_3$ or $CuFeS_2$ (ore of copper) ; Zinc Blende, ZnS (ore of zinc) etc., Gangue ❤ Water

Ore 💔 Water

Froth


away from water
air inlet
ore particles get attached to bubbles

Frothers ✓ Jyada



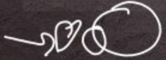
These form stable froth which rises to the top of the flotation cell. Oil like pine oil, camphor oil etc., are used as **Frothers**.

These are added in small quantity.

Froth Stabilizer (Aniline & Cresol)

The stabiliser are added to the frothers so that the froth can be stable for longer period.

Collectors



Potassium or sodium ethyl xanthate is used as a **Collector**.

By Chemical Separation Method

Leaching

Hall's Process

Used for red bauxite

$$\text{Bauxite ore} + Na_2CO_3 \xrightarrow{\text{Fused}} NaAlO_2 \xrightarrow{\text{Hydrolysis}} Al(OH)_3 + NaOH$$

$$Al(OH)_3 + NaOH \xrightarrow{CO_2} Al(OH)_3 + Na_2CO_3$$

$$Al(OH)_3 + Na_2CO_3 \xrightarrow[\Delta]{1500^\circ C} Al_2O_3$$

Cyanide Process

VV Imp

Yield ↑ O_2 ↑

(a) Formation of cyanide complex

$$Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$$

In absence of air reaction is reversible.

$$4Na_2S + 5O_2 + 2H_2O \longrightarrow 2Na_2SO_4 + 2S + 4NaOH$$

In presence of air reaction is irreversible.

Conversion of concentrated ore into oxide form

Roasting (sulphide, hallide)

Calcination (Sulphate oxide)

Reduction of ore to the metal

1.Reduction by Carbon (Smelting)

$PbO + C \longrightarrow Pb + CO$

CO $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$

Flux

Metal → oxide

Imp → 〃

a) Acidic Flux

$FeO + SiO_2 \longrightarrow FeSiO_3$

(basic impurity) (acidic flux) (slag)

b) Basic Flux

acidic basic flux

$SiO_2 + CaO \longrightarrow CaSiO_3$

~~(basic impurity)~~ ~~(acidic flux)~~ (slag)

3.) Self reduction (Auto reduction)

$$\underset{\text{(unroasted ore)}}{PbS} + \underset{\text{(roasted ore)}}{2PbO} \xrightarrow[\text{In absence of air}]{\text{High temperature}} \underset{\text{(Self reduction)}}{3Pb + SO_2\uparrow}$$

4.Reduction by metal(Alumino Thermite Process)

$Cr_2O_3 + Al \longrightarrow Al_2O_3 + 2Cr + Q\ cal$ Exothermic

$Fe_2O_3 + Al \longrightarrow Al_2O_3 + 2Fe + Q\ cal$ *

Krolls process

$TiCl_4 + Na$

$TiCl_4 + Mg$

5.) Thermal decomposition

$$Ag_2O \xrightarrow[300°C]{\Delta} 2Ag\downarrow + 1/2O_2\uparrow$$

$$HgO \xrightarrow[400°C]{\Delta} Hg\uparrow + 1/2O_2\uparrow$$

6.) Electrolytic Reduction

(Common)

Electrolysis is carried out in large cells and a small amount of another suitable electrolyte is added.

(i) Lowers the melting point of the main electrolyte

(ii) Enhances its conductivity

(iii) Reduces corrosion troubles

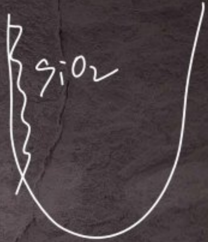
Refining of Metals

Impure metal (10-15%)

Poling Process

Melt

This process is used for the purification of copper and tin.



(A) Purification of Impure Copper

Flux SiO_2

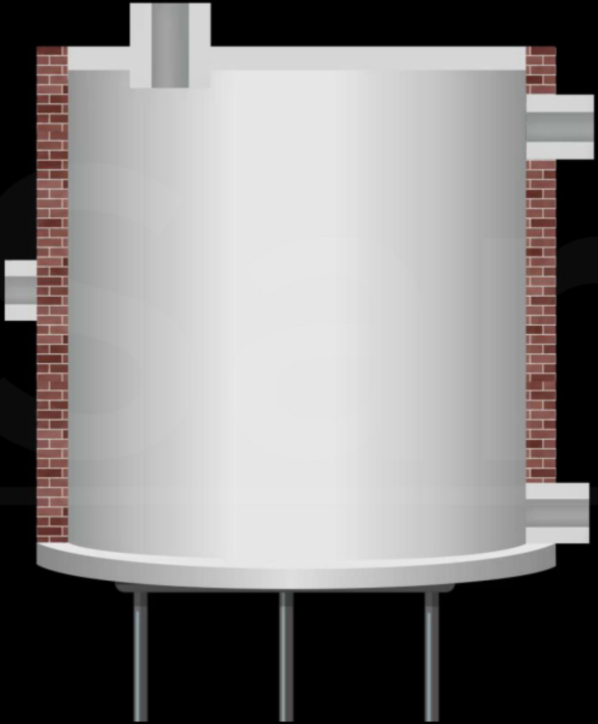
Fe is oxidised to FeO which forms a slag of $FeSiO_3$ with SiO_2 lining of the furnace.

RA

This molten copper is treated with powdered anthracite and then stirred with a pole of green wood.

$$\text{Green wood} \longrightarrow \text{Hydrocarbons} \longrightarrow CH_4$$

$$4CuO + CH_4 \longrightarrow 4Cu\ (\text{pure metal}) + CO_2 + 2H_2O$$



ii) Liquation

This method is used for the refining of metals having low melting point and are associated with high melting impurities.

Ex. Pb, Sn, Sb, Bi and Hg.

iii) Distillation

Metals having low boiling point are refined by this method, for example, zinc, cadmium and mercury.

iv) Vapour Phase Refining

a) Van-Arkel Process

$$Ti(s) + 2I_2(g) \xrightarrow{523\ K} TiI_4(g)$$

$$TiI_4(g) \xrightarrow{1700\ K} Ti(s) + 2I_2(g)$$

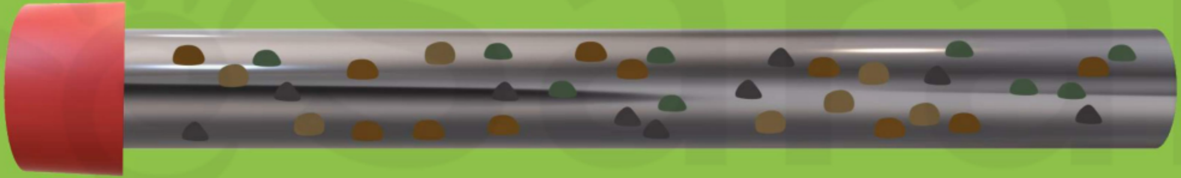
(b) Mond's process

$$Ni_{(Impure)} + 4CO \xrightarrow{\Delta} [Ni(CO)_4] \xrightarrow{\Delta} Ni_{(pure)} + 4CO$$

v) Zone Refining or Fractional Crystallisation

Ge, Si, Ga used as semiconductors are refined in this manner. Indium is also refined similarly.

This refining method is based on the fact that impurities tend to remain dissolved in molten state (Phase rule).



Cupellation (removal of Lead from Silver or Gold)

Amalgamation Process

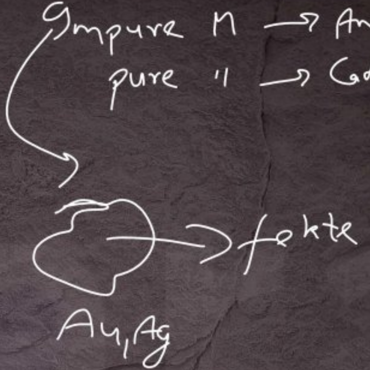
For noble metal Au, Ag from the native ore.

Electro-refining of Metals

Metals such as Cu, Ag, Zn, Sn, Pb, Al, Ni, Au are refined by this method.

On passing the electric current, pure metal from the anode dissolves and gets deposited at the cathode.

Impure M → Anode
pure " → Cathode



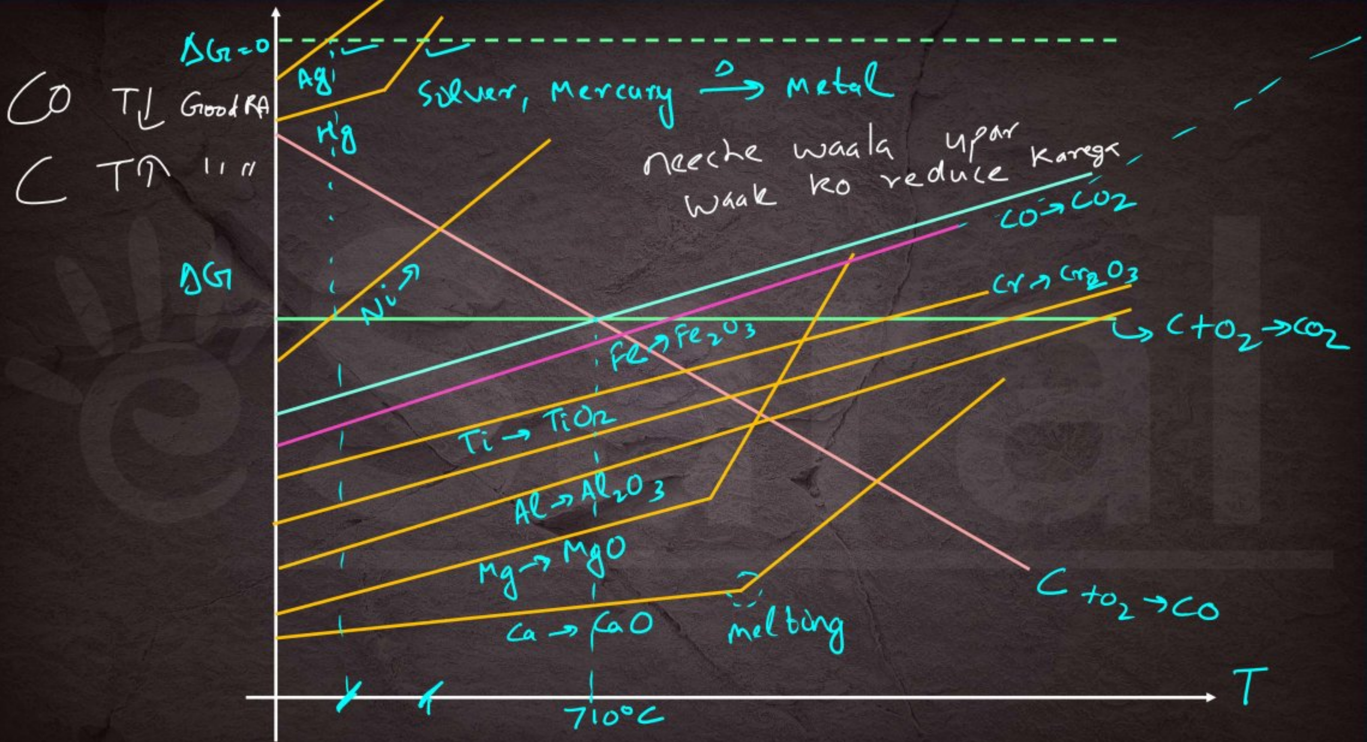
The soluble impurities go into the solution while insoluble or less electropositive impurities settle down below the anode as anode mud or sludge.

Electrorefining of Cu

Anode	Impure copper
Cathode	Pure copper
Electrolyte	An aqueous solution of $CuSO_4$ + 5% dil H_2SO_4

Electrorefining of Pb (Bett's process)

Anode	Impure Lead
Cathode	Pure Lead
Electrolyte	A mixture of $PbSiF_6$ and H_2SiF_6


ΔG=0
CO T↓ Good RA
C T↑ '' ''
Ag
Hg
Silver, Mercury $\xrightarrow{\Delta}$ Metal
neeche waala upar waale ko reduce karega
ΔG
Ni →
CO → CO₂
Cr → Cr₂O₃
C + O₂ → CO₂
Fe → Fe₂O₃
Ti → TiO₂
Al → Al₂O₃
Mg → MgO
Ca → CaO
melting
C + O₂ → CO
710°C
T

Extraction of Gold (Au)

(i) Crushing & Grinding

(ii) Leaching Process

Macarthur-Forrest / cyanide process

Extraction of Silver (Ag)

(A) From Argentite (Ag_2S)

(i) Concentration

As it is a sulphide ore, so froth flotation process is used.

(iii) Refining

(a) Amalgamation process

(b) Purification by electrolytic method

Pure Ag → Cathode

Impure Ag → Anode

Electrolyte → $AgNO_3$

Extraction of Copper (Cu)

Main Ore

Copper pyrites ($CuFeS_2$)

Extraction from pyrites by pyrometallurgical process (Smelting Process)

It also occurs as

Copper glance Cu_2S

Malachite $Cu(OH)_2.CuCO_3$

Azurite $Cu(OH)_2.2CuCO_3$

Learn

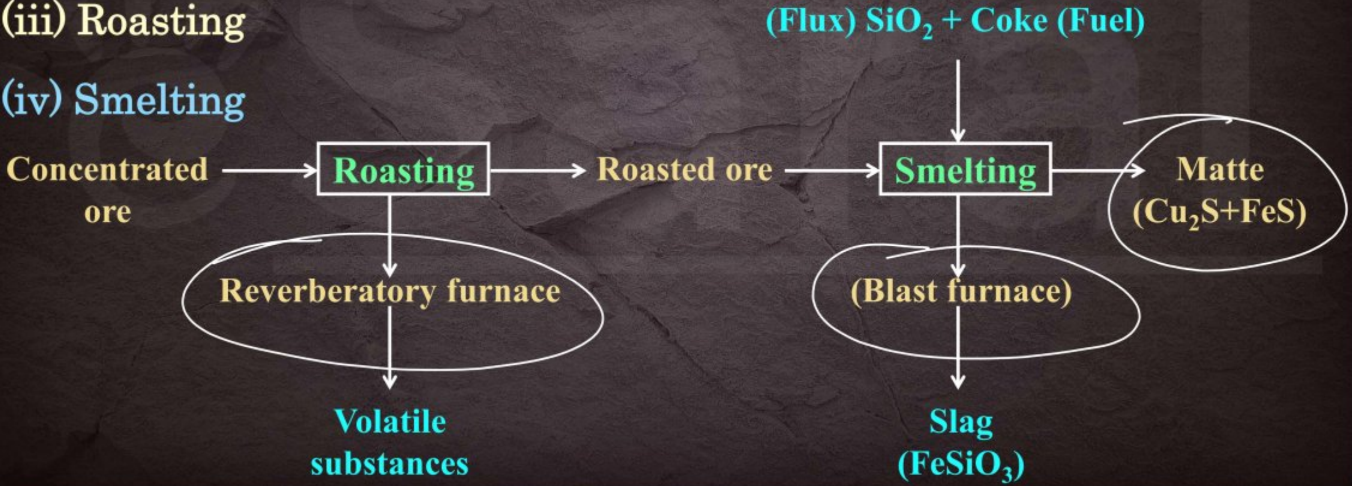
(i) Crushing & Grinding

(ii) Concentration

Copper pyrite ($CuFeS_2$) → **Crushing & grinding** → **Froth flotation** → Concentrated ore

(iii) Roasting

(iv) Smelting



(Flux) SiO_2 + Coke (Fuel)

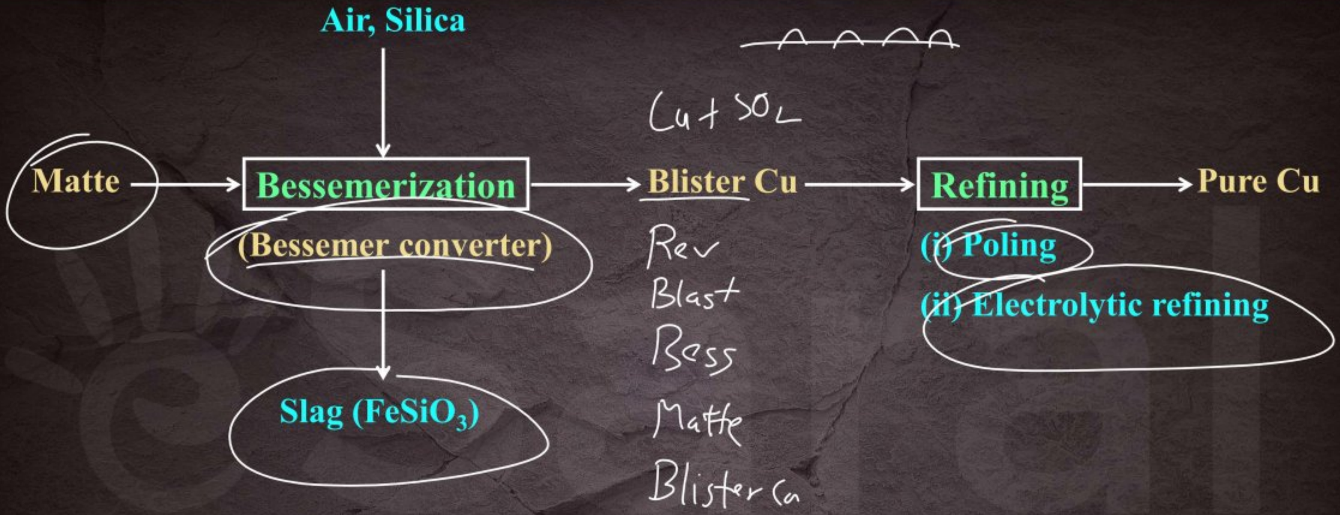
Concentrated ore → **Roasting** → Roasted ore → **Smelting** → Matte (Cu_2S+FeS)

Reverberatory furnace

Volatile substances

(Blast furnace)

Slag ($FeSiO_3$)



Air, Silica

Matte → **Bessemerization** → Blister Cu → **Refining** → Pure Cu

(Bessemer converter)

Slag ($FeSiO_3$)

(i) Poling

(ii) Electrolytic refining

Cu + SO_2

Rev

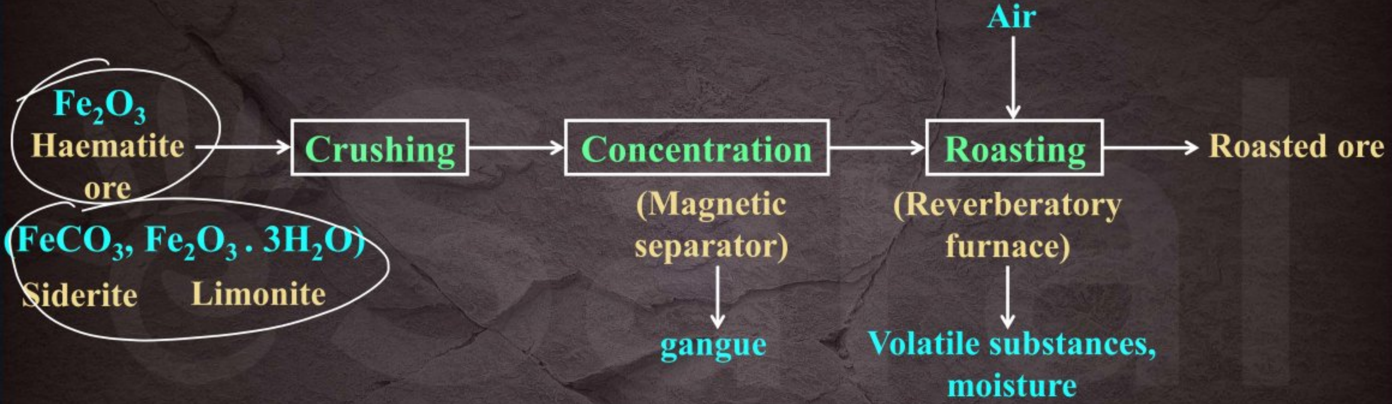
Blast

Bess

Matte

Blister Cu

Extration of Iron (Fe)



Fe_2O_3
Haematite ore

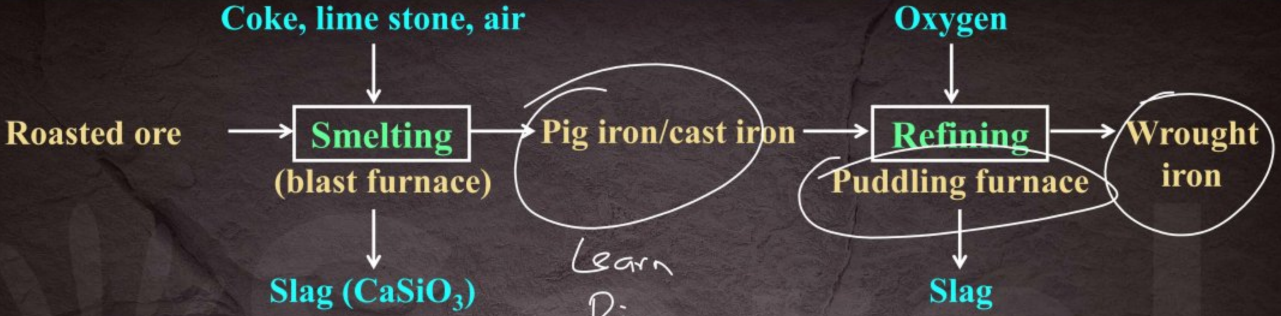
($FeCO_3$, $Fe_2O_3 . 3H_2O$)
Siderite Limonite

→ **Crushing** → **Concentration** → **Roasting** → Roasted ore

Concentration: (Magnetic separator) → gangue

Air → Roasting

Roasting: (Reverberatory furnace) → Volatile substances, moisture



Coke, lime stone, air

Roasted ore → **Smelting** (blast furnace) → Pig iron/cast iron → **Refining** Puddling furnace → Wrought iron

Oxygen

Slag ($CaSiO_3$)

Slag

Learn
Pig
Puddling
Wrought

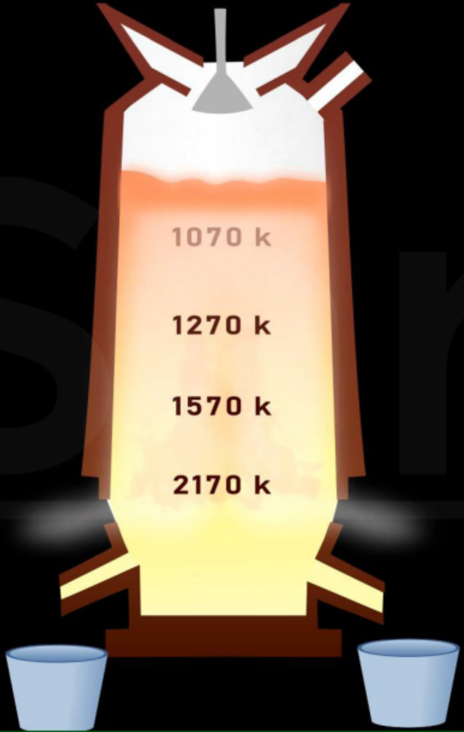
(a) Puddling Process

(b) Bessemerisation Process

(c) Open hearth Process

(d) L. D. Process

Thus we get pure iron.


1070 k
1270 k
1570 k
2170 k

(a) Zone of combustion (1500 - 16000°C) $C + O_2 \rightarrow CO_2$

(b) Zone of reduction (400 - 700°C) $Fe_2O_3 + CO$

(c) Zone of slag formation and reduction (800 - 1000°C)

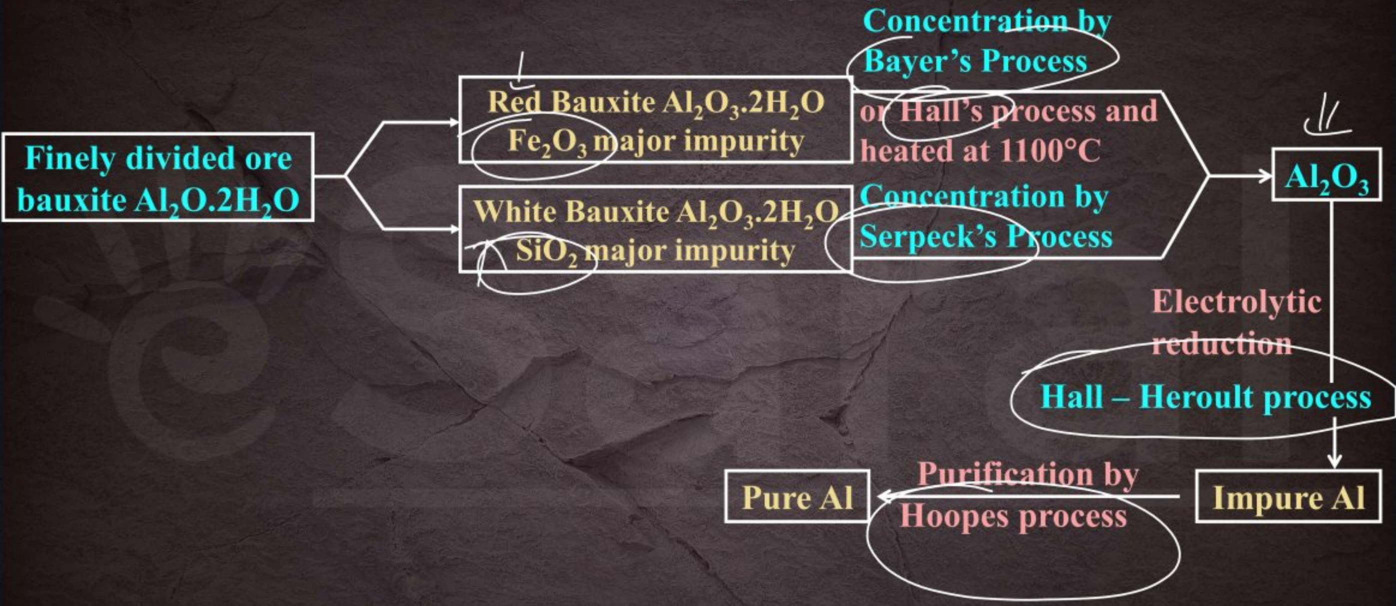
$$CO_2 + C \longrightarrow 2CO$$

$$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2\uparrow$$

$$FeO + CO \longrightarrow Fe + CO_2\uparrow$$

(d) Zone of fusion (1200 - 1300°C) → Iron melts

Flow chart of Al from $Al_2O_3.2H_2O$ (Bauxite)



Finely divided ore bauxite $Al_2O.2H_2O$

Red Bauxite $Al_2O_3.2H_2O$
Fe_2O_3 major impurity

White Bauxite $Al_2O_3.2H_2O$
SiO_2 major impurity

Concentration by Bayer's Process or Hall's process and heated at 1100°C

Concentration by Serpeck's Process

Al_2O_3

Electrolytic reduction

Hall – Heroult process

Impure Al

Purification by Hoopes process

Pure Al

Extraction of Lead (Pb)

Galena (PbS)

Ore – Galena Pbs

- (a) Carbon reduction process
- (b) Self reduction process

Refining process

(i) Liquation

(ii) Bett's Electrorefining

Electrolyte $\longrightarrow$ $Pb[SiF_6] + H_2SiF_6 +$ Gelatine (to adjust viscosity)

Extraction of Magnesium (Mg)

(i) From Carnallite($KCl.MgCl_2.6H_2O$)

(ii) From Magnesite($MgCO_3$)

(iii) From Sea water (Dow's process)

Electrolysis of fused anhydrous $MgCl_2$

Magnesium Chloride obtained by any of the above methods is fused and mixed with Sodium Chloride and Calcium Chloride in the temperature range of 973 – 1023 K.

GROUP-15 ELEMENTS

(N,	P,	As,	Sb,	Bi)
↑	↑	↑	↑	↑
नानी	पापा	आशु	सब	बीमार

(i) The common oxidation states of these elements are –3, +3 and +5.

Dinitrogen

Laboratory Preparation

$$NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + 2H_2O(\ell) + NaCl\ (aq)$$

$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$$

Reactions with metals :-

$$6Li + N_2 \xrightarrow{\text{Heat}} 2Li_3N$$

Reaction with Non-Metals

$$N_2(g) + 3H_2(g) \xrightleftharpoons{773k} 2NH_3(g)$$

Ammonia

$$\underset{\text{Urea}}{NH_2CONH_2} + 2H_2O \longrightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2 \ *$$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + 2H_2O + CaCl_2$$

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

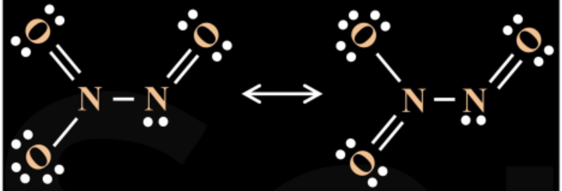
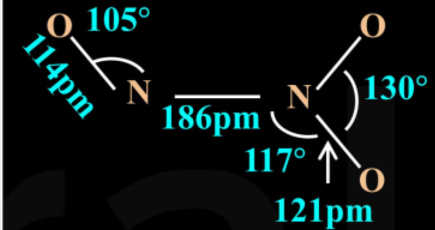
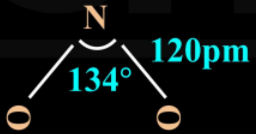
M Imp

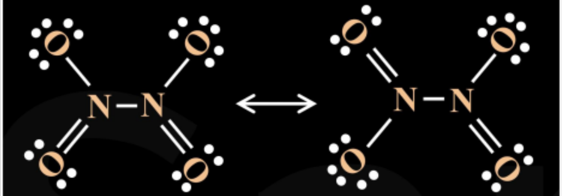
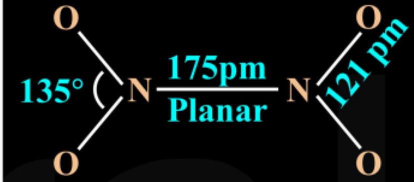
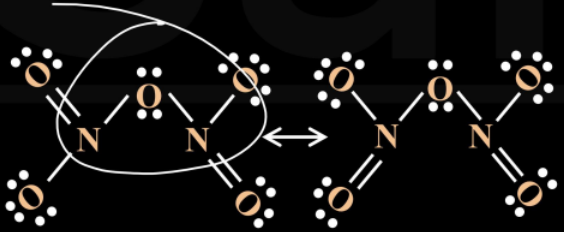
$$\underset{\text{(blue)}}{Cu^{2+}(aq)} + 4NH_3\ (aq) \rightleftharpoons \underset{\text{(deep blue)}}{\boxed{[Cu(NH_3)_4]^{2+}(aq)}}$$

deep blue

Structure of Oxides of Nitrogen

Formula	Resonance structures	Bond Parameters
N_2O	 $\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}=N=\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} \longleftrightarrow :N\equiv N-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:$	N — N — O 113pm 119pm Linear
NO	 $:N=\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} \longleftrightarrow :\overset{\cdot\cdot}{N}=\overset{\cdot\cdot}{O}$	N — O 115pm

Formula	Resonance structures	Bond Parameters
N_2O_3		
NO_2		 **Angular**

Formula	Resonance structures	Bond Parameters
N_2O_4		
N_2O_5		

Nitrous Acid (HNO_2)

Preparation

(a) $\text{M}-\text{nitrite} \xrightarrow[\text{HCl or } H_2SO_4]{\text{dil.acid}} HNO_2$

(b) $N_2O_3 + H_2O \longrightarrow 2HNO_2$

Oxidising as well as a RA

Nitric Acid ✓✓

Laboratory Method

By heating KNO_3 or $NaNO_3$ and concentrated H_2SO_4 in a glass retort.

$$KNO_3\ /\ NaNO_3 + H_2SO_4 \longrightarrow KHSO_4\ /\ NaHSO_4 + HNO_3$$

Large Scale Preparation (Ostwald's Process)

Imp

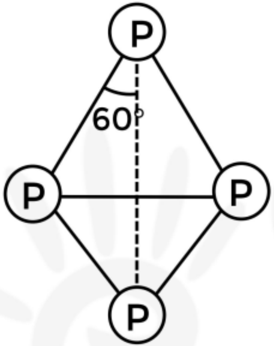
$$4NH_3(g) + \underset{\text{(from air)}}{5O_2(g)} \xrightarrow[\text{500K, 9bar}]{\text{Pt/Rh}-\text{gauge catalyst}} 4NO(g) + 6H_2O(g)$$

(i) Nitric acid usually acquires yellow or brown colour due to its decomposition by sunlight into NO_2.

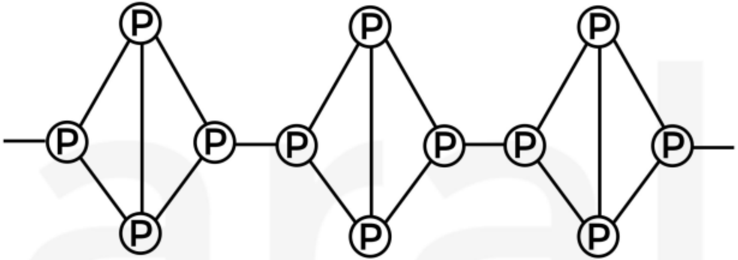
Nitric acid acts as a strong oxidising agent as it decomposes to give nascent Oxygen easily.

$$S + 6HNO_3 \xrightarrow[\text{and hot}]{\text{Conc.}} H_2SO_4 + 6NO_2 + 2H_2O$$

Allotropic Forms of Phosphorus



White Phosphorus



Red Phosphorus

If white Phosphorus is heated to about 250°C, or a lower temperature in the presence of sunlight, then red phosphorus is formed.

Phosphine

→ Holme's signal

↳ RA

$PH_3 \rightarrow Br_2$

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

$$Ca_3P_2 + 6HCl \longrightarrow 3CaCl_2 + 2PH_3$$

Laboratory preparation: it is prepared by heating white Phosphorus with concentrated NaOH solution in an inert atmosphere of CO_2.

$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$$

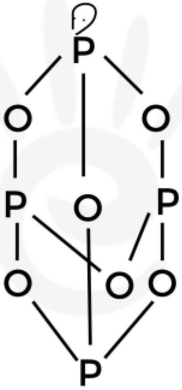
(sodium hypophosphite)

Properties

It is a colourless gas with rotten fish smell and is highly poisonous.

It explodes in contact with traces of oxidising agents like HNO_3, Cl_2 and Br_2 vapours.

Phosphorus Trioxide (P_4O_6)

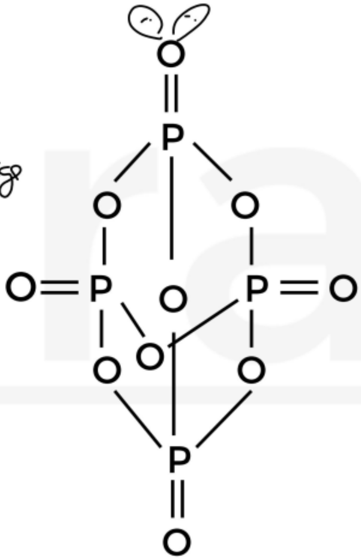


Learn

① no of POP linkage

② no of lp

Phosphorus (V) Oxide (P_4O_{10})



Oxygen Family Group 16 Elements
(O, S, Se, Te, Po)
Oye Salike se Teepo

Electron Gain Enthalpy

S > Se > Te > Po > O

Learn

Dioxygen

Laboratory Method

$2KClO_3 \xrightarrow[MnO_2]{Heat} 2KCl + 3O_2$

$2Ag_2O(s) \longrightarrow 4Ag(s) + O_2(g)$

$2Pb_3O_4(s) \longrightarrow 6PbO(s) + O_2(g)$

$2HgO(s) \longrightarrow 2Hg(\ell) + O_2(g)$

$2PbO_2(s) \longrightarrow 2PbO(s) + O_2(g)$

$2H_2O_2(aq) \longrightarrow 2H_2O(\ell) + O_2(g)$ Finely divided MnO_2 catalyst

Examples of neutral oxides are
CO,H_2O, NO and **N_2O.**

Learn

Ozone Preparation

$$3O_2 \longrightarrow 2O_3$$

ΔH^{-} (298 K) = + 142 kJ mol^{-1} Endothermic

Silent Electrical Discharge is used

This ozone layer in stratosphere protects the earth's surface from an excessive concentration of ultraviolet (UV) radiations.

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

Another threat to this ozone layer is probably posed by the use of freons which are used in aerosol sprays and as refrigerants.

OA

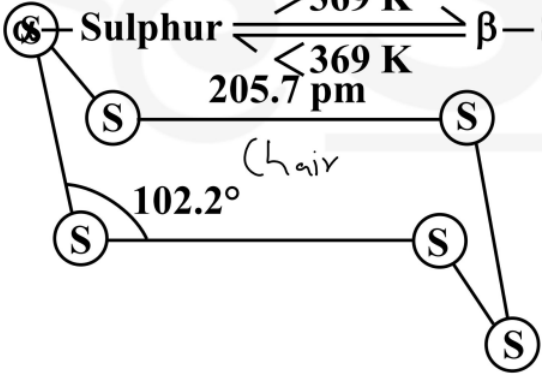
$$O_3 + 2H^+ + 2e \longrightarrow O_2 + H_2O$$

$$E^\circ = +2.07\ V$$

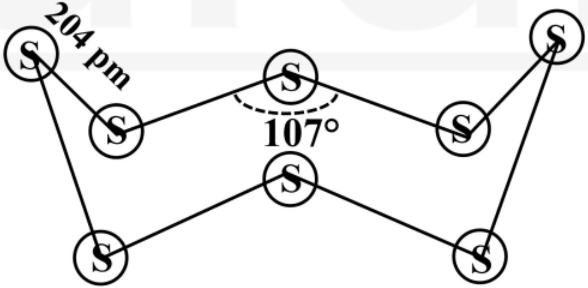
Allotropic Forms of Sulphur

The stable form at room temperature is Rhombic Sulphur → α ,which transforms to Monoclinic → β Sulphur when heated above 369 K.

$$\alpha\text{—Sulphur} \underset{<369\text{ K}}{\overset{>369\text{ K}}{\rightleftharpoons}} \beta\text{—Sulphur}$$



Crown



Hydrogen Sulphide(H_2S)

By the action of dil. HCl or H_2SO_4 on Iron Pyrites.

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$$

It is a colourless gas having an offensive smell of rotten eggs.

It burns in air with blue flame

$$2H_2S + O_2 \longrightarrow 2H_2O + S$$

It act as a reducing agent. It reduces halogen into corresponding hydroacid.

$$H_2S + X_2 \longrightarrow 2HX + S$$

Sulphuric Acid

Industrial Manufacturing (Contact process)

(i) Burning of Sulphur or Sulphide ores in air to generate SO_2.

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$$

The SO_3 gas from the catalytic converter is absorbed in concentrated H_2SO_4 to produce oleum.

Dilution of Oleum with water gives H_2SO_4 of the desired concentration.

Concentrated sulphuric acid is a strong dehydrating agent.

Halogen Family Group 17 Elements
(F, Cl, Br, I, At)

First Class Break Indian Auto

Electron Gain Enthalpy

Cl > F > Br > I

Bond energy order

$Cl_2 > Br > F_2 > I_2$ Learn

$2F_2(g) + H_2O(\ell) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$

$X_2(g) + H_2O(\ell) \longrightarrow HX(aq) + HOX(aq)$

(where X = Cl or Br)

$4I^-(aq) + 4H^+(aq) + O_2(g) \longrightarrow 2I_2(s) + 2H_2O(\ell)$

Learn

O_2F_2 oxidises Plutonium to PuF_6 and the reaction is used in removing Plutonium as PuF_6 from spent nuclear fuel.

ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment.

Fluorine

Moissan Process

$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

$HF + KF \longrightarrow KHF_2$

[KF decreases the m.p. of the mix. depending upon the composition]

$KHF_2 \xrightarrow{\text{Electrolysis}} H_2\text{(at cathode)} + F_2\text{(at anode)}$

Chlorine

Deacon's Process

$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$

$8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$
(excess)

$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$
(excess)

$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$
(cold and dilute)

$6\ NaOH + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$
(hot and conc.)

Imp
rxns of Cl

Learn

Aqua Regia

3 : 1

HCl HNO_3

When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., Gold, Platinum.

Interhalogen Compounds

ICl_3 ClF_3

ICl_7

Interhalogen compounds are more reactive than halogens (except fluorine).

Noble Gases Family Group 18 Elements (He, Ne, Ar, Kr, Xe, Rn)

He Never Argues, Kal Xero Run pe out hua tha

$XeO_4 \rightarrow$ hydrolysis ✗

$Xe^+PtF_6^-$ is the first noble gas compound discovered.

$$2XeF_2(s) + 2H_2O(l) \longrightarrow 2Xe\,(g) + 4\,HF(aq) + O_2(g)$$

$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6\,HF$$

Hydrolysis

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$$

$$2XeF_6 + SiO_2 \longrightarrow SiF_4\uparrow + 2XeOF_4$$

violet

$$XeF_2 + 2HCl \longrightarrow 2HF + Xe + Cl_2$$

$$XeF_4 + 4KI \longrightarrow 4KF + Xe + 2I_2$$

Learn

Naming of Oxyacids

$H_2\overset{+4}{S}O_3$ ous

$H_2\overset{+6}{S}O_4 \longrightarrow$ **Sulphuric acid**

$H\overset{+7}{Cl}O_4 \longrightarrow$ **Per – Chloric acid**

prefix **Root word** **suffix**

3 parts of a name

$H\overset{+5}{Cl}O_3 \longrightarrow$ Chloric acid

Rule –1 for **Suffix**

(i) Sulphuric acid, sulphurous acid

$HClO_4 \longrightarrow$ **Per Chloric Acid**

Rule – 2 'Meta' Prefix

$\overset{+5}{H_3PO_4} \xrightarrow{-H_2O} \overset{+5}{HPO_3}$ **Meta phosphoric acid**

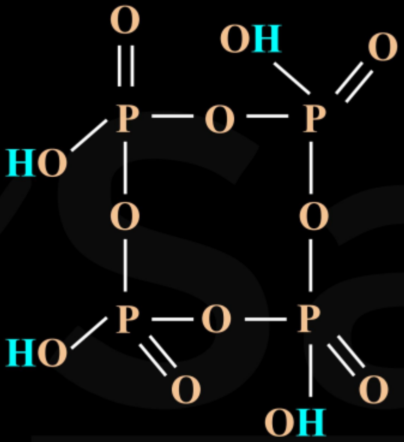
HPO_3 & HPO_2 do not exist in their metameric actually they exist in their Polymeric form

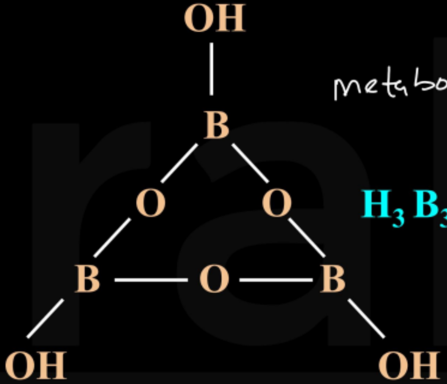
$nH_3PO_4 \xrightarrow{-nH_2O} (HPO_3)_n \longrightarrow$ **Polymeric from**

$H_4P_4O_{12}$

$P_4O_{12}^{-4}$

Meta acids → H_3PO_4 → derivatives





metaboric

$H_3B_3O_6$

General Form

$H_nP_nO_{3n}$ ⟶ Cyclic Structure

Or $P_nO_{3n}^{-n}$

Rule – 3 'Ortho' Prefix

It is provided to ic from of that Oxyacid whose Meta derivative is possible

H_3PO_4 also ortho Phosphoric acid

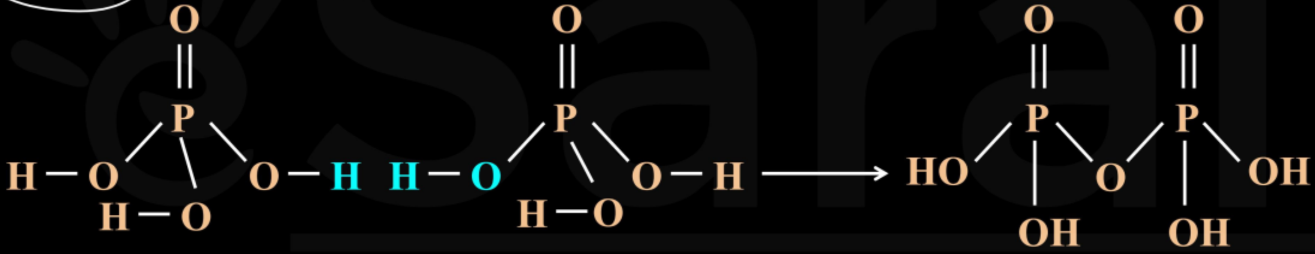
H_3BO_3 → ortho B.A

[Exception H_3PO_3 → Ortho Phosphourous acid]

Rule - 4 'Pyro' Prefix

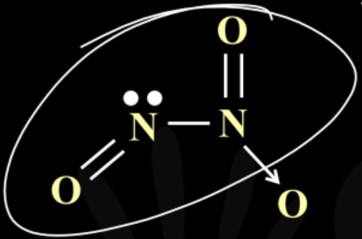
$2H_2SO_4 \xrightarrow{-H_2O} H_2S_2O_7$ [Pyro Sulphuric acid (Oleum)]

$2H_3PO_4 \xrightarrow{-H_2O} H_4P_2O_7$



Oxo linkage is a characteristic property of Pyro acids.

$2HNO_2 \xrightarrow{-H_2O} N_2O_3$ (Nitrous Anhydride)



More Stable

$H_2SO_3 \xrightarrow{-O} H_2SO_2$

$H_3PO_3 \xrightarrow{-O} H_3PO_2$

Rule - 5 'Hypo' Prefix

Hypo prefix is provided to that oxyacid which is obtained by the removel one Oxygen atom from the ous form of the oxyacid.

Exception

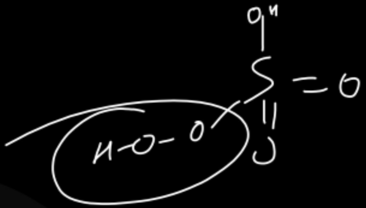
Hypo Phosphoric acid $H_4P_2O_6$ X

$$2H_3PO_4 \xrightarrow{-H_2O} H_4P_2O_7 \xrightarrow{-O} H_4P_2O_6$$

Pyro phosphoric Acid Hypo phosphoric Acid

Exception – instead of ous, ic

Rule – 6 'Per' Prefix



H_2SO_5

Per prefix is provided to that Oxyacid which is obtained by the addition of Oxygen atom in the ic from of Oxyacid.

$$\underset{\text{(ic)}}{\text{(P.A)}} \xrightarrow{+\text{O}} \text{Per P.A}$$

5
B

13
Al

31
Ga

49
In

81
Tl

The Boron Family

[illegible]

Bengan Aloo Gajar in Thela

Atomic and Ionic radii order

B < Ga < Al < In < Tl

3d

Al > Ga AR

Boiling point order

B.P. B > Al > Ga > In > Tl Learn

Melting point order

M.P. B > Al > Tl > In > Ga Learn

Ionization Enthalpy

B > Tl > Ga > Al > In Learn

(i) Preparation of B_2O_3 from Borax or Colemanite

$$Na_2B_4O_7 + HCl/H_2SO_4 \longrightarrow NaX + H_2B_4O_7$$

$$H_2B_4O_7 + 5H_2O \longrightarrow 4H_3BO_3 \xrightarrow{\Delta} B_2O_3 + H_2O$$

Learn

Preparation of Borax

$$\underset{\text{Colemanite}}{2CaO.\ 3B_2O_3} + 2Na_2CO_3 \longrightarrow 2CaCO_3\downarrow + Na_2B_4O_7 + 2NaBO_2$$

$$\Big\downarrow \text{ Filtered - } CaCO_3 \text{(as residue)}$$

$$\underbrace{Na_2B_4O_7 + NaBO_2}_{\text{in solution}}$$

$$\underset{\text{in filtrate}}{NaBO_2} + \underset{\text{as residue}}{Na_2B_4O_7 \cdot 10H_2O} \xleftarrow[\text{and allowed to crystallise out and filtered}]{\text{Concentrated}} Na_2B_4O_7 + NaBO_2$$

$$\Big\downarrow \text{ CO}_2 \text{ Passed and crystallise out again} \qquad [4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3]$$

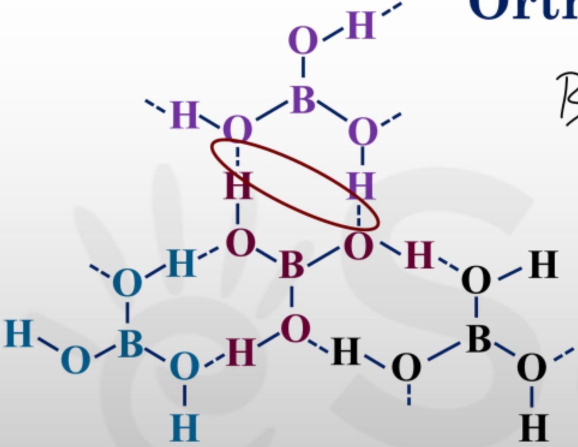
$$Na_2B_4O_7.\ 10H_2O\downarrow$$

Heating

$$\left(\underset{\text{Borax}}{Na_2B_4O_7.10H_2O} \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underset{\text{Sodium metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}\right)$$

[Heating effect]

Orthoboric acid



Basicity = 1

lp accepting Lewis acid

H^+ ✗

Heating of Boric acid

$$H_3BO_3 \xrightarrow{100^\circ C} HBO_2 \xrightarrow{140^\circ C} H_2B_4O_7 \xrightarrow[\text{red hot}]{\Delta} B_2O_3$$

Metaboric acid Tetra boric acid Glassy mass

Al_2O_3 Preparation

(i) $2Al(OH)_3 \xrightarrow{300°C} Al_2O_3 + 3H_2O$

(ii) $Al_2(SO_4)_3 \xrightarrow{\Delta} Al_2O_3 + 3SO_3$

Alum

(iii) $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \xrightarrow{\Delta} Al_2O_3 + 2NH_3 + 4SO_3 + 25H_2O$

$AlCl_3$ Preparation

(i) Its anhydrous form is deliquescent and fumes in air.

$2Al + 6HCl\ (vap.) \longrightarrow 2AlCl_3 + 3H_2$

(over heated) dry

Alumns

$M_2SO_4 . M'_2(SO_4)_3 \cdot 24\ H_2O$

where

M = Na^+, K^+, Rb^+, Cs^+, As^+, Tl^+,

M' = Al^{+3}, Cr^{+3}, Fe^{+3}, Mn^{+3}, Co^{+3}

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ Potash alum

The Carbon Family

Chemistry Sir Gives Sanki Problems

5 **C** → $1s^2\ 2s^2\ 2p^2$

13 **Si** → $[Ne]\ 3s^2\ 3p^2$

31 **Ge** → $[Ar]\ 3d^{10}\ 4s^2\ 4p^2$

49 **Sn** → $[Kr]\ 4d^{10}\ 5s^2\ 5p^2$

81 **Pb** → $[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$

Melting and Boiling Points

M.P. C > Si > Ge > Pb > Sn

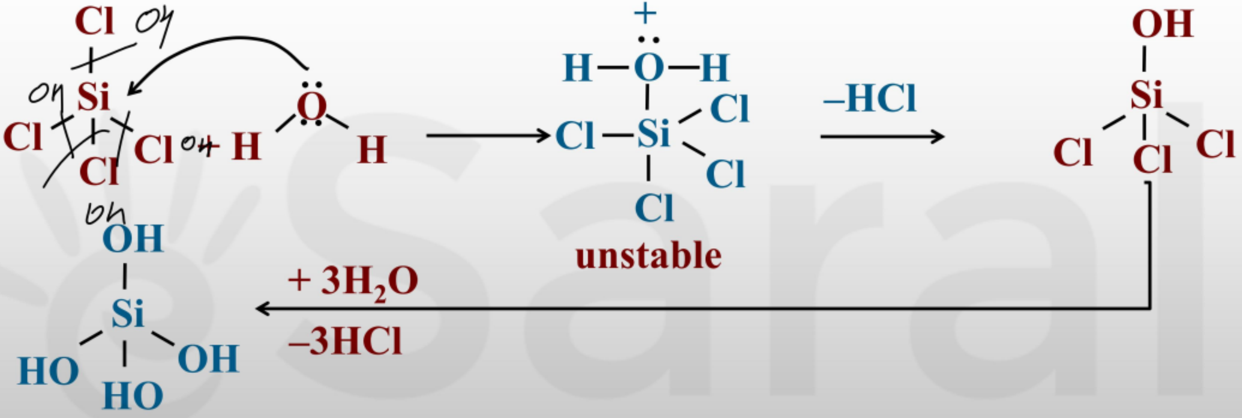
B.P. C > Si > Ge > Sn > Pb

Learn

Electronegativity

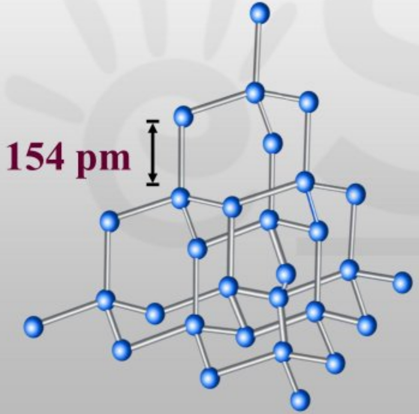
The electronegativity values for elements from Si to Pb are almost the same.

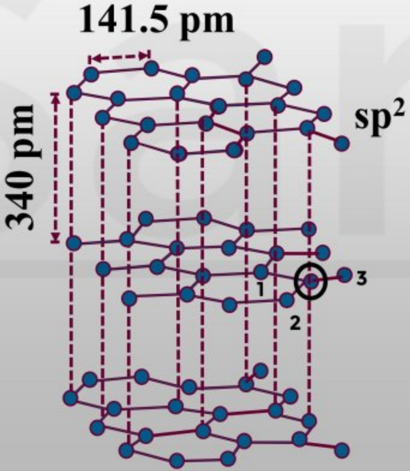
Hydrolysis of $SiCl_4$ (Mechanism)



Silicic acid

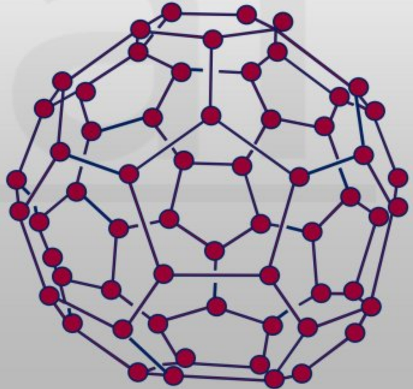
Allotropes of Carbon





Fullerenes

$C \rightarrow 3C$ C_{60} 5,6



Carbide

C_1 unit **Be_2C , Al_4C_3**

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

C_2 unit **CaC_2, BaC_2**

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + CH \equiv CH$$

C_3 unit **Mg_2C_3**

$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3 - C \equiv CH$$

Silicon (Si)

(one of most abundant element)

Silica is found in the free state in sand, flint and quartz and in the combined state as silicates like

Fle

(i) F~~el~~dspar	$K_2O. Al_2O_3. 6SiO_2$
(ii) Kaolinite	$Al_2O_3. 2SiO_2. 2H_2O$
(iii) Asbestos	$CaO. 3MgO. 4SiO_2$

Learn

Compounds of Silicon

Catenation → oxygen

Silane

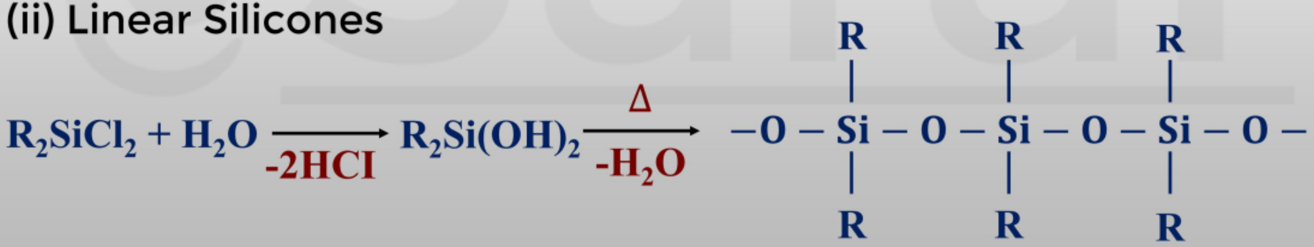
$Si_nH_{2n+2} \rightarrow SiH_4$ & Si_2H_6

Only these two are found

Silicones

$R_2Si(OH)_2$

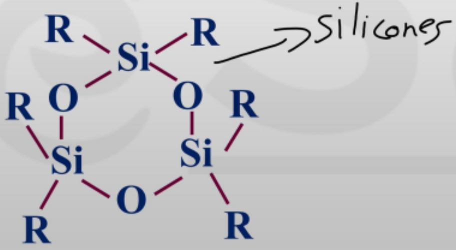
(ii) Linear Silicones



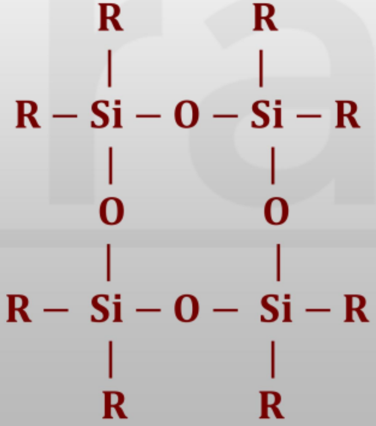
$$R_2SiCl_2 + H_2O \xrightarrow[-2HCl]{} R_2Si(OH)_2 \xrightarrow[-H_2O]{\Delta} -O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-$$

(iii) Cyclic Silicones

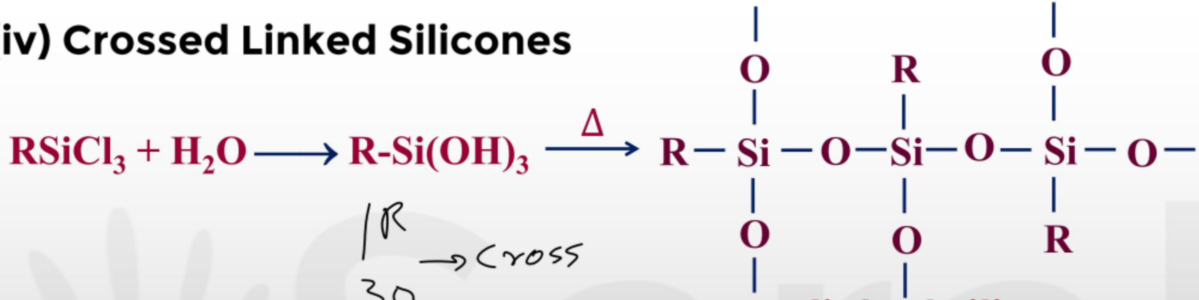
Silicones may have the cyclic structure also having 3, 4, 5 and 6 silicon atoms within the ring.



cyclic silicones are non planar



(iv) Crossed Linked Silicones



$$RSiCl_3 + H_2O \longrightarrow R\text{-}Si(OH)_3 \xrightarrow{\Delta} R-\overset{\overset{|}{\overset{O}{|}}}{\underset{\underset{|}{\underset{O}{|}}}{Si}}-O-\overset{\overset{R}{|}}{\underset{\underset{|}{\underset{O}{|}}}{Si}}-O-\overset{\overset{|}{\overset{O}{|}}}{\underset{\underset{R}{|}}{Si}}-O-$$

1 R

3 O → cross

cross linked silicone

3 dimensional network

Silicates

Learn the examples

(1) Ortho silicates (Ex. Zircon, Willemite)

(2) Pyro Silicates (Ex. Hemimorphite)

(3) Cyclic Silicate (Wollastonile, Benitotite, Beryl, Emrald)

(4) Single chain silicate (Pyroxene Silicate) (Ex. Diopsite)

(5) Double chain Silicate (Amphiboles) (Ex. Asbestos)

(6) Sheet Silicate (Ex. Clay talc, Micas)

(7) 3-D Silicate (Ex. fledspars, zeolites, ultramarine, quartz)

(1) $CO + H_2$ is called as water gas

Isotopes of Hydrogen

Properties	protium(P)	Deuterium(D)	Tritium(T)
e-, p+ , n^0	1,1,0	1,1,1	1,1,2
abundance	99.98%	0.02%	trace
Comman name	Simple hydrogen	Heavy hydrogen	Radioactive hydrogen

Isomers of molecular hydrogen

ortho-hydrogen

1. one with its two proton nuclear spins aligned parallel.
2. Presence in nature = 75%

para-hydrogen

1. The other with its two proton spins aligned antiparallel.
2. Presence in nature = 25%

Dihydrogen, H_2

Laboratory Preparation of Dihydrogen

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$$

Sodium Zincate

Commercial Production of Dihydrogen

(i) Electrolysis of acidified water using platinum electrodes gives hydrogen.

$$2H_2O\ (\ell) \xrightarrow[\text{traces of acid}]{\text{Electrolysis}} 2H_2(g) + O_2(g)$$

Water

The hardness of water is of two types $((Ca^{2+}, Mg^{2+}))$

(i) Temporary hardness

(ii) Permanent hardness

Temporary hardness is due to the presence of magnesium and calcium bicarbonates.

Permanent hardness is due to presence of sulphate and chlorides

Temporary hardness of water can be removed by

Learn

(i) Boiling
(ii) Clark's method

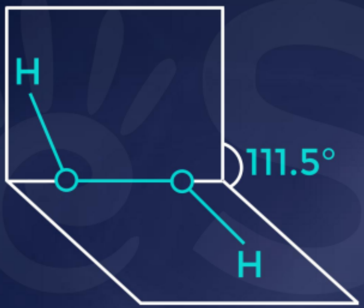
Permanent Hardness

(i) Treatment with washing soda (sodium carbonate)
(ii) Calgon's method ($Na_6P_6O_{18}$)
(iii) Ion-exchange method (By Zeolite)
(iv) Ion exchange method (By synthetic resins)

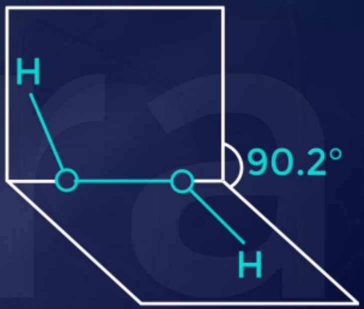
Hydrogen Peroxide (H_2O_2)

Structure

Hydrogen peroxide has a non-planar structure.



Gas phase



Solid phase

(a) H_2O_2 structure in gas phase, dihedral angle is 111.5°.

(b) H_2O_2 structure in solid phase at 110K, dihedral angle is 90.2°.

Storage Imp

H_2O_2 decomposes slowly on exposure to light.

$$2H_2O_2(\ell) \longrightarrow 2H_2O(\ell) + O_2(g)$$ (glass, metal)

It is stored in wax-lined glass or plastic vessels in dark.

Acetanilide or Glycerol or Urea can be added as a stabiliser. It is kept away from dust because dust can induce explosive decomposition of the compound.

(iii) As a rocket propellant

$$NH_2.NH_2 + 2H_2O_2 \longrightarrow N_2 + 4H_2O$$

[highly exothermic and large increase in volume]

Group 1 Elements : Alkali Metals

S-block

Hydration Enthalpy

The hydration enthalpies of alkali metal ions decrease with increase in ionic sizes.

$\phi \uparrow$ HE $\uparrow$

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

$$4Li + O_2 \longrightarrow 2Li_2\overset{-2}{O} \text{ (oxide)}$$

$$2Na + O_2 \longrightarrow Na_2\overset{-1}{O_2} \text{ (peroxide)}$$

$$M + O_2 \longrightarrow M\overset{-1/2}{O_2} \text{ (superoxide)}$$

Learn

(M = K, Rb, Cs)

With ammonia
Deep blue

VVVV Imp Color due to ammoniated e^-

Paramagnetic

The alkali metals dissolve in liquid ammonia giving deep blue solutions which are conducting in nature.

$$M + (x + y)NH_3 \longrightarrow [M(NH_3)_x]^+ + [e(NH_3)y]^-$$

The blue colour of the solution is due to the ammoniated electron which absorbs energy in the visible region of light and thus imparts blue colour to the solution.

The solutions are paramagnetic and on standing slowly liberate hydrogen resulting in the formation of NH_2^-.

LiCl is deliquescent and crystallises as a hydrate, $LiCl.2H_2O$ whereas other alkali metal chlorides do not form hydrates.

Lithium nitrate when heated gives lithium oxide, Li_2O, whereas other alkali metal nitrates decompose to give the corresponding nitrite.

$$4LiNO_3 \longrightarrow \underline{2Li_2O} + 4NO_2 + O_2$$

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

Sodium Carbonate (Washing Soda), $Na_2CO_3 . 10H_2O$

Preparation Solvay Process

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$2NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \longrightarrow NH_4Cl + NaHCO_3$$

$$2NaHCO_3 \longrightarrow Na_2CO_3\ (\text{crystals}) + CO_2 + H_2O$$

Uses

(i) It is used in water softening, laundering and cleaning.

(ii) It is used in paper, paints and textile industries.

Sodium Hydroxide (Caustic Soda), NaOH

Brine

1. Sodium hydroxide is generally prepared commercially by the electrolysis of sodium chloride in Castner-Kellner cell.

Cathode $Na^+ + e^- \xrightarrow{Hg} Na(Hg)$

$$Na(Hg) + H_2O \longrightarrow NaOH + Hg + \frac{1}{2}H_2$$

Uses

(i) The manufacture of soap, paper, artificial silk and a number of chemicals.

(ii) In petroleum refining.

(iii) In the purification of bauxite.

(iv) In the textile industries for mercerising cotton fabrics.

Sodium Hydrogen Carbonate (Baking Soda), $NaHCO_3$

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$

Uses

1. Sodium hydrogen carbonate is a mild antiseptic for skin infections.

2. It is used in fire extinguishers.

Group 2 Elements : Alkaline Earth Metals

The alkaline earth metals are less reactive than the alkali metals. The reactivity of these elements increases on going down the group.

AEM < AM

Reactivity Towards Air

Beryllium and magnesium are kinetically inert to oxygen and water because of the formation of an oxide film on their surface. However, powdered beryllium burns brilliantly on ignition in air to give BeO and Be_3N_2.

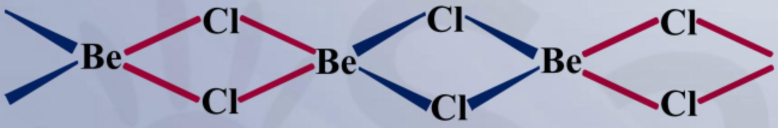
All the elements except beryllium combine with hydrogen upon heating to form their hydrides, MH_2. BeH_2, however, can be prepared by the reaction of $BeCl_2$ with $LiAlH_4$.

$$2BeCl_2 + LiAlH_4 \longrightarrow \boxed{2BeH_2} + LiCl + AlCl_3$$

Beryllium halides are essentially covalent and soluble in organic solvents.

Be ϕT

Beryllium chloride has a chain structure in the solid state.



Learn

Bridge Bonding

Calcium Oxide or Quick Lime, CaO

$$CaCO_3 \xrightleftharpoons{heat} CaO + CO_2$$

Calcium Hydroxide (Slaked lime), $Ca(OH)_2$

Calcium hydroxide is prepared by adding water to quick lime, CaO.

When carbon dioxide is passed through lime water it turns milky due to the formation of calcium carbonate.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

On passing excess of carbon dioxide, the precipitate dissolves to form calcium hydrogen carbonate.

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca\,(HCO_3)_2$$

Calcium Carbonate, $CaCO_3$ (Marble)

$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$

$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$

Calcium Sulphate (Plaster of Paris), $CaSO_4 \cdot \frac{1}{2} H_2O$

It is a hemihydrate of calcium sulphate. It is obtained when gypsum, $CaSO_4 \cdot 2H_2O$, is heated to 393 K.

$2(CaSO_4 \cdot 2H_2O) \longrightarrow 2(CaSO_4 \cdot \frac{1}{2} H_2O) + 3H_2O$

Transition Elements

d & f block

Zn, Cd, Hg are not transition metals.

Electronic Configuration

$(n-1)d^{1-10}ns^{1-23}$

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
	साइन्स	टीचर	very	cruel	मन	फे	को	नी	क्यू	जान	जलाती हो।
As usual				$4s^1$					$4s^1$		
Others are				$3d^5$					$3d^{10}$		

M.P.

no of upe ↑ MP ↑

5 upe

Cr → Maximum

Cr, Mo, W: 6 no. of unpaired e^-s are involved in metallic bonding

0

Zn, Cd, Hg: Lowest m.p.

Due to no unpaired e^-

For metallic bonding

Density

5d >> 4d > 3d

Due to Lanthanide contraction

Ex. : Ti < Zr << Hf

Fe < Ni < Cu

Fe < Cu < Au

Fe < Hg < Au

Learn

Oxidation states of the Ist transition series most common ones are in bold types

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			+ 1					+ 1	
	+ 2	+ 2	+ 2	+ 2	+ 2	+ 2	+ 2	+ 2	+ 2
+ 3	+ 3	+ 3	+ 3	+ 3	+ 3	+ 3	+ 3		
	+ 4	+ 4	+ 4	+ 4	+ 4	+ 4	+ 4		
		+ 5	+ 5	+ 5					
			+ 6	+ 6	+ 6				
				+ 7					

All Cu (II) halides are known except the Iodide.
In this case, Cu^{2+} Oxidises I^- to I_2

$$2Cu^{2+} + 4I^- \longrightarrow \overset{+1}{Cu_2}I_2(s) + I_2$$

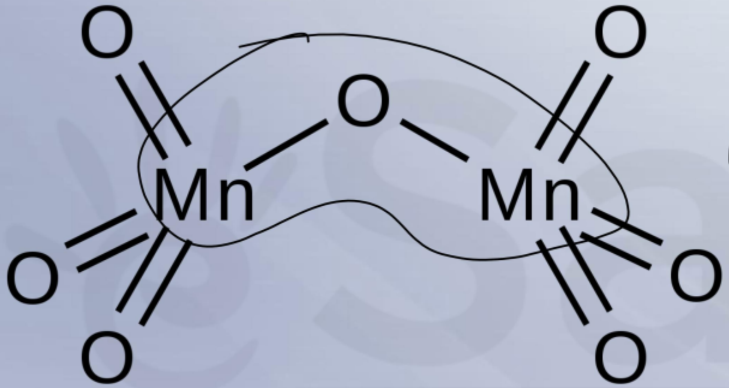
However, many Copper (I) compounds are unstable in aqueous solution and undergo disproportionation.

$\phi\uparrow$ Cu^{2+} $HE\uparrow$

$$2Cu^+ \longrightarrow Cu^{2+} + Cu$$

The stability of Cu^{2+}(aq.) rather than Cu^+(aq) is due to the much more negative hydration enthalpy of Cu^{2+}(aq.) than Cu^+, which more than compensates for the second Ionisation Enthalpy of Cu.

Learn



Mn_2O_7

Colour (aquated)

d^{10} d^{0} → colourless

$Ti^{4+} \longrightarrow$ Colourless

$V^{4+} \longrightarrow$ Blue

$V^{2+} \longrightarrow$ Violet

$Cr^{3+} \longrightarrow$ Green

$Sc^{3+} \longrightarrow$ Colourless

$Ti^{3+} \longrightarrow$ Purple

$V^{3+} \longrightarrow$ Green

$Cr^{2+} \longrightarrow$ Blue

Learn

$Mn^{2+} \longrightarrow$ Light pink

$Fe^{3+} \longrightarrow$ Yellow

$Ni^{2+} \longrightarrow$ Green

$Zn^{2+} \longrightarrow$ Colourless

$Mn^{3+} \longrightarrow$ Violet

$Fe^{2+} \longrightarrow$ Light green

$Co^{2+} \longrightarrow$ Pink

$Cu^{2+} \longrightarrow$ Blue

Ni → hydrogenation

$TiCl_3$ ⟶ **Used as the Ziegler-Natta catalyst in the production of polythene.**

V_2O_5 ⟶ **Convert SO_2 to SO_3 in the contact process for making H_2SO_4**

$FeSO_4 + H_2O_2$ ⟶ **Used as Fenton's reagent for oxidizing Alcohols to Aldehydes.**

Iron(III) catalyses the reaction between Iodide and persulphate ions.

$$2I^- + S_2O_8^{2-} \longrightarrow I_2 + 2SO_4^{2-}$$

Alloys

The best known are ferrous alloys. Chromium, Vanadium, Tungsten, Molybdenum and Manganese are used for the production of a variety of steels and stainless steel.

Alloys of transition metals with non transition metals such as brass (Copper-Zinc) and bronze (Copper-Tin), are also of considerable industrial importance.

Ferric comounds are easily hydrolysed as compared to ferrous compounds.

Chromate-Dichromate

$$\underset{\text{(Chromite Ore)}}{4FeCr_2O_4} + 8Na_2CO_3 + 7O_2 \xrightarrow[\text{Red hot in presence of air}]{1000° - 1300°C} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2\uparrow$$

Dissolve in water and filter

Residue (Fe_2O_3)

Filtrate (Na_2CrO_4)

$$2Na_2CrO_4 + \underset{\text{conc.}}{H_2SO_4} \longrightarrow Na_2SO_4\downarrow + Na_2Cr_2O_7 + H_2O$$

$\left.\begin{array}{l}\text{It's solubility upto}\\ 32°\text{C increases and}\\ \text{then decreases}\end{array}\right\}$ Hence, suitable temp. is to be employed to crystallise out Na_2SO_4 first.

Then $Na_2Cr_2O_7$ is crystallised out as $Na_2Cr_2O_7{\cdot}2H_2O$ on evaporation.

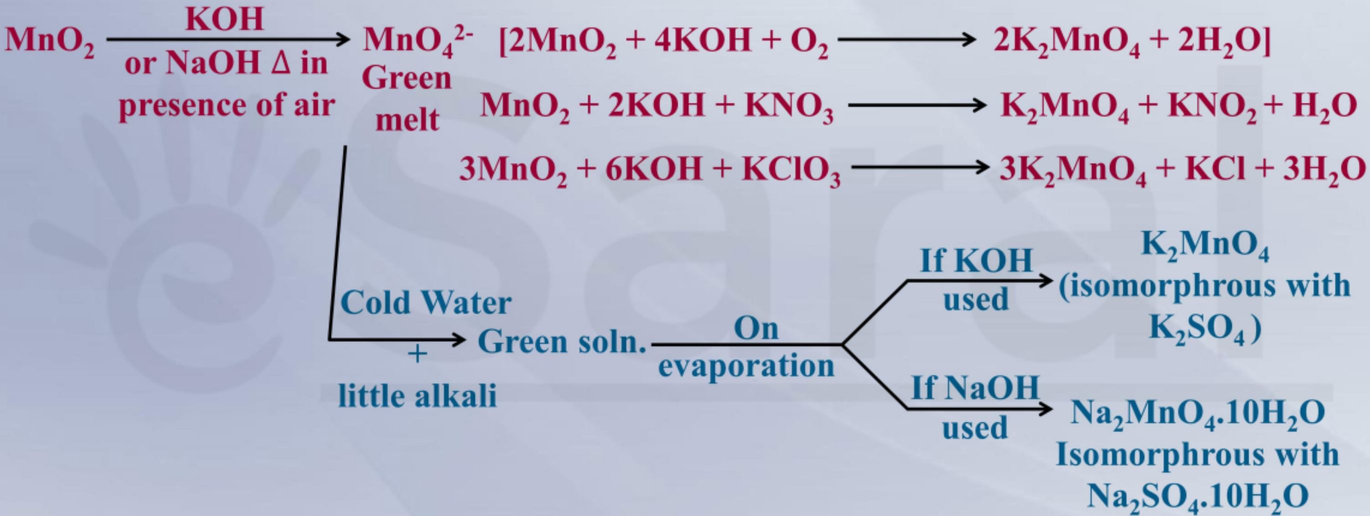
$$\underset{\text{Hot conc.}}{Na_2Cr_2O_7} + 2KCl \xrightarrow[\text{Decomposition}]{\text{Double}} \overset{\text{Titration}}{\boxed{K_2Cr_2O_7}} + 2NaCl$$

NaCl crystallises out first and filtered off.

Then $K_2Cr_2O_7$ crystallised out on cooling

The Chromates and Dichromates are interconvertible in aqueous solution depending upon pH of the solution.

Manganate & Permanganate



$MnO_2 \xrightarrow[\text{or NaOH } \Delta \text{ in presence of air}]{KOH} MnO_4^{2-}$ Green melt

$[2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O]$

$MnO_2 + 2KOH + KNO_3 \longrightarrow K_2MnO_4 + KNO_2 + H_2O$

$3MnO_2 + 6KOH + KClO_3 \longrightarrow 3K_2MnO_4 + KCl + 3H_2O$

$\xrightarrow[\text{+ little alkali}]{\text{Cold Water}}$ Green soln. $\xrightarrow[\text{evaporation}]{\text{On}}$

$\xrightarrow[\text{used}]{\text{If KOH}}$ K_2MnO_4 (isomorphrous with K_2SO_4)

$\xrightarrow[\text{used}]{\text{If NaOH}}$ $Na_2MnO_4.10H_2O$ Isomorphrous with $Na_2SO_4.10H_2O$

The green solution of manganate is quite stable in Alkali, but in pure water and in presence of acids, deposits MnO_2 and gives a purple solution of Permanganate. Learn

$$\overset{\text{Manganate}}{3K_2MnO_4} + 2H_2O \longrightarrow \underset{\textbf{Purple}}{\overset{\text{Permanganate}}{2KMnO_4}} + \underset{\textbf{Dark Brown}}{MnO_2\downarrow} + 4KOH$$

Permanganate is diamagnetic whereas manganate is paramagnetic. Learn

Lanthanides (Rare Earths or Lanthanones)

Lanthanides are reactive elements so are not found in free state in nature.

The general configuration of Lanthanides may be given as $4f^{1-14}5s^{2}5p^{6}5d^{0-1}6s^{2}$.

Atomic Number	Element	Symbol	Outer electronic configuration	
			Atomic	+3 ion
58	Cerium	Ce	$4f^{1}\ 5d^{1}6s^{2}$	$4f^{1}$
59	Praseodymium	Pr	$4f^{3}\ 6s^{2}$	$4f^{2}$
60	Neodymium	Nd	$4f^{4}\ 6s^{2}$	$4f^{3}$
61	Promethium	Pm	$4f^{5}\ 6s^{2}$	$4f^{4}$
62	Samarium	Sm	$4f^{6}\ 6s^{2}$	$4f^{5}$

Atomic Number	Element	Symbol	Outer electronic configuration	
			Atomic	+3 ion
63	Europium	Eu	$4f^7\,6s^2$	$4f^6$
64	Gadolinium	Gd	$4f^7\,5d^1\,6s^2$	$4f^7$
65	Terbium	Tb	$4f^9\,6s^2$	$4f^8$
66	Dysprosium	Dy	$4f^{10}\,6s^2$	$4f^9$
67	Holmium	Ho	$4f^{11}\,6s^2$	$4f^{10}$
68	Erbium	Er	$4f^{12}\,6s^2$	$4f^{11}$
69	Thulium	Tm	$4f^{13}\,6s^2$	$4f^{12}$
70	Ytterbium	Yb	$4f^{14}\,6s^2$	$4f^{13}$
71	Lutetium	Lu	$4f^{14}\,5d^1\,6s^2$	$4f^{14}$

For Lanthanides, the +3 Oxidation is common.

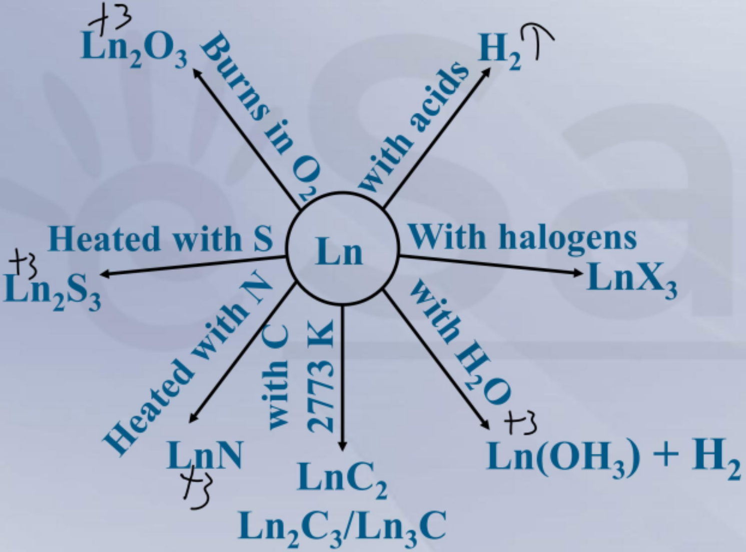
Alloy

Alloys of Lanthanides with Fe are called Misch metals, which consists of a Lanthanoid metal (~ 95%) and Iron (~ 5%) and traces of S, C, Ca and Al.

Basic Nature

$La(OH)_3$ is most basic in nature while $Lu(OH)_3$ least basic.

Chemical Reactions of The Lanthanoids



$Ln \xrightarrow{\text{Burns in } O_2} \overset{+3}{Ln_2O_3}$

$Ln \xrightarrow{\text{with acids}} H_2\uparrow$

$Ln \xrightarrow{\text{With halogens}} LnX_3$

$Ln \xrightarrow{\text{with } H_2O} \overset{+3}{Ln(OH_3)} + H_2$

$Ln \xrightarrow{\text{with C 2773 K}} LnC_2$

Ln_2C_3/Ln_3C

$Ln \xrightarrow{\text{Heated with N}} \underset{+3}{LnN}$

$Ln \xrightarrow{\text{Heated with S}} \overset{+3}{Ln_2S_3}$

Uses of d&f block elements

Group 11 metals are called coinage metals.

UK copper coins are copper-coated steel.
Silver UK coins are Cu/Ni alloy.

AgBr is used in photography industry.

Gunmetal is an alloy of copper, tin, zinc and lead.

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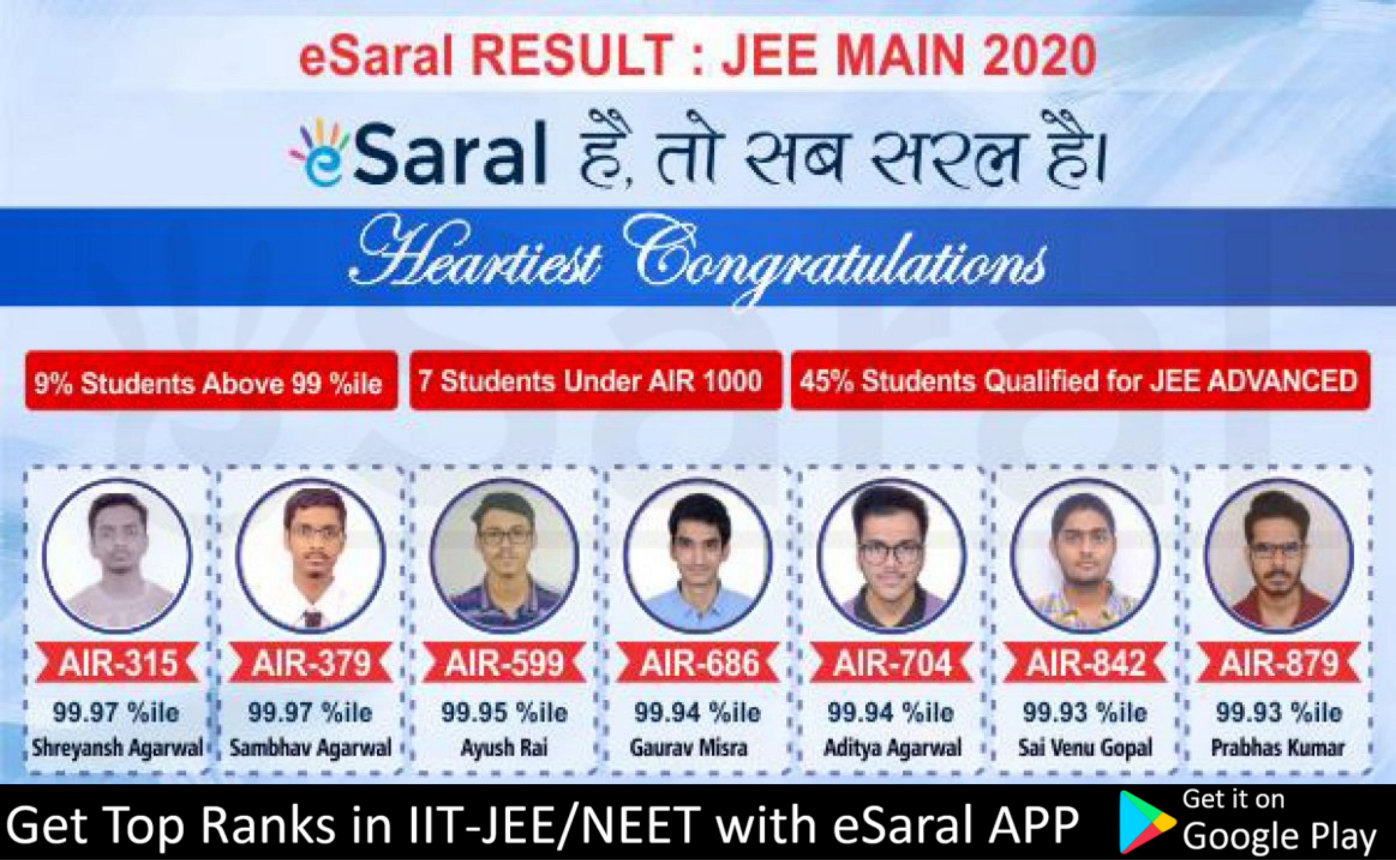

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