p–BLOCK ELEMENTS

IMPORTANT CONCEPTS :

Back bonding	**Dimerisation**
Inert pair effect	**Oxyacids**
Hydrolysis	**Allotropes**
Silicates and Silicones	**Drying agent and bleaching agents**
Reactions and compounds (Group 13-18)	

BACK BONDING

It is formed between two covalently bonded adjacent atoms.

Conditions for back bonding :

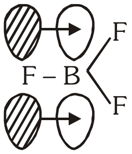
(i) Both bonded atoms must belong to 2nd period or one bonded atom must belong to 2nd period and the other must belong to 3rd period.

(ii) One bonded atom must possess vacant orbital and the other bonded atom must possess lone pair.

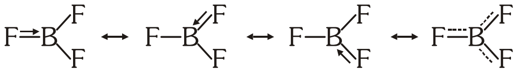
- **As a result of back bonding between the bonded atoms, bond length decreases and bond energy increases.**

Back bonding :

It is a partial sideways overlap in which there is a slight electron transference from electron rich atom to electron deficient atom. As a result the electron deficiency of the deficient atom gets slightly compensated.



F–donor
B–acceptor



(B–F) B.O = 4/3 = 1.33

Types of back bonding :

Based on type of orbital : (2 types)

pπ-pπ back bonding

pπ-dπ back bonding

pπ-pπ back bonding :

Order of strength : $2p - 2p > 2p - 3p > 2p - 4p$ ....

Size ↑ extent of B.B. ↓

It is used to explain following observations :-

(a) Abnormal bond length and bond energy of B-F bond in BF_3.

(b) Lewis acidic order of **Boron** and **Beryllium** halides.

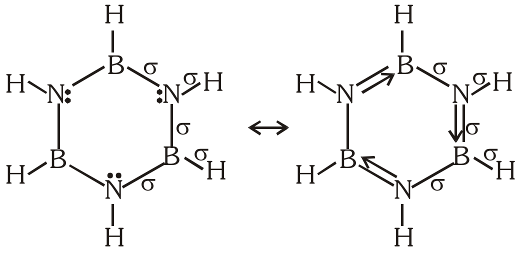
$$\underbrace{BF_3 < BCl_3}_{\substack{\text{BB effective} \\ \text{so Lewis acid} \\ \text{strength}\downarrow}} < BBr_3 < BI_3$$

$$BeF_2 < BeCl_2 < BeBr_2 < BeI_2$$

(c) **Hybridisation :** If a lone pair participates in back bonding then it is not considered in hybridisation.

Ex. $B_3N_3H_6$ (inorganic benzine or borazene or borazole)

- Hybridisation of B as well as N = sp^2



- Inorganic benzene is more reactive than organic benzene as in it the **bonds are polar,** although over all molecule is non polar.

(d) If back bonding is present then tendency to form dimer or polymer decreases.

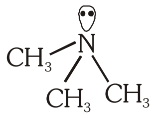
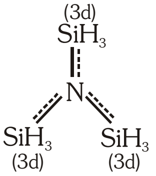
Ex. BF_3, BeF_2

pπ-dπ back bonding :

$$\underset{\substack{\text{2nd period}\\\text{with lp}}}{p} \Longrightarrow \underset{\substack{\text{3rd period}\\\text{empty}}}{d}$$

it is used to explain following observations :

(a) Hybridisation

Ex. Trimethyl amine	Trisilyl amine
$(CH_3)_3N$	$(SiH_3)_3N$
	
• sp^3 hybrid (N)	• sp^2 hybrid (N)
• trigonal pyramidal	• trigonal planar
• Lewis base (due to presence of lp)	• Not Lewis base
	• Bond angle increases

(b) Acidic strength

$CH_3-\ddot{\underset{\cdot\cdot}{O}}\,\vdots\,H$ Methyl alcohol	$SiH_3-\ddot{\underset{\cdot\cdot}{O}}\,\vdots\,H$ Silyl alcohol
• No back bonding	• Back bonding present in conjugate base
• Less acidic	• More acidic

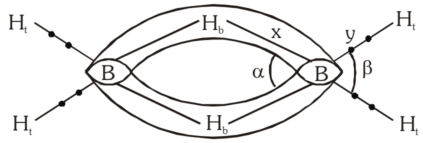
DIMERISATION / POLYMERISATION

Types of Dimerisation

3C—2e	3C—4e
B_2H_6	$(BeCl_2)_2$
$(BeH_2)_2$	$(BeCl_2)_n$
$(BeH_2)_n$	$(AlCl_3)_2$
$Al_2(CH_3)_6$	$(ICl_3)_2$
$Ga_2(CH_3)_6$	

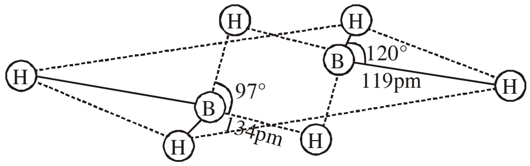
(A) By banana Bond or by 3C–2e bond or by e^- deficient bond

(a) B_2H_6



$\alpha < \beta$ = BA

$x > y$ = BL



$2C - 2e^-$ bonds = 4 $3C - 2e^-$ bonds = 2 The structure of diborane, B_2H_6

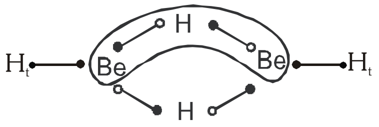
Hybridisation state = sp^3

Electron deficient molecule (act as Lewis acid)

- All four terminal hydrogen and two boron atoms are present in same plane both bridging H are present in perpendicular plane.
- If substitution reaction takes place than only four terminal hydrogen atom will be substituted.

$$B_2H_6 \rightleftharpoons BH_4^- + BH_2^+ \text{ , } B_2H_6 + 4CH_3\text{–}Cl \rightarrow B_2H_2(CH_3)_4 + 4HCl$$

(b) $(BeH_2)_2$ (dimer of BeH_2 in vapour state)

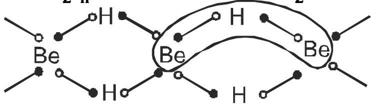


Hybridisation state = sp^2

Planar

electron deficient molecule

(c) $(BeH_2)_n$ (polymer of BeH_2 in solid state)



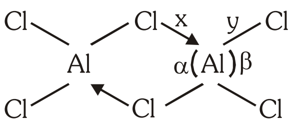
Hybridisation state = sp^3

Non-planar

electron deficient molecule

(B) By-coordinate Bond / 3C-4e bond

(a) Al_2Cl_6 (dimer of $AlCl_3$ in liquid or solid state)



BA = $\alpha < \beta$

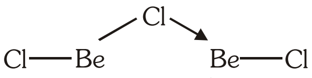
BL = $x > y$

Hybridisation state = sp^3

Non-planar

octet complete

(b) $(BeCl_2)_2$ (dimer of $BeCl_2$ in vapour state)

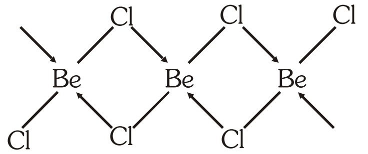


Hybridisation state = sp^2

Planar

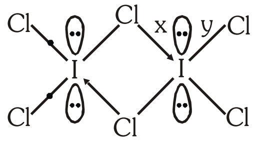
electron deficient molecule

(c) $(BeCl_2)_n$ (polymer of $BeCl_2$ in solid state)



Hybridisation state = sp^3
Non-planar
octet complete

(d) I_2Cl_6 (dimer of ICl_3)



Hybridisation state = sp^3d^2
Planar
super octet complete (12 electrons)

Note :

(i) BCl_3, BBr_3 & BI_3 do not form dimer due to smaller size of boron & large size of halogen (due to more steric repulsion)

(ii) BF_3 cannot form dimer due to its back bonding.

(iii) AlF_3 cannot form dimer due to its ionic nature.

INERT PAIR EFFECT

	Group-13	Group-14	Group-15
(group oxidation state)	$\underbrace{ns^2np^1}_{+3}$	$\underbrace{ns^2np^2}_{+4}$	$\underbrace{ns^2np^3}_{+5}$

- While moving down the group the stability of lower oxidation state (2 less than group oxidation state) progressively increases, for the last element of the group the stability of lower oxidation state becomes even greater than the group oxidation state. **This is called inert pair effect.**
- For the last element group oxidation state is highly oxidising in nature.

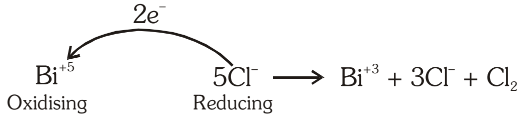
Group-13		Group-14		Group-15	
B	+3	C	+4	N	+5
Al	+3	Si	+4	P	+5
Ga	+3 > +1	Ge	+4 > +2	As	+5 > +3
In	+3 > +1	Sn	+4 > +2	Sb	+5 > +3
Tl	**+3 < +1**	**Pb**	**+4 < +2**	**Bi**	**+ 5 < +3**

Reason : As we move down the group there is presence of d & f-orbitals in inner shells which have poor shielding effect hence Z_{eff} increases. As a result the ns^2 electron pair becomes more and more tightly held to the nucleus and becomes reluctant to participate in bonding.

Examples :

1. $PbCl_2$ is more stable than $PbCl_4$.
2. TlCl is more stable than $TlCl_3$
3. $GaCl_3$ is more stable than $TlCl_3$
4. $SnCl_4$ is more stable than $PbCl_4$
5. Thalium (III) iodide does not exist.
6. PbI_4 does not exist.
7. Only BiF_5 exists but $BiCl_5$ does not exist ?

Ans. $\underset{\text{(Oxidising)}}{Bi^{+5}} + \underset{\text{(Less reducing)}}{5F^-} \longrightarrow \underset{\text{(Stable)}}{BiF_5}$



OXY ACID

General Formula of Oxy acid : $H_xZ_yO_z$ (Z = non metal)

- Compounds which contain Z-OH bond are known as oxyacids.

- $$\underbrace{\begin{array}{c}\text{Acidic oxide}\\ \text{or}\\ \text{Non metallic oxide}\end{array}}_{\text{Anhydrides of oxyacids}} + H_2O \underset{\Delta}{\rightleftharpoons} \text{Oxyacids}$$

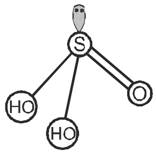
$$\text{Anhydrides of their corresponding oxyacids} \left\{ \begin{array}{l} CO_2 + H_2O \rightarrow H_2CO_3 \\ (\text{So } CO_2 \text{ is anhydride of } H_2CO_3) \\ SO_3 + H_2O \rightarrow H_2SO_4 \\ Cl_2O_7 + H_2O \rightarrow 2HClO_4 \\ Mn_2O_7 + H_2O \rightarrow \underset{\text{Permanganic acid}}{2HMnO_4} \\ CrO_3 + H_2O \rightarrow \underset{\text{Chromic acid}}{H_2CrO_4} \\ N_2O_5 + H_2O \rightarrow 2HNO_3 \\ N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3 \ \textbf{(Special case)} \\ (N_2O_4 \text{ is mixed anhydride of } HNO_2 \ \& \ HNO_3) \\ Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4 \\ (Cl_2O_6 \text{ is mixed anhydride of } HClO_3 \text{ and } HClO_4) \end{array} \right.$$

- Oxidation state of central atom does not change.

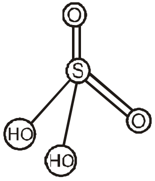
Pyro	**Meta**	**Per oxy acid**	**Hypo**	
2 mole oxy acid $\downarrow -H_2O$ pyro acid	1 mole oxy acid $\downarrow -H_2O$ meta acid	$\downarrow$ Z—O—O—H	Ous acid $\downarrow -O$ Hypo us acid	ic acid $\downarrow -O$ Hypo ic acid
Ex. $H_2S_2O_5$ $H_2S_2O_7$ $H_4P_2O_7$	**Ex.** HPO_3 HBO_2	**Ex.** H_2SO_5 $H_2S_2O_8$ HNO_4 CH_3CO_3H $C_6H_5CO_3H$	**Ex.** HOX H_3PO_2	**Ex.** $H_4P_2O_6$

OXY ACIDS OF SULPHUR

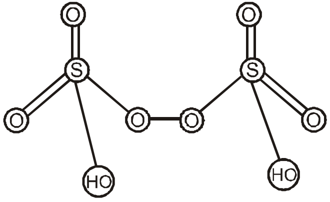
sulphurous acid



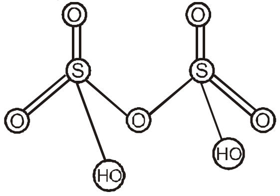
sulphuric acid



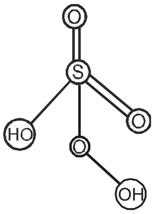
peroxodi sulphuric acid (Marshall's)



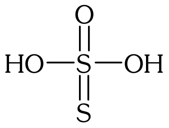
pyro sulphuric acid



Peroxo monosulphuric acid
(Caro acid)

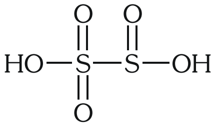


Thiosulphuric acid



$\mathrm{HO{-}\underset{\underset{S}{\|}}{\overset{\overset{O}{\|}}{S}}{-}OH}$

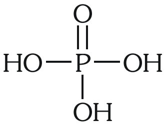
Pyrosulphurous acid



$\mathrm{HO{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}\overset{\overset{O}{\|}}{S}{-}OH}$

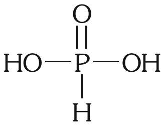
OXY ACID OF PHOSPHORUS

Phosphoric acid

(i) 

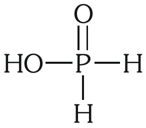
$\mathrm{HO{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}OH}$

Phosphorous
(phosphonic) acid

(ii) 

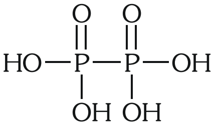
$\mathrm{HO{-}\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}{-}OH}$

Hypo phosphorous
(phosphinic) acid

(iii) 

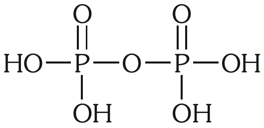
$\mathrm{HO{-}\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}{-}H}$

Hypo phosphoric acid

(iv) 

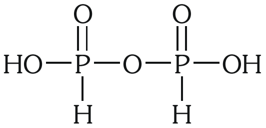
$\mathrm{HO{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}OH}$

Pyro phosphoric acid

(v) 

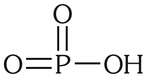
$\mathrm{HO{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}O{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}OH}$

Pyro phosphorous acid

(vi) 

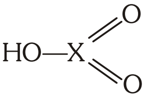
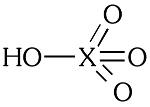
$\mathrm{HO{-}\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}{-}O{-}\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}{-}OH}$

Meta phosphoric acid

(vii) 

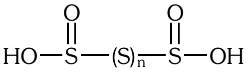
$\mathrm{O{=}\overset{\overset{O}{\|}}{P}{-}OH}$

OXY ACIDS OF HALOGENS

Hypohalous	**Halous**	**Halic**	**Per halic**
HO—X	O=X—OH		
+1	+3	+5	+7
HOCl	$HClO_2$	$HClO_3$	$HClO_4$
HOBr	—	$HBrO_3$	$HBrO_4$
HOI	—	HIO_3	HIO_4

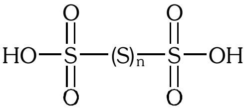
OXY ACIDS CONTAINING S-S LINKAGE

Polythionus
$H_2S_nO_4$
o.s.=+3



$\mathrm{HO{-}\overset{\overset{O}{\|}}{S}{-}(S)_n{-}\overset{\overset{O}{\|}}{S}{-}OH}$

Polythionic
$H_2S_nO_6$
o.s.=+5



$\mathrm{HO{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}(S)_n{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}OH}$

[Number of S-S-linkage = number of sulphur atom-1]

Important points : $H_2S_2O_3$
$H_2S_2O_4$ (S-S bond)
$H_2S_2O_5$
$H_2S_2O_6$
$H_2S_2O_7$ →[S-O-S]
$H_2S_2O_8$→[S-O-O-S]

Trick for drawing structure of oxy compound

Oxy compounds	Group present
$X_2O_6^{-q}$ $X_2O_7^{-q}$ $X_2O_8^{-q}$	[X-X] [X-O-X] [X-O-O-X]

Some important points

(1) Oxy acid of phosphorus having +1 & +3 oxidation state (having P-H bond) can act as reducing agent or give disproportionation reaction on heating.

$$\overset{+3}{H_3PO_3} \xrightarrow{\Delta} \overset{+5}{H_3PO_4} + \overset{-3}{PH_3}$$

$$H_3PO_3 + Ag_2O \longrightarrow H_3PO_4 + 2Ag\downarrow$$

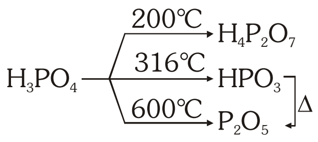
Order of reducing nature.

$$\begin{bmatrix} H_3PO_2 & > & H_3PO_3 & > & H_3PO_4 \\ \text{Two P}-\text{H} & & \text{One P}-\text{H} & & \text{Zero P}-\text{H} \\ \text{bonds} & & \text{bond} & & \text{bond} \end{bmatrix}$$

Note : Nitrogen compound having +1 & +3 oxidation state gives disproportion to reaction in acidic medium.

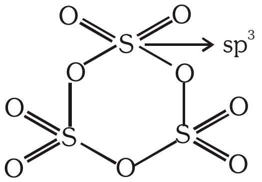
$$\overset{+3}{HNO_2} \xrightarrow{H^+} \overset{+5}{HNO_3} + \overset{+2}{NO}$$

(2) **Heating effect of phosphoric acid**



(3) **Heating effect of boric acid** $2H_3BO_3 \xrightarrow[-2H_2O]{100°C} 2HBO_2 \xrightarrow[-H_2O]{\Delta} B_2O_3$

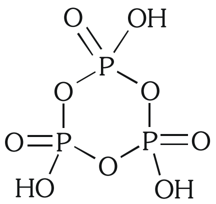
(4) **SO_3 exists as a cyclic trimer (S_3O_9)**



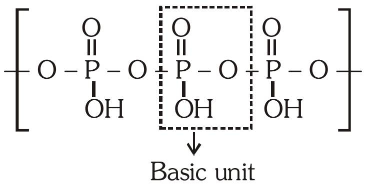
6 S=O bonds
3 S–O–S bonds
sp^3 hybrid 'S', Non planar

(5) **Metaphosphoric acid exists as dimer, cyclic trimer or polymer**

$(HPO_3)_3$



$(HPO_3)_n$



(6) **Acidic nature of oxy acids.**

General concept :

For same elements $\begin{pmatrix} \text{Acidic nature} & \propto & \text{Oxidation number of} \\ \text{of oxyacids} & & \text{active element} \end{pmatrix}$

$(\text{Acidic nature of oxyacids} \propto \text{EN of active element})$ for different elements

Exception :

- $\boxed{\textbf{for oxy acids of P}}$

$$\left(\text{Acidic nature} \propto \frac{1}{\text{Oxidation number}}\right)$$

Example : $H_3PO_2 > H_3PO_3 > H_3PO_4$ (acidic order)

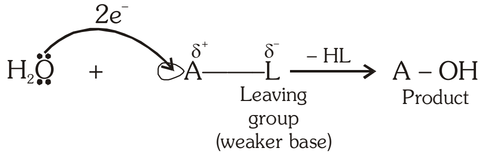
HYDROLYSIS

Chemical reaction of H_2O with a covalent compound.

Condition :

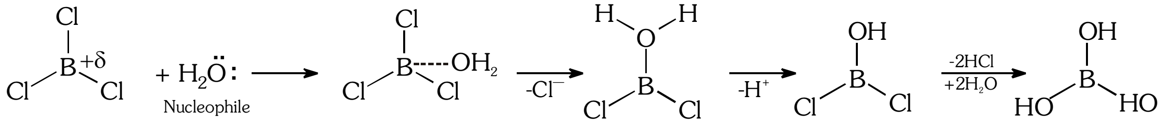
One atom must possess vacant orbital and positive charge.

Mechanism : (SN^2 mechanism)



- Weaker base goes out and a stronger base substitutes it.

  Example



- For hybridisation of transition state

  Reactant ⟶ Transition state

  Ex. : $sp \longrightarrow sp^2$

  $sp^2 \longrightarrow sp^3$

  $sp^3 \longrightarrow sp^3d$

Important examples of hydrolysis

Hydrolysis of some important covalent molecules.

(a) $BeCl_2 + 2H_2\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}} \longrightarrow Be(OH)_2 + 2HCl$

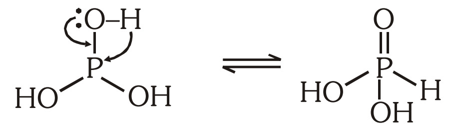
(b) $MgCl_2 + 2H_2\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}} \longrightarrow Mg(OH)_2 + 2HCl$

(c) $BCl_3 + 3H_2\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}} \longrightarrow B(OH)_3 + 3HCl$

or H_3BO_3

(orthoboric acid)

(d) $PCl_3 + 3H_2\underset{\bullet\bullet}{\overset{\bullet\bullet}{O}} \longrightarrow P(OH)_3 + 3HCl$

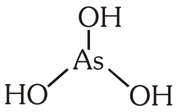


(P=O is more stable than P–O bond)

(Hydrolysis + Tautomerism) (H_3PO_3) (Phosphorous acid)

(Basicity = 2)

(e) $AsCl_3 + 3H_2\ddot{O} \longrightarrow As(OH)_3 + 3HCl$



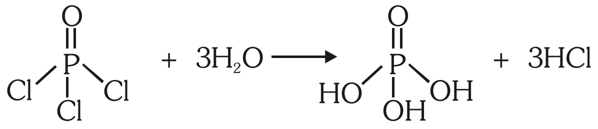
No tautomerism & only hydrolysis
(As=O is not formed due to large size of As)

(f) $AlCl_3 + \underset{\text{(steam)}}{3H_2\ddot{O}} \longrightarrow \underset{\text{(white gelatinous ppt)}}{Al(OH)_3} + 3HCl$

$AlCl_3 + \underset{\text{(normal)}}{6H_2\ddot{O}} \longrightarrow \underbrace{[Al(H_2O)_6]^{+3} + 3Cl^-}_{\text{Ionic compound due to hydration}}$

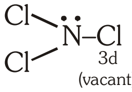
(g) $PCl_5 + H_2\ddot{O} \longrightarrow PCl_3\boxed{(Cl_2) + H_2}O \longrightarrow POCl_3 + 2HCl$

two axial bonds



H_3PO_4 = phosphoric acid

- **Hydrolysis is not a redox reaction**

(h)  $+ H_2\ddot{O} \longrightarrow NH_3 + 3HOCl$

3d (vacant)

(Hypochlorous acid)

(i) $NF_3 + H_2\ddot{O} \longrightarrow$ No reaction

- **Partial hydrolysis**

due to ionic character

(j) $SbCl_3 + H_2\ddot{O} \longrightarrow \underset{\text{(Antimonyl chloride)}}{SbOCl} + 2HCl$

(k) $BiCl_3 + H_2\ddot{O} \longrightarrow \underset{\text{(Bismuthyl chloride)}}{BiOCl} + 2HCl$

(Bismuthyl chloride)
(white ppt also known as **white pearl**)

Hydrolysis of interhalogen compounds

(a) **Type xx' :** $Cl-F + H_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} \longrightarrow \underset{\text{Halogen acid}}{HF} + \underset{\text{Oxy acid (Hypochlorous acid)}}{HOCl}$

x = oxy acid (same oxidation number)

x' = Halogen acid

(b) **Type xx'_3 :** $ClF_3 + H_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} \longrightarrow HF + \underset{\text{(Chlorous acid)}}{HClO_2}$

(c) **Type xx'_5 :** $ClF_5 + H_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} \longrightarrow HF + \underset{\text{(Chloric acid)}}{HClO_3}$

(d) **Type xx'_7 :** $IF_7 + H_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} \longrightarrow HF + \underset{\text{(Periodic acid)}}{HIO_4}$

Hydrolysis of oxyacids

(a) $\underset{\text{(Pyro sulphuric acid)}}{H_2S_2O_7} + H_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} \longrightarrow \underset{\text{(Sulphuric acid)}}{2H_2SO_4}$

(b) $\underset{\text{(Peroxo disulphuric acid)}}{H_2S_2O_8} + H_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} \longrightarrow H_2SO_4 + \underset{\text{(Caro's acid)}}{H_2SO_5}$

$$\downarrow$$

$$\text{Net} \Rightarrow 2H_2SO_4 + H_2O_2$$

(c) $\underset{\text{(Pyro phosphoric acid)}}{H_4P_2O_7} + H_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} \longrightarrow \underset{\text{(Phosphoric acid)}}{2H_3PO_4}$

(d) $\underset{\text{(Peroxo diphosphoric acid)}}{H_4P_2O_8} + H_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} \longrightarrow H_3PO_4 + H_3PO_5$

$$\downarrow$$

$$\text{Net product} \Rightarrow 2H_3PO_4 + H_2O_2$$

Hydrolysis of oxides (N, P, S, Cl)

(a) $SO_2 + H_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} \longrightarrow \underset{\text{(Sulphurous acid)}}{H_2SO_3}$

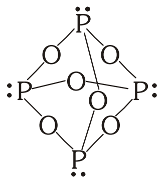
(b) $SO_3 + H_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} \longrightarrow \underset{\text{(Sulphuric acid)}}{H_2SO_4}$

(c) $Cl_2O_7 + H_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} \longrightarrow \underset{\text{(Perchloric acid)}}{2HClO_4}$

(d) $N_2O_5 + H_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} \longrightarrow \underset{\text{(Nitric acid)}}{HNO_3}$

(e) $P_4O_6 + H_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} \longrightarrow \underset{\text{(Phosphorous acid)}}{H_3PO_3}$

(f) $P_4O_{10} + H_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} \longrightarrow \underset{\text{(Phosphoric acid)}}{H_3PO_4}$

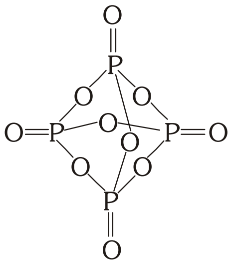


P_4O_6

→ sp^3 hybrid 'P'

→ 6 P–O–P bonds

→ lp on 'P' = 4



P_4O_{10}

→ sp^3 hybrid 'P'

→ 6 P–O–P bonds

→ 4 P = O bonds

Hydrolysis of Xe-fluoride

(a) $2XeF_2(s) + 2H_2O(\ell) \rightarrow 2Xe\ (g) + 4\ HF(aq) + O_2(g)$ **(It is redox reaction not hydrolysis)**

Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3

(b) $XeF_6 + 3H_2O \rightarrow XeO_3 + 6\ HF$

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

$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

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

(c) $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$ **(Redox + hydrolysis both)**

Hydrolysis of ionic compounds

(a) Carbides (b) Nitrides (c) Phosphides

Hydrolysis of non-metals and halogen

(a) $F_2 + H_2\ddot{\underset{\cdot\cdot}{O}} \longrightarrow 2HF + 1/2\ O_2$ (O_3 is also produced in small amount & mixture of O_2 & O_3 is known as ozonide)

(Phosphoric acid)

- 'F₂' is the only non-metal that can oxidise H_2O as it is a powerful oxidising agent. Other halogens & non-metals undergo disproportionation with water in basic medium. (Redox reaction)

(b) $P_4 + H_2\ddot{\underset{\cdot\cdot}{O}} \longrightarrow PH_3 + H_3PO_2 \xrightarrow{NaOH} PH_3 + NaH_2PO_2$

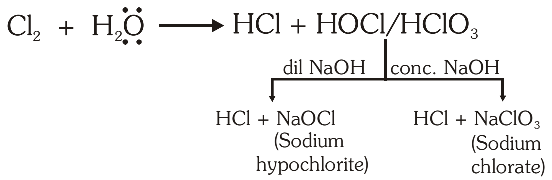
(Sodium hypophosphite)

To speed up the reaction

(c) $S_8 + H_2\ddot{\underset{\cdot\cdot}{O}} \longrightarrow H_2S + H_2S_2O_3 \xrightarrow{NaOH} H_2S + Na_2S_2O_3$

Thiosulphuric acid

Sodium thiosulphate (Hypo) used in photography

(d) 

$$Cl_2 + H_2\ddot{O} \longrightarrow HCl + HOCl/HClO_3$$

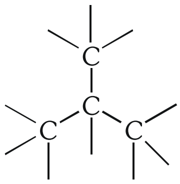
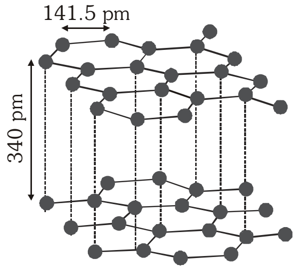
dil NaOH $\rightarrow$ $HCl + NaOCl$ (Sodium hypochlorite)

conc. NaOH $\rightarrow$ $HCl + NaClO_3$ (Sodium chlorate)

ALLOTROPES

(A) Allotropes of Carbon

Crystalline	**Amorphous**
Ex. Diamond	**Ex.** Coke
Graphite	Charcoal
Fullerene	Coal, C-lamp black

DIAMOND	**GRAPHITE**
	
Each carbon bonded with four other carbon atom sp^3 hybridisation	Each carbon bonded with three other carbon atom sp^2 hybridisation
tetrahedral structure	hexagonal layer structure
Insulator due to absence of free electrons	Conductor due to presence of delocalised electrons
Hard due to presence of strong sigma bond and 3D structure	Soft due to presence of weak van der Waals forces between two layers
Density = 3.35 gm/cm^3	Density = 2.22 gm/cm^3
High melting point (giant molecule)	Low melting point
Bond length (C—C) = 1.54Å	Bond length (C—C) = 1.41Å

Special Point :

(i) Thermodynamically graphite is more stable than diamond.

(ii) Aqueous solution of graphite is known as **aquadag**.

(iii) Graphite is also known as **plumbago (used in lead pencil)**

(iv) Graphite use as a dry lubricants.

(v) **Hardest allotrope** of carbon is diamond, **softest allotrope** is lamp black, **purest allotrope** is fullerene

Fullerene

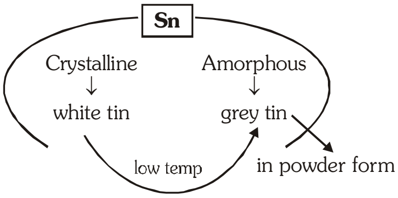
- C-60 & C-70 are common fullerene.
- C-60 is also known as Buckmeinster fullerene (Bucky ball)

- There are 32 rings $32 \begin{cases} 12 \text{ pentagonal} \\ 20 \text{ hexagonal} \end{cases}$
- Each carbon atom bonded with 3 other carbon by sigma & double bond (resonance)
- sp^2 hybridisation & aromatic in nature

✍ **Dangling Bond**

In diamond or graphite some surface carbon atom have free valency. These carbon atoms form new bonds with impurities. These new bonds are known as dangling bond.

(B) ALLOTROPES OF TIN



(C) ALLOTROPES OF PHOSPHOROUS

(a) white/yellow phosphorous (b) Red phosphorous (c) Black phosphorous

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

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

$$\begin{tikzcd}
\text{Red Phosphorous} \arrow[r, "803K", "\text{high P}"'] & \alpha\text{-Black Phosphorous} \\
\text{White Phosphorous} \arrow[u, "573K", "\text{inert medium}"'] \arrow[r, "473K", "\text{high P}"'] & \beta\text{-Black Phosphorous}
\end{tikzcd}$$

(D) ALLOTROPES OF SULPHUR

I.

S

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

II. (a) density of αS > βS

(b) Both are puckered crown shape having S_8 units

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

(d) S_6 is chair form of S

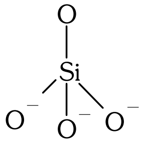
III. Effect of temperature :

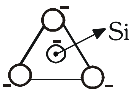
$S_{8(\alpha)} \xrightarrow{95.5°C} S_{8(\beta)} \xrightarrow{119°C} S_{(liq)} \xrightarrow{130-200°C}$ Viscosity of liquid increase $\xrightarrow{>200°C}$ viscosity decrease

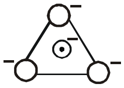
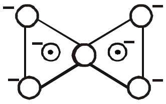
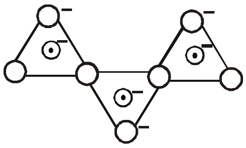
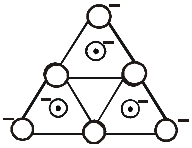
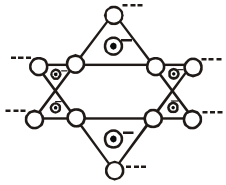
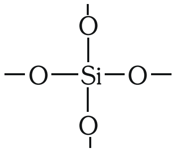
(A) SILICATES

Basic / structural unit : SiO_4^{-4}

SiO_4^{-4} have a tendency of polymerisation





Silicate	No. of shared oxygen per unit	General formula	Structure	Example
Ortho silicate	0	SiO_4^{-4}		Zircon $ZrSiO_4$
Pyro silicate	1	$Si_2O_7^{-6}$		Hemi morphite $Zn_3Si_2O_7 \cdot Zn(OH)_2 \cdot 2H_2O$
Single chain silicate	2	$(SiO_3^{-2})_n$		$LiAlSi_2O_6$ Spodumene
Cyclic silicate	2	$(SiO_3^{-2})_n$		Beryl ($Be_3Al_2Si_6O_{18}$)
Sheet silicate	3	$(Si_2O_5^{-2})_n$		Talc $Mg_3(OH)_2(Si_2O_5)_2$
3-D silicate	4	$(SiO_2)_n$	 $-O-\underset{\underset{O}{\mid}}{\overset{\overset{O}{\mid}}{Si}}-O-$	Silica (SiO_2)

(B) Sodium Zeolite [$Na_2Al_2Si_2O_8$]/[$Na_2O.Al_2O_3.2SiO_2.xH_2O$]

(i) It is a 3-D silicate

(ii) It is used in

(a) For softening of hard water

(b) For cracking of hydrocarbon & isomerisation

Ex. ZSM-5 (Zeolite) is used to convert ethyl alcohol into petrol.

(C) SILICA : Generally silica is inert but it can react with NaOH & HF.

(a) $\underset{\text{base}}{2NaOH} + \underset{\text{acid}}{SiO_2} \rightarrow Na_2SiO_3 + H_2O$

[Na_2SiO_3 known as water glass or water soluble]

(b) $SiO_2 + 4HF \rightarrow 2H_2O + SiF_4$

$SiF_4 + 2HF \rightarrow \underset{\text{hexa fluoro silicic acid}}{H_2[SiF_6]}$

- This process is also known as **Etching of glass.**

(D) SILICONES

Silicones are organometallic polymer which contain R_2SiO as a basic unit.

Properties :

(i) Silicones are chemically inert due to presence of strong sigma bond.

(ii) Silicones have water repelling nature due to presence of alkyl group.

(iii) Silicones are insulator due to absence of free electrons.

Preparation :

Alkyl chloro silane $\xrightarrow{\text{hydrolysis}}$ product $\xrightarrow{\text{condensation}}$ silicones

R_3SiCl : dimer (used to stop chain formation)

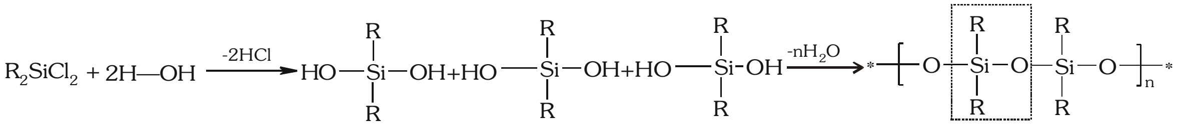
R_2SiCl_2 : linear polymer

$RSiCl_3$: cross link polymer

(a) Dimer silicone:

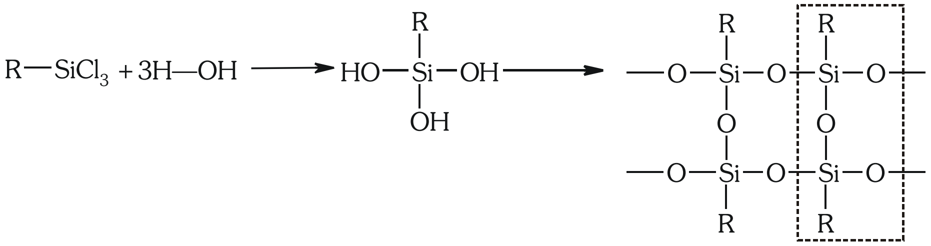
$$2R_3Si—Cl + 2H—OH \xrightarrow{-2HCl} R_3Si—OH + HO—SiR_3 \xrightarrow{-H_2O} R_3Si—O—SiR_3$$

(b) Linear chain silicone



$(R_2SiO)_n$

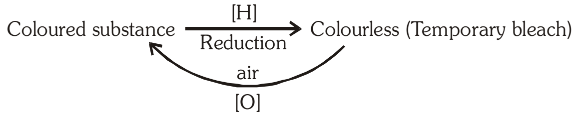
(c) Cross linked silicone



$(R_2Si_2O_3)_n$

BLEACHING AGENTS AND DEHYDRATING AGENTS

(A) BLEACHING AGENTS

- Bleaching can be done by oxidation or reduction.
- Coloured substance $\xrightarrow[\text{Oxidation}]{[O]}$ Colourless (Permanent bleach)
- 

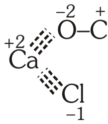
Examples :

	By oxidation	By Reduction
(1)	O_3 (Dry bleach)	SO_2 (with moisture)
(2)	H_2O_2 (with moisture)	
(3)	Cl_2 (with moisture)	

- **Bleaching powder :** Used in textile industries. Bleaches by oxidation.

  $CaCl_2 . Ca(OCl)_2 . Ca(OH)_2 . 2H_2O$ (average oxidation number of Cl = 0)

  or



(Oxidation number of Cl = +1 and −1)

(B) DEHYDRATING AGENTS

Example : [P_4O_{10}, (Conc.) H_2SO_4, CaO (Quick line), $CaCl_2$ (Anhydrous)]

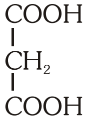
- $\text{Acid} \xrightarrow[\text{agent}]{\text{dehydrating}} H_2O + \text{Oxide}$

Example :

- $HCOOH \xrightarrow[H_2SO_4]{\text{conc.}} H_2O + CO$ (Lab preparation of CO)

- 

  $\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow[H_2SO_4]{\text{conc.}} CO + CO_2 + H_2O$ (Lab preparation of CO & CO_2)

- 

  $\begin{matrix} COOH \\ | \\ CH_2 \\ | \\ COOH \end{matrix} \xrightarrow[H_2SO_4]{\text{conc.}} 2H_2O + O{=}C{=}C{=}C{=}O$ (Carbon suboxide)

  (Malonic acid)

- $2HClO_4 \xrightarrow{P_4O_{10}} H_2O + Cl_2O_7$

- $2HNO_3 \xrightarrow{P_4O_{10}} H_2O + N_2O_5$

- Charring of sugar (dehydration) :

$$C_{12}H_{22}O_{11} \xrightarrow[H_2SO_4]{\text{conc.}} 11\ H_2O + C \text{ (Black mass)}$$

Some extra points :

(i) NH_3 can not be dried by conc. H_2SO_4, P_4O_{10} and $CaCl_2$

(ii) Alcohols, phenols can not be dried by metal hydrides.

(iii) $MgCl_2.6H_2O$ and $AlCl_3.6H_2O$ can not be dried by heating alone.

BORON FAMILY (GROUP 13)

INTRODUCTION

The p-block elements are those elements of the periodic table in which the differentiating electron (or the last electron) enters the p-subshell of the last (outermost) shell. Since the maximum capacity of any atomic orbital is of two electrons with opposite spins (Pauli's principle), the maximum number of electrons that can be accommodated in any p-subshell is six. As a result, the p-block of the periodic table consists of six group: 13 (III A), 14(IV A), 15(V A), 16(VI A), 17(VIIA) and 18 (zero group). On the basis of electronic configuration, the element He is to be excluded from the p-block as its last electron enters the s-subshell of the last shell.

BORON FAMILY

Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to boron, and gallium, indium and thallium are almost exclusively metallic in character,

GENERAL CHARACTERISTICS

Physical properties :

- Boron is non-metallic in nature.
- It is extremely hard and black coloured solid. It exists in many allotropic forms.
- Due to very strong crystalline lattice, boron has unusually high melting point.
- Rest of the member are soft metals with low melting point and high electrical conductivity. Gallium with low melting point (303 K), could exist in liquid state during summer. Its **high boiling point (2676 K) makes it a useful material for measuring high temperatures.**

Chemical properties

Reactivity towards air

- Boron is unreactive in crystalline form.
- Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack.
- Amorphous boron and aluminium metal on heating in air form B_2O_3 and Al_2O_3 respectively. With dinitrogen at high temperature they form nitrides.

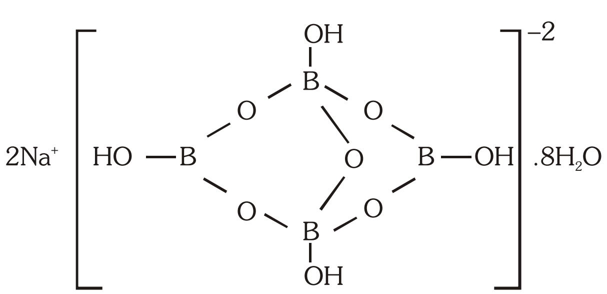
$2E(s) + 3\,O_2\,(g) \xrightarrow{\Delta} 2\,E_2O_3(s)$; $2E(s) + N_2(g) \xrightarrow{\Delta} 2\,EN\,(s)$.

The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of indium and thallium are basic in their properties.

COMPOUNDS OF BORON

(I) Borax ($Na_2B_4O_7.10H_2O$)

$2Na^+[B_4O_5(OH)_4]^{-2}.8H_2O$



Important points :

B–O–B linkage = 5

Total B–O bonds = 14

Two Boron-sp^2 hybridised

Two Boron-sp^3 hybridised

(i) From Colemanite.

When colemanite powder is heated with Na_2CO_3 solution, the following reaction occurs with the precipitation of $CaCO_3$.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3 \downarrow + Na_2B_4O_7 + 2NaBO_2$$

The filtrate is cooled when white crystals of borax are precipitated. The mother liquor on treatment with CO_2 converts $NaBO_2$ to $Na_2B_4O_7$ which precipitates out on crystallization.

$$4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$$

(ii) From orthoboric acid.

Borax is obtained by the action of Na_2CO_3 on orthoboric acid.

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2\uparrow$$

Properties :

(i) Borax is a white powder, less soluble in cold water, more soluble in hot water.

(ii) Its aqueous solution is alkaline because of its hydrolysis to weak acid H_3BO_3 and strong alkali NaOH.

$$Na_2B_4O_7 + 7H_2O \longrightarrow 4H_3BO_3 + 2NaOH$$

(iii) **Action of heat.**

When borax powder is heated, it first swells due to loss of water in the form of steam but at 740°C it becomes converted into colourless transparent borax bead.

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10\ H_2O\uparrow$$

$$Na_2B_4O_7 \xrightarrow{740°C} 2NaBO_2 + B_2O_3 \text{ (borax bead)}$$

Borax-bead test :

Borax reacts with certain metal salts such as, Ni^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+} etc. to form coloured metaborates. The colour of the metaborates can be used to identify the metallic ions (cations) in salts.

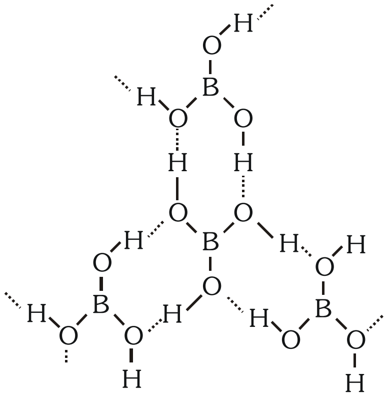
$$Na_2B_4O_7\cdot 10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{740°C} \underbrace{2NaBO_2 + B_2O_3}_{\text{glassy mass}} \rightarrow CuO + B_2O_3 \longrightarrow Cu(BO_2)_2 \text{ (blue bead)}$$

Uses : Borax is used

1. in borax bead test
2. in purifying gold
3. as flux during welding of metals and
4. in production of glass.

(II) ORTHO BORIC ACID [H_3BO_3/$B(OH)_3$]

Orthoboric acid is greasy to touch less soluble in cold water but more soluble in hot water. In the solid state, the $B(OH)_3$ units are hydrogen bonded together into two dimensional sheets with almost hexagonal symmetry.



(A) Preperation :

(i) It is precipitated by treating a concentrated solution of borax with mineral acid.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3 \downarrow$$

$$Na_2B_4O_7 + HCl + 5H_2O \rightarrow 2NaCl + 4H_3BO_3 \downarrow$$

(ii) From Colemanite: Powdered colemanite is suspended in water and excess SO_2 is passed through it. On filtering and cooling the filtrate, white crystals of H_3BO_3 are obtained.

$$Ca_2B_6O_{11} + 4SO_2 + 11H_2O \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$$

(B) Properties:

It is a weak monobasic acid soluble in water and in aqueous solution the boron atom completes its octet by accepting OH^- from water molecules:

$$B(OH)_3(aq) + 2H_2O(\ell) \rightleftharpoons [B(OH)_4]^-(aq) + H_3O^+(aq), \qquad (Pk_a = 9.25)$$

It, therefore, functions as a Lewis acid and not as a proton donor like most acids.

(C) Test for Borate radical :

When boric acid is heated with ethyl alcohol, the evolved gas is burned forming a green edged flame.

$$H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\text{ethyl borate (volatile)}}{B(OC_2H_5)_3} + 3H_2O$$

Uses :

1. It is an antiseptic and its water solution is used as an eyewash.
2. It is also used in glass, enamel and pottery industry.

(III) DIBORANE (B_2H_6)

Binary compounds of boron with hydrogen are called boron hydrides or boranes.

Preparation :

(i) $4BF_3 + 3LiAlH_4 \xrightarrow{\text{ether}} 2B_2H_6 + 3LiF + 3AlF_3$

(ii) $2NaBH_4 + I_2 \xrightarrow{\text{ether}} B_2H_6 + 2NaI + H_2$

(iii) $2BF_3 + 6NaH \xrightarrow{453\text{ K}} B_2H_6 + 6NaF$ (Industrial method)

Properties :

(i) B_2H_6 is colourless gas and highly reactive (boiling point 183 K).

(ii) It catches fire spontaneously in air and explodes with O_2. Reaction with oxygen is extremely exothermic.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O \qquad \Delta H = -2160 \text{ kJ mol}^{-1}$$

Mixtures of diborane with air or oxygen in flame spontaneously producing large amount of heat. Diborane has a higher heat of combustion per unit weight of fuel than most other fuels. It is therefore used as a rocket fuel.

At red-heat the boranes decomposes to boron and hydrogen.

(iii) Reaction with water is instantaneous.

$$B_2H_6 + 6H_2O \longrightarrow 2B(OH)_3 + 6H_2$$

(iv) The electron deficient 3c-2e B–H–B bridges are sites of nucleophilic attack.

Small amines such as NH_3, CH_3NH_2 and $(CH_3)_2NH$ give unsymmetrical cleavage of diborane.

$$B_2H_6 + 2NH_3 \longrightarrow [H_2B(NH_3)_2]^+ + [BH_4]^-$$

Large amines such as $(CH_3)_3N$ and pyridine give symmetrical cleavage of diborane.

$$2(CH_3)_3N + B_2H_6 \longrightarrow 2H_3B \leftarrow N(CH_3)_3$$

$$B_2H_6 + 2CO \xrightarrow{200°C,\ 20\text{ atm}} 2BH_3CO \text{ (borane carbonyl)}$$

(v) The reaction with ammonia depends on conditions.

$$B_2H_6 + NH_3 \xrightarrow[\text{low temperature}]{\text{Excess } NH_3} B_2H_6 \,.\, 2NH_3 \text{ or } [H_2B(NH_3)_2]^+ [BH_4]^- \text{ (ionic compound).}$$

$$\xrightarrow[\text{higher temperature } (> 200°C)]{\text{Excess } NH_3} (BN)_x \textbf{ boron nitride/BORAZONE. (Inorganic graphite)}$$

$$\xrightarrow[\text{higher temperature } (200°C)]{\text{Ratio } 2NH_3 : 1\, B_2H_6} B_3N_3H_6 \textbf{ borazole/BORAZINE. (Inorganic benzene)}$$

Borazole is much more reactive than benzene.

COMPOUNDS OF ALUMINIUM :

ALUM

(a) Alums are double sulphates with their general formula $M_2SO_4.M'_2(SO_4)_3.24H_2O$

where M= monovalent radical like Na^+ , K^+, NH_4^+ and M' = Trivalent radical like Al^{+3}, Cr^{+3}. Fe^{+3}.

(b) The different alums are -

(i) Potash alum - $K_2SO_4.Al_2(SO_4)_3.24H_2O$

(ii) Chrome alum - $K_2SO_4\ Cr_2(SO_4)_3.\ 24\ H_2O$

(iii) Iron alum - $(NH_4)_2SO_4.\ Fe_2(SO_4)_3.\ 24H_2O$

(iv) Ammonium alum - $(NH_4)_2SO_4.\ Al_2(SO_4)_3.\ 24H_2O$

(c) In alums each metal ion is surrounded by six water molecules.

(d) Lithium does not form alum because Li ion is too small to have a coordination number of six.

(e) **Pseudo alums** : Double sulphates of divalent ions and trivalent ions with 24 water molecules in their crystals are known as **pseudo alums**.

Eg. $MSO_4.X_2\,(SO_4)_3.24H_2O$

M = divalent or Bivalent ion

X = Trivalent metal ion

Properties :

(a) It is a white crystalline solid highly soluble in water.

(b) On heating it undergoes dehydration and swells up.

(c) It is highly acidic in aqueous solution due to the hydrolysis of aluminium sulphate to sulphuric acid

(d) It is a double salt and its aqueous solution gives reaction of all the constituents ions K^+, Al^{+3}, SO_4^{-2}.

Uses :

(i) Alum is used to stop bleeding.

(ii) It is used for purification of water.

(iii) It is used as a mordant in dyeing industry.

(iv) Alum is used for tanning of leather.

CARBON FAMILY (GROUP 14)

PHYSICAL PROPERTIES

- All group 14 members are solids.
- Carbon and silicon are non-metals, germanium is metalloid whereas tin and lead are soft metals with low melting points.
- Melting points and boiling points of group 14 elements are much higher than those of corresponding elements of group 13 due to stronger metallic bonding.

COMPOUNDS OF CARBON

(A) Carbon Monoxide (CO)

(I) Preparation

(i) It is formed together with CO_2, when carbon or carbonaceous matter is oxidized by air or oxygen. It is also produced when CO_2 is reduced by red- hot carbon; this reaction is of importance in metal extractions.

$$C(s) + CO_2(g) \longrightarrow 2CO(g)$$

(ii) In the laboratory it can be prepared by dehydrating methanoic acid with concentrated sulphuric acid .

$$HCOOH\ (liq) \xrightarrow[\text{conc.}H_2SO_4]{373\,K} CO(g) + H_2O$$

(II) Physical Properties

(i) Carbon monoxide is a colourless, odourless gas which burns in air with a blue flame, forming CO_2.

(ii) It is sparingly soluble in water and is a neutral oxide.

(iii) CO is toxic, because it forms a complex with haemoglobin in the blood and this complex is more stable than oxy-haemoglobin. This prevents the haemoglobin in the red blood corpuscles from carrying oxygen round the body. This causes oxygen deficiency, leading to unconsciousness and then death.

(iv) It acts as good reducing agents for all metal oxide.

(B) CARBON DIOXIDE (CO_2)

Preparation :

(i) Complete combustion of carbon containing compounds.

$$CH_4 + O_2 \longrightarrow CO_2 + H_2O$$

(ii) In the laboratory it can be conveniently made by the action of dilute hydrochloric acid on marble chips :

$$CO_3^{2-}(aq) + 2H^+(aq) \longrightarrow CO_2(g) + H_2O(\ell)$$

(iii) Industrially it is produced as a by-product during the manufacture of quicklime and in fermentation processes:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)\ ; \qquad C_6H_{12}O_6(aq)\{glucose\} \longrightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

Properties :

(i) It is a colourless, odourless and heavy gas.

(ii) Carbon dioxide is the acid anhydride of carbonic acid, which is a weak dibasic acid and ionises in two steps as follows :

$$H_2CO_3(aq) + H_2O\ (\ell) \rightleftharpoons HCO_3^-(aq) + H_3O^+\ (aq)$$

$$HCO_3^-\ (aq) + H_2O\ (\ell) \rightleftharpoons CO_3^{2-}\ (aq) + H_3O^+\ (aq)$$

H_2CO_3 / HCO_3^- buffer system helps to maintain pH of blood between 7.26 to 7.42.

A solution of carbonic acid in water will slowly turn blue litmus red and when the solution is boiled, all the CO_2 is evolved.

(iii) Carbon dioxide readily reacts with alkalies forming the carbonate and, if CO_2 is in excess, the hydrogen carbonate. This is the basis of the lime-water test for CO_2 gas.

$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(liq)\ ; \qquad CaCO_3(s) + H_2O(liq) + CO_2(g) \rightarrow Ca(HCO_3)_2(aq)$$

The above reaction accounts for the formation of temporarily hard water.

(iv) Gaseous CO_2 is extensively used to carbonate soft drinks. Being heavy and non–supporter of combustion it is used as fire extinguisher. A substantial amount of CO_2 is used to manufacture urea.

(C) Carbides :

On the basis of type of bonding carbides are of three types :-

(I) Salt like carbides (ionic carbides)

(II) Covalent carbides (giant molecular carbides)

(III) Interstitial carbides.

(I) Salt like carbides (ionic carbides) :

(a) These are formed by strong electropositive elements of groups 1, 2 and 13

(b) These are transparent crystalline substances and do not conduct electric current in the solid state.

(c) These are easily hydrolysed by water or dilute acids to give aliphatic hydrocarbons,

(i) **Methanides (Methides)** – Methanides are the carbides which give methane on hydrolysis. They contain C^{4-} ions.

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

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

(ii) **Acetylides** – These are the carbides which yield acetylene on hydrolysis.

They contain the ion C_2^{2-}.

e.g. $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$ or $C_2^{2-} + 2H^+ \longrightarrow C_2H_2$

(iii) **Allylides** – These carbides give methylacetylene or allylene (CH_3–C≡CH) on hydrolysis.

They contain C_3^{4-} ions.

e.g. $Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3\text{–}C\equiv CH$

(II) Covalent carbides (giant molecular carbides)

(a) Covalent carbides are the compounds of carbon with elements having similar electronegativity.

(b) These are covalent, polymeric, thermally stable, extremely hard, high melting and technically inert solid.

(c) B_4C and SiC are two main covalent carbides.

(III) Interstitial carbides.

Transition metals like Ti, Zr, Hf, V, Nb, Ta and Mo form these carbides. The metals retains their **close packed lattice** and carbons are incorporated in their interstitial spaces. These carbides are extremely hard and have very high melting points. The carbides of V and Ta are very hard hence they are used for manufacture of high speed cutting tools.

GLASS

(a) Glass is a hard, brittle transparent, amorphous solid or supercooled liquid made up of silicates of Na, Ca and other metals like Pb, Zn etc.

(b) Being amorphous solid (not a true solid) it has no sharp melting and melts at high temperature.

(c) Glass has no definite chemical formula, however it may be represented as :

$$xM_2O.yM'O.6SiO_2$$

where M = monovalent metals (eg : Na, K)

M' = bivalent metals Ca, Pb, Zn etc. x and y are integers.

(d) $CaO + Na_2CO_3 + 6SiO_2 \xrightarrow{1700K} \underbrace{Na_2SiO_3 + CaSiO_3 + 4SiO_2}_{\text{Glass}} + CO_2$

Different Types of Glass

(i) **Soda or Soft glass or Sodalime glass :** It is common glass. Contain Na & Ca metal carbonate. Used for formation of tube, window.

(ii) **Potash or Hard glass :** It is a mixture of potassium and calcium silicates. It fuses with difficulty. It is used for making hard glass apparatus.

(iii) **Flint glass :** It is mixture of potassium and lead silicates. It has a very high refractive index and is used for making electric bulbs and optical instruments.

(iv) **Crooke's glass :** It is a optical glass containing CeO_2 which prevents the entry of UV rays.

(v) **Pyrex glass or borasil or borosilicate glass :** It is used to make lab appliances as it is resistant to heat, shock and common reagents. It is a mixture of zinc and barium boro silicates and alumina silicate.

Small part of SiO_2 is replaced by boric oxide/borax.

Low coefficient and thermal expansion, can with stand sudden change in temperature so used for making lab glass wares.

SOME GASEOUS FUELS

(a) Water gas or syn gas = $CO + H_2$

(b) Producer gas = $CO + N_2$

(c) Semi water gas = $CO + N_2 + H_2$

(d) Natural gas = CH_4

(e) Coal gas = $[CO_2 + CO + H_2 + CH_4]$

NITROGEN FAMILY (GROUP 15)

Group 15 includes nitrogen phosphorus, arsenic, antimony and bismuth.

PHYSICAL PROPERTIES:

- Dinitrogen is a diatomic gas while all others are solids.
- Except nitrogen, all the elements show allotropy.
- As we go down the group, there is a shift from non-metallic to metallic through metalloidic character. Nitrogen and phosphorus are non-metal, arsenic and antimony are metalloid and bismuth is a typical metal.

CHEMICAL PROPERTIES

Oxidation States and trends in a chemical reactivity :

- The common oxidation states of these elements are –3, +3 and +5. The tendency to exhibit –3 oxidation state decreases down the group , bismuth hardly forms any compound in –3 oxidation state.
- Nitrogen also exhibits +1, +2, +4 oxidation states when it reacts with oxygen. Phosphorus also shows +1 and +4 oxidation states in some oxyacids.
- In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution.

  For example, $3\,HNO_2 \longrightarrow HNO_3 + H_2O + 2\,NO$
- Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and –3 both in alkali and acid. However +3 oxidation state in case of arsenic , antimony and bismuth become increasingly stable with respect to disproportionation.

Reactivity towards hydrogen :

- All the elements of Group 15 form hydrides of the type EH_3 where E=N, P, As, Sb or Bi.
- The stability of hydrides decreases from NH_3 to BiH_3. Consequently the reducing character of the hydrides increases. Ammonia is only a mild reducing agent while BiH_3 is the strongest reducing agent amongst all the hydrides. Due to weaker Bi–H bond.

Reactivity towards oxygen :

- All these elements form two types of oxides : E_2O_3 and E_2O_5 . The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic , that of arsenic and antimony amphoteric and those of bismuth is predominantly basic.

Reactivity towards halogens :

- These elements react to form two series of halides : EX_3 and EX_5 .
- All the trihalides of these elements except those of nitrogen are stable. In case of nitrogen, only NF_3 is known to be stable. Trihalides except BiF_3 are predominantly covalent in nature.

COMPOUND OF NITROGEN

NITROGEN GAS (N_2) :

Nitrogen is an important and essential constituent of proteins and amino acids. Nitrates and other nitrogen compounds are extensively used in fertilizers and explosive.

(a) Preparation :

(i) **Laboratory method of preparation :**

$$NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + H_2O\,(\ell) + NaCl_{(aq)}$$

N_2 is collected by the downward displacement of water.

This reaction takes place in two steps as given below :

$$NH_4Cl + NaNO_2 \rightarrow NH_4NO_2 + NaCl\ ;\ NH_4NO_2 \xrightarrow{\Delta} N_2\uparrow + 2H_2O.$$

(ii) **By heating ammonium dichromate :**

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2\uparrow + 4H_2O + Cr_2O_3$$

(iii) **Very pure nitrogen can be obtained by heating sodium or barium azide.**

$$Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$$

$$2NaN_3 \xrightarrow{300°C} 3N_2 + 2Na$$

(iv) **Industrial methods of preparation :**

From liquified air by fractional distillation : The boiling point of N_2 is –196°C and that of oxygen is –183°C and hence they can be separated by fractional distillation of air.

(b) Properties :

(i) N_2 is a colourless, odourless gas very less soluble in water. It is neither combustible nor a supporter of combustion.

(ii) **Reaction with oxygen:** Dinitrogen combines with dioxygen only at very high temperature (at about 2000K) to form nitric oxide.

This reaction is endothermic. $N_2 + O_2 \longrightarrow 2NO$

(c) Uses :

(i) For providing an inert atmosphere during many industrial processes where presence of air or O_2 is to be avoided.

(ii) For manufacture of NH_3 by the Haber's process.

(iii) Liquid dinitrogen is used as a refrigerent to preserve biological materials, food items & cryosurgery.

AMMONIA (NH_3)

(a) Preparation :

(i) By the action of any base or alkali on any ammonium salt :

$$NH_4NO_3 + NaOH \xrightarrow{\Delta} NH_3\uparrow + NaNO_3 + H_2O$$

$$(NH_4)_2SO_4 + Ca(OH)_2 \xrightarrow{\Delta} 2NH_3\uparrow + CaSO_4 + 2H_2O$$

This is a general method and is used as a test for ammonium salts.

Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.

$$NH_2CONH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$$

(ii) Industrial methods of preparation :

Haber's process : $N_2 + 3H_2 \xrightleftharpoons[\text{Iron oxide+}K_2O\text{ \& }Al_2O_3]{500^0C,200atm} 2NH_3$

In accordance with Le Chatelier's principle, high pressure would favour the formation of ammonia. The optimum conditions for the production of ammonia are a pressure of 200×10^5 Pa (about 200 atm), a temperature of ~ 700 K and the use of a catalyst such as iron oxide with small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium.

(b) Physical properties : Ammonia is a colourless gas with a pungent odour.

(c) Chemical properties :

(i) Its aqueous solution is weakly basic due to the formation of OH^- ions.

$$NH_3\,(g) + H_2O\,(\ell) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

(ii) It forms ammonium salts with acids, e.g., NH_4Cl, $(NH_4)_2SO_4$ etc. As a weak base, it precipitates the hydroxides of many metals from their salt solutions. For example ,

$$FeCl_3\,(aq) + NH_4OH\,(aq) \longrightarrow \underset{\text{(brown ppt)}}{Fe_2O_3 \,.\, xH_2O\,(s)} + NH_4Cl\,(aq)$$

$$ZnSO_4\,(aq) + 2NH_4OH\,(aq) \longrightarrow \underset{\text{(white ppt)}}{Zn(OH)_2\,(s)} + (NH_4)_2SO_4\,(aq)$$

(iii) The presence of lone pair of electrons on the nitrogen atoms of the ammonia molecule makes it a Lewis base. It donates the electrons pair and forms linkage with metal ions and the formation of such complex compounds finds applications in detection of metal ions such as Cu^{2+} , Ag^+

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

$$\underset{\text{(colourless)}}{Ag^+\,(aq)} + Cl^-\,(aq) \rightleftharpoons \underset{\text{(white ppt)}}{AgCl\,(s)}$$

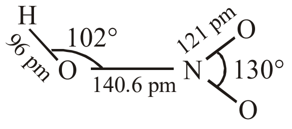
$$\underset{\text{(white ppt)}}{AgCl\,(s)} + 2\,NH_3\,(aq) \longrightarrow \underset{\text{(colourless)}}{[Ag\,(NH_3)_2]Cl\,(aq)}$$

OXIDES OF NITROGEN :

Nitrogen forms a number of oxides, N_2O, NO, N_2O_3, NO_2 or N_2O_4 and N_2O_5. All these oxides of nitrogen exhibit pπ-pπ multiple bonding between nitrogen and oxygen.

Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide]	N_2O	+ 1	$NH_4NO_3 \xrightarrow{Heat} N_2O + 2\,H_2O$	colourless gas , neutral
Nitrogen monoxide [Nitrogen(II) oxide]	NO	+ 2	$2\,NaNO_2 + 2\,FeSO_4 + 3\,H_2SO_4$ $\longrightarrow Fe_2(SO_4)_3 + 2\,NaHSO_4$ $+ 2\,H_2O + 2\,NO$	colourless gas , neutral
Dinitrogen trioxide [Nitrogen(III) oxide]	N_2O_3	+ 3	$2\,NO + N_2O_4 \xrightarrow{250\,K} 2\,N_2O_3$	blue solid , acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO_2	+ 4	$2\,Pb(NO_3)_2 \xrightarrow{673\,K} 4\,NO_2 + 2\,PbO + O_2$	brown gas, acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N_2O_4	+ 4	$2\,NO_2 \underset{Heat}{\overset{cool}{\rightleftharpoons}} N_2O_4$	colourless solid / liquid , acidic
Dinitrogen pentoxide [Nitrogen(IV) oxide]	N_2O_5	+ 5	$4\,HNO_3 + P_4O_{10} \longrightarrow 4\,HPO_3 + 2\,N_2O_5$	colourless solid, acidic

NITRIC ACID (HNO_3)



Structure of HNO_3

(a) **Preparation :**

In the laboratory, nitric acid is prepared by heating KNO_3 or $NaNO_3$ and concentrated H_2SO_4 in a glass retort.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

On a large scale it is prepared mainly by **Ostwald's process.**

This method is based upon catalytic oxidation of NH_3 by atmospheric oxygen.

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

Nitric oxide thus formed combines with oxygen giving NO_2.

$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

Nitrogen dioxide so formed, dissolves in water to give HNO_3.

$$3\,NO_2\,(g) + H_2O\,(\ell) \longrightarrow 2\,HNO_3\,(aq) + NO\,(g)$$

NO thus formed is recycled and the aqueous HNO_3 can be concentrated by distillation upto ~ 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4.

(b) Physical properties :

(i) It is a colourless liquid. Freezing point is 231.4 K and boiling point is 355.6 K. Laboratory grade nitric acid contains ~ 68% of the HNO_3 by mass and has a specific gravity of 1.504.

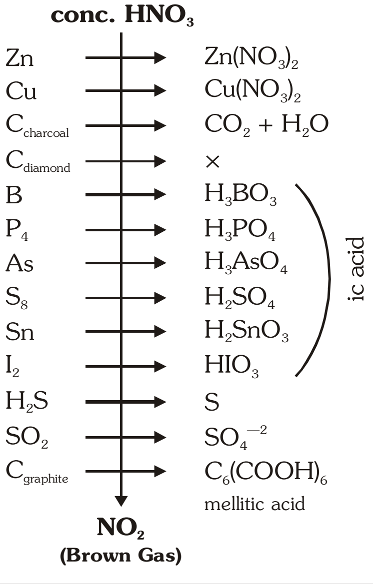
(ii) In the gaseous state, HNO_3 exists as a planar molecule.

(iii) In aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.

$$HNO_3\,(aq) + H_2O\,(\ell) \longrightarrow 2H_3O^+\,(aq) + NO_3^-\,(aq)$$

(iv) Concentrate nitric acid is a strong oxidising agent and attacks most metals except Au & Pt. The product of oxidation depend upon the concentration of the acid, temperature and nature of metal.

(v) Concentrate HNO_3 also oxidises non-metals and their compounds.



Types of Metal	conc. HNO_3	dil. HNO_3	very dil. HNO_3
negative SRP metal	Metal nitrate + NO_2	Metal nitrate + N_2O	Metal nitrate + $NH_4NO_3/(NH_3)$
positive SRP metal & Pb	Metal nitrate + NO_2	Metal nitrate + NO	×
Metalloids, Non-metals & Sn	ic-acid + NO_2	×	×

EX.

- $Zn(NO_3)_2 + N_2O \xleftarrow{\text{dil.}HNO_3} Zn \xrightarrow{\text{conc.}HNO_3} Zn(NO_3)_2 + NO_2$
- $Cu(NO_3)_2 + NO \xleftarrow{\text{dil.}HNO_3} Cu \xrightarrow{\text{conc.}HNO_3} Cu(NO_3)_2 + NO_2$

SOME EXCEPTIONAL POINTS

- **Mg and Mn form H_2 gas on reaction with very dilute HNO_3**
- **Be, Al, Fe, Cr do not react with conc. HNO_3 due to fromation of protective oxide layer.**
- **Au and Pt (Noble metals) do not react with conc. HNO_3**
- **Sn reacts with conc. HNO_3 and forms H_2SnO_3 (metastannic acid)**
- **Au and Pt react only with aqua regia (3 part of conc. HCl and 1 part of conc. HNO_3)**

$3HCl + HNO_3 \rightarrow NOCl + 2H_2O + Cl^-$

$$Au + 3Cl^- \rightarrow AuCl_3 \xrightarrow{HCl} \underset{\text{tetrachloro auric acid}}{HAuCl_4}$$

$$Pt + 4Cl^- \rightarrow PtCl_4 \xrightarrow{2HCl} \underset{\text{hexachloro platinic acid}}{H_2PtCl_6}$$

conc. HNO_3 + skin → yellow spot (protein → xanthoprotein)

- **The major use of nitric acid is in the manufacture of ammonium nitrate for fertilizers and other nitrates for use in explosives and pyrotechnics. It is also used for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds. Other major uses are in the pickling of stainless steel, etching of metals and as an oxidiser in rocket fuels.**

COMPOUNDS OF PHOSPHORUS :

Phosphine (PH_3) :

(a) Preparation :

(i) Phosphine is prepared by the reaction of calcium phosphide with water.

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

(ii) In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO_2.

$$P_4 + 3\,NaOH + 3\,H_2O \longrightarrow PH_3 + \underset{\text{(sodium hypophosphite)}}{3\,NaH_2PO_2}$$

(iii) When pure, it is non inflammable but becomes inflammable owing to the presence of P_2H_4 or P_4 vapours. To purify it from the impurities , it is absorbed in HI to form phosphonium iodide (PH_4I) which on treating with KOH gives off phosphine.

$$PH_4I + KOH \longrightarrow KI + H_2O + PH_3$$

(b) Properties :

(i) It is a colourless gas with rotten fish smell and is highly poisonous. It is slightly soluble in water. The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2.

(ii) When absorbed in copper sulphate or mercuric chloride, the corresponding phosphides are obtained.

$$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2\downarrow + 3H_2SO_4$$

$$3HgCl_2 + 2\,PH_3 \longrightarrow Hg_3P_2\downarrow \text{(brownish black)} + 6\,HCl$$

(iii) Phosphine is weakly basic and like ammonia, gives phosphonium compounds with acids

e.g. $PH_3 + HBr \longrightarrow PH_4Br$

- **Uses :** The spontaneous combustion of phosphine is technically used in **Holme's signals.** Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.
- It is also used in the production of smoke screens. Calcium phosphide reacts with water producing phosphine which burns in air to give clouds of phosphorus pentaoxide and that acts as smoke screens.

PHOSPHOROUS HALIDES

Phosphorous forms two types of halides, PX_3 (X = F, Cl, Br, I) and PX_5 (X = F, Cl, Br).

Phosphorous Trichloride (PCl_3)

(a) Method of preparation

(i) It is obtained by passing dry chlorine over heated white phosphorus.

$P_4 + 6Cl_2 \rightarrow 4PCl_3$

(ii) It is also obtained by the action of thionyl chloride with white phosphorus.

$P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$

(b) Properties

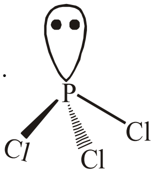
(i) It is a colourless oily liquid and hydrolyses in the presence of moisture.

$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

(ii) It reacts with organic compounds containing –OH group such as CH_3COOH, C_2H_5OH.

$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_4$

$3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$



PHOSPHORUS PENTACHLORIDE (PCl_5)

(a) Method of preparation

(i) Phosphorus pentachloride is prepared by the reaction of white phosphorus with excess of dry chlorine.

$P_4 + 10Cl_2 \rightarrow 4PCl_5$

(ii) It can also be prepared by the action of SO_2Cl_2 on phosphorus.

$P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$

(b) Properties

(i) PCl_5 is a yellowish white powder and in moist air, it hydrolyses to $POCl_3$ and finally gets converted to phosphoric acid.

$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$

(ii) When heated, it sublimes but decomposes on stronger heating.

$$PCl_5 \xrightarrow{\text{Heat}} PCl_3 + Cl_2$$

(iii) It reacts with organic compounds containing –OH group converting them to chloro derivatives.

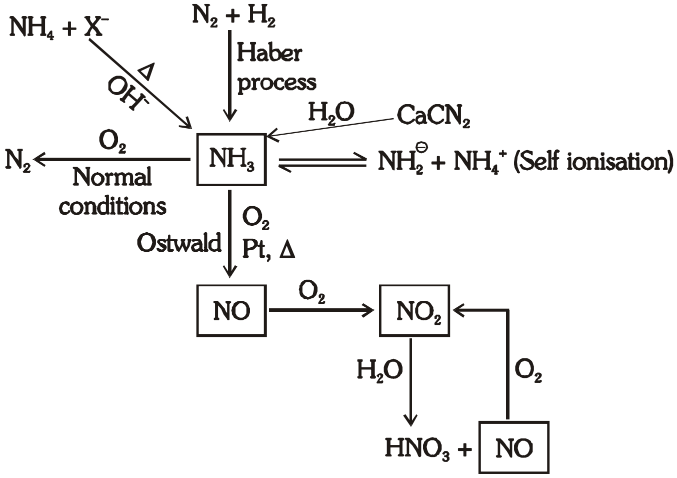
$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$

(iv) Finally divided metals on heating with PCl_5 give corresponding chlorides.

$2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$

$Sn + 2PCl_5 \rightarrow SnCl_4 + 2PCl_3$

(v) It is used in the synthesis of some organic compounds, e.g., C_2H_5Cl, CH_3COCl.



NCERT QUESTIONS (REASONING)

Q. **Why BiH_3 is the strongest reducing agent amongst all the hydrides of Group 15 elements ?**

Ans. In hydrides of nitrogen family on moving down the group M–H bond length increases so bond strength decreases hence tendency to release hydrogen increases and reducing nature increases.

Increasing order of reducing nature is $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

Q. **Write the reaction of thermal decomposition of sodium azide.**

Ans. Thermal decomposition of sodium azide gives dinitrogen gas.

$2NaN_3 \rightarrow 2Na + 3N_2$

Q. **Why N_2 is less reactive at room temperature?**

Ans. N_2 is less reactive at room temperature because of the high bond enthalpy of N≡N bond.

Q. **Why does $R_3P = O$ exist but $R_3N = O$ does not (R = alkyl group)?**

Ans. Due to presence of vacant d orbital phosphorous can form five covalent bond, while nitrogen restricts its covalency to four due to absence of vacant d orbitals.

Q. **Why does nitrogen show catenation properties less than phosphorus?**

Ans. N–N bond is weaker than the single P–P bond due to high interelectronic respulsion of non-bonding electrons as a result the catenation tendency is weaker in nitrogen.

Q. **Mention the conditions required to maximise the yield of ammonia.**

Ans. In accordance with Le Chatelier's principle, high pressure would favour the formation of ammonia. The optimum conditions for the production of ammonia are a pressure of 200×10^5 Pa (about 200 atm), a temperature of ~ 700 K and the use of a catalyst such as iron oxide with small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium.

Q. **How does ammonia react with a solution of Cu^{2+}?**

Ans. The presence of a lone pair of electrons on the nitrogen atom of the ammonia molecule makes it a Lewis base. It donates the electron pair and forms linkage with metal ions and the formation of such complex compounds finds applications in detection of Cu^{2+}.

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

Q. **Illustrate how copper metal can give different products on reaction with HNO_3.**

Ans. $3Cu + 8\,HNO_3(\text{dilute}) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

$Cu + 4HNO_3(\text{conc.}) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

Q. **Why is nitrogen di-oxide paramagnetic in gaseous state but the solid obtained on cooling it is diamagnetic.**

Ans. NO_2 contains odd number of electrons in its valence shell. On cooling it forms dimer and converted to stable N_2O_4 which is a colourless solid and diamagnetic in nature.

Q. **Why NH_3 gas cannot be dried by passing over P_2O_5 , $CaCl_2$ and H_2SO_4 ?**

Ans. $CaCl_2 + 8NH_3 \longrightarrow CaCl_2.8NH_3$

$P_2O_5 + 6NH_3 + 3H_2O \longrightarrow 2(NH_4)_3PO_4$

$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4$

So it is dried by passing over quick lime (CaO).

$CaO + H_2O \longrightarrow Ca(OH)_2$

Q. **Why inert atmosphere of CO_2 is taken in the formation of PH_3 by the reaction of white phosphorous with conc. NaOH solution.**

Ans. To decrease the partial pressure of O_2 in atmosphere.

Q. **Why does PCl_3 fumes in moisture?**

Ans. PCl_3 hydrolyses in the presence of moisture giving fumes of HCl

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

Q. **What happens when PCl_5 is heated?**

Ans. When heated, it sublimes but decomposes on stronger heating

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

Q. **Can PCl_5 act as an oxidising as well as reducing agent? Justify.**

Ans. It can act as an oxidising as well as reducing agent due to oxidising nature of P(V) and reducing nature of Cl^-

OXYGEN FAMILY (GROUP 16)

INTRODUCTION

Oxygen, sulphur, selenium, tellurium and polonium constitute group 16 of the periodic table. This is sometimes known as group of chalcogens (ore forming elements) because a large number of metals ores are oxides or sulphides.

Physical Properties :

- Oxygen and sulphur are non-metal, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life 13.8 days).
- The melting and boiling points increase with an increase in atomic number down the group. The larger difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity; oxygen exist as diatomic molecules (O_2) whereas sulphur exists as polyatomic molecule (S_8).

CATENATION

Tendency for catenation decreases down the group. This property is prominently displayed by sulphur (S_8). The S—S bond is important in biological system and is found in some proteins and enzymes such as cysteine.

Chemical Properties

Oxidation states and trends in chemical reactivity :

The elements of group 16 exhibit a number of oxidation states. The stability of -2 oxidation state decreases down the group. Except oxygen other elements of the group exhibit + 2, + 4, + 6 oxidation states but + 4 and + 6 are more common. Sulphur, selenium and tellurium usually show + 4 oxidation in their compounds with oxygen and +6 oxidations state with fluorine. The stability of +6 oxidation state decreases down the group and stability of + 4 oxidation state increases (inert pair effect). Bonding in + 4 and + 6 oxidation states are primarily covalent.

(i) Reactivity with hydrogen :

All the elements of group 16 form hydrides of the type H_2E (E = O, S, Se, Te, Po).

(ii) Reactivity with oxygen : All these elements form oxides of the EO_2 and EO_3 types where E = S, Se, Te or Po. Ozone (O_3) and sulphur dioxide (SO_2) are gases while selenium dioxide (SeO_2) is solid. Reducing property of dioxide decreases from SO_2 to TeO_2 ; SO_2 is reducing while TeO_2 is an oxidising agent. Besides EO_2 type sulphur, selenium and tellurium also form EO_3 type oxides (SO_3, SeO_3, TeO_3). Both types of oxides are acidic in nature.

(iii) Reactivity toward the halogens : Elements of group 16 form a larger number of halides of the type EX_6, EX_4 and EX_2 where E is an element of the group –16 and X is an halogen. The stabilities of the halides decrease in the order F > Cl > Br > I. Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. They have octahedral structure. Sulphur hexafluoride SF_6 is exceptionally stable for steric reasons.

Amongst tetrafluorides, SF_4 is a gas , SeF_4 liquid and TeF_4 a solid

All elements except selenium form dichlorides and dibromides. The well known monohalides are dimeric in nature, Examples are S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2 and Se_2Br_2. These dimeric halides undergo disproportionation as given $2Se_2Cl_2 \longrightarrow SeCl_4 + 3Se$.

COMPOUNDS OF OXYGEN

DIOXYGEN (O_2)

(a) Preparation of DiOxygen (O_2) :

By thermal decomposition of oxides of metals.

$$2\,HgO \xrightarrow{450^0C} 2\,Hg + O_2; \quad 2\,Ag_2O \xrightarrow{350^0C} 4\,Ag + O_2$$

$$3\,MnO_2 \xrightarrow{\Delta} Mn_3O_4 + O_2; \quad 2\,Pb_3O_4 \xrightarrow{\Delta} 6\,PbO + O_2$$

$$KClO_3 \xrightarrow{\Delta} 2\,KCl + 3O_2 \text{ (laboratory method)}$$

$$4\,K_2Cr_2O_7 \xrightarrow{\Delta} 4\,K_2CrO_4 + 2\,Cr_2O_3 + 3O_2\ ;\ 2\,KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$$

$$2PbO_2(s) \xrightarrow{\Delta} 2PbO(s) + O_2(g)$$

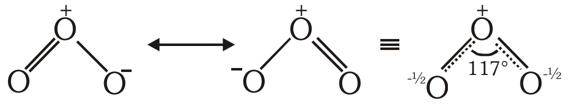
Properties:

- Dioxygen is a colourless and odourless gas.
- Oxygen atom has three stable isotopes: ^{16}O, ^{17}O and ^{18}O. Molecular oxygen.
- O_2 is paramagnetic (by MOT)
- Dioxygen directly reacts with nearly all metals and non-metals except some metals (e.g., Au, Pt) and some noble gases.

OZONE (O_3) :

Preparation : It is prepared by passing silent electric discharge through pure and dry oxygen.

$$3O_2 \longrightarrow 2O_3 \quad \Delta H^{\ominus}(298K) = +142 \text{ kJ mol}^{-1}$$



Mixture obtained contains 5-10% ozone by volume and this mixture is called ozonised oxygen.

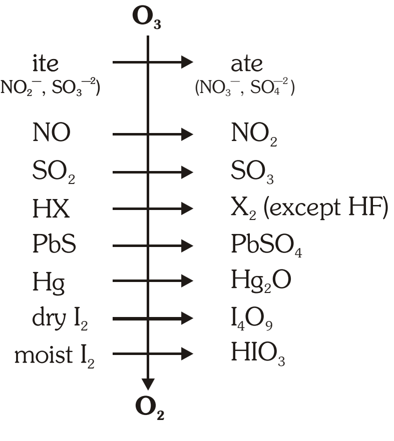
Since the formation of ozone from oxygen is an endothermic process, it is necessary to use a silent electrical discharge in its preparation to prevent its decomposition. If concentrations of ozone greater than 10 per cent are required, a battery of ozonisers can be used, and pure ozone (b.p. 385 K) can be condensed in a vessel surrounded by liquid oxygen.

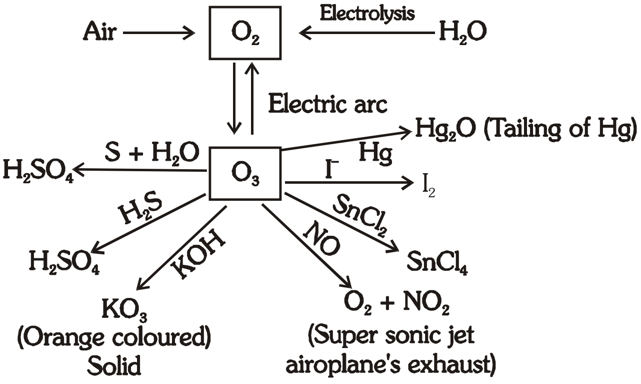
Properties :

- Pure ozone is a pale blue gas, dark blue liquid and violet-black solid.
- Ozone is thermodynamically unstable with respect to oxygen since its decomposition into oxygen results in the liberation of heat (ΔH is negative) and an increase in entropy (ΔS is positive). These two effects reinforce each other, resulting in large negative Gibbs energy change (ΔG) for its conversion into oxygen. Therefore, high concentrations of ozone can be dangerously explosive.

Oxidising behaviour of ozone :

Due to the ease with which it liberates atoms of nascent oxygen ($O_3 \rightarrow O_2 + O$), it acts as a powerful oxidising agent. For example, it oxidises lead sulphide to lead sulphate and iodide ions to iodine.





Tests for Ozone

Tailing of mercury : Pure mercury is a mobile liquid but when brought in contact with O_3 its mobility decreases and it starts sticking to glass surface forming a type of tail due to the dissolution of Hg_2O (mercury sub-oxide) in Hg.

$$2\,Hg + O_3 \longrightarrow Hg_2O + O_2$$

Estimation of Ozone : When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating O_3 gas.

$$2KI + H_2O + O_3 \rightarrow O_2 + I_2 + 2KOH$$

$$I_2 \xrightarrow{(Na_2S_2O_3.5H_2O)} 2NaI + \underset{\text{(sodium tetra thionate)}}{Na_2S_4O_6}$$

Depletion of ozone layer : Experiments have shown that nitrogen oxides (particularly nitric oxide) combine very rapidly with ozone and there is, thus, the possibility that nitrogen oxides emitted from the exhaust systems of supersonic jet aeroplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.

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

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

COMPOUNDS OF SULPHUR :

Hydrogen Sulphide (H_2S)

Preparation :

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

It is prepared in kipp's apparatus

Properties :

(i) Colourless gas with rotten egg smell .

(ii) Moderately soluble in water but solubility decreases with increasing temperature.

(iii) It gives black ppt with lead acetate

$$(CH_3COO)_2\underset{\text{salt}}{Pb} + \underset{\text{acid}}{H_2S} \longrightarrow \underset{\text{black ppt}}{PbS} + 2CH_3COOH$$

Reducing behaviour :

Acts as a strong reducing agent as it decomposes evolving hydrogen.

$$H_2S + SO_2 \xrightarrow{\text{moisture}} H_2O + S;$$

$$\underset{\text{yellow}}{2FeCl_3} + H_2S \xrightarrow{\text{redox}} \underset{\text{green}}{2FeCl_2} + S + 2HCl$$

SO_2 (Sulphur Dioxide)

Preparation :

(i) $S + O_2$ or air $\xrightarrow{\text{Burn}} SO_2$

(ii) By reaction of metal sulphites with dilute HCl (Laboratory method)

$$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + SO_2 + H_2O$$

Similarly bisulphites also give SO_2 with dilute HCl

$$NaHSO_3 + HCl \longrightarrow NaCl + SO_2 + H_2O$$

(iii) By heating sulphides (metal sulphide ores) in excess of air.

$$2\,ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

By this method SO_2 is obtained in large scale

Properties :

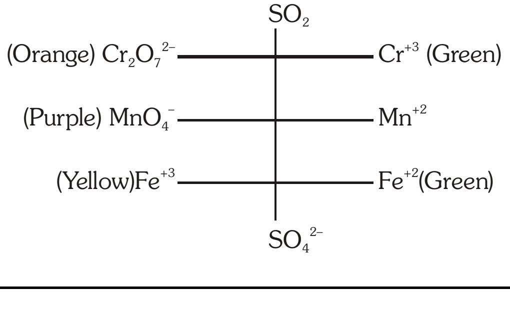
(i) Colourless gas with pungent smell.

(ii) It is heavier than air and is highly soluble in water.

(iii) Acidic Nature : Acidic oxide and thus dissolve in water forming sulphurous acid.

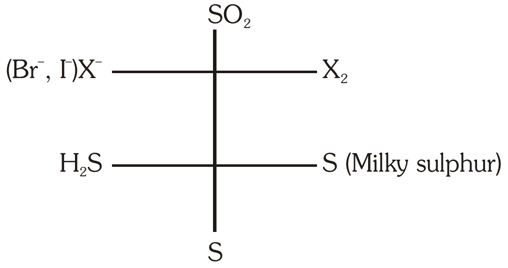
$$SO_2 + H_2O \longrightarrow H_2SO_3$$

Reducing nature :



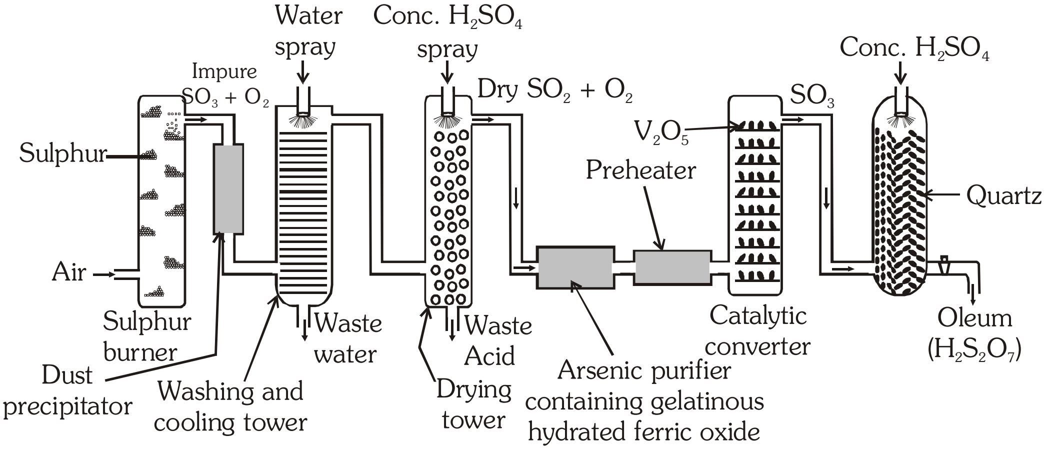
The above reactions are not given by CO_2, so they are used to distinguish between SO_2 and CO_2

Oxidising nature : Acts as oxidising agent with strong reducing agent



SULPHURIC ACID (H_2SO_4) :

Manufacture by contacts process :



Flow diagram for the manufacture of sulphuric acid

Sulphuric acid is one of the most important industrial chemicals worldwxide.

Sulphuric acid is manufactured by the contact process which involves three steps :

(i) burning of sulphur or sulphide ores in air to generate SO_2

(ii) Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5), and

(iii) Absorption of SO_3 in H_2SO_4 to give Oleum ($H_2S_2O_7$)

The SO_2 produced is purified by removing dust and other impurities such as arsenic compounds.

The key step in the manufacture of H_2SO_4 is the catalytic oxidation of SO_2 with O_2 to give SO_3 in the presence of V_2O_5 (catalyst).

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)\ \Delta_r H^{-} = -196.6\ \text{kJ mol}^{-1}.$$

The reaction is exothermic reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favourable conditions for maximum yield. But the temperature should not be very low other wise rate of reaction will become slow.

Dilution of oleum with water gives H_2SO_4 of the desired concentration. In the industry two steps are carried out simultaneously to make the process a continuous one and also to reduce the cost.

$$SO_3 + H_2SO_4 \longrightarrow \underset{\text{(Oleum)}}{H_2S_2O_7} \quad ; \quad H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

The sulphuric acid obtained by Contact process is 96-98% pure.

Properties : Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K. The acid freezes at 283 K and boils at 611 K. It dissolves in water with the evolution of a larger quantity of heat.

The chemical reaction of sulphuric acid are as a result of the following characteristics : (a) low volatility (b) strong acidic character (c) strong affinity for water and (d) ability to act as an oxidising agent in aqueous solution,

(i) Sulphuric acid ionises in two steps.

$$H_2SO_4(aq) + H_2O(\ell) \rightarrow H_3O^+ (aq) + HSO_4^- (aq) \text{ ; } Ka_1 = \text{very larger } (K_{a_1} > 10)$$

$$HSO_4^-(aq) + H_2O(\ell) \rightarrow H_3O^+ (aq) + SO_4^{2-} (aq) \text{ ; } Ka_2 = 1.2 \times 10^{-2}$$

The larger value of K_{a_1} ($K_{a_1} > 10$) means that H_2SO_4 is largely dissociated into H^+ and HSO_4^-. Greater the value of dissociation constant (K_a) the stronger is the acid.

(ii) **The acid forms two series of salts :** Normal sulphates (such as sodium sulphate and copper sulphate and acid sulphate (e.g., sodium hydrogen sulphate)

(iii) Sulphuric acid, because of its low volatility can be used to manufacture more volatile acid from their corresponding salts.

$$2MX + H_2SO_4 \rightarrow 2HX + M_2SO_4 (X = F, Cl, NO_3)$$

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

(M = Metal)

$$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$$

(iv) Concentrated sulphuric acid is a strong dehydrating agent. Many wet gases can be dried by passing them through sulphuric acid, provided the gases do not react with the acid. Sulphuric acid removes water from organic compound; it is evident by its charring action on carbohydrates.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O \text{ (charring action of sugar)}$$

$$H_2C_2O_4 \xrightarrow[-H_2O]{H_2SO_4} CO + CO_2$$

(v) Hot concentrated sulphuric acid is moderately strong oxidising agent. In this respect it is intermediate between phosphoric and nitric acids. Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to SO_2.

$$Cu + \text{conc. } 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O$$

$$3S + \text{conc. } 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

$$C + \text{conc. } 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

$$KBr + \text{conc.} H_2SO_4 \longrightarrow KHSO_4 + 2H_2O + Br_2 + SO_2$$

NCERT QUESTIONS (REASONING)

Q. **H_2S is less acidic than H_2Te. Why?**

Ans. Due to the decrease in bond (E–H) dissociation enthalpy down the group, acidic character increases.

Q. **Why is H_2O a liquid and H_2S a gas?**

Ans. Hydrogen bonds are present between H_2O molecules while between H_2S molecules, vander Waal's forces are present.

Q. **Why is dioxygen a gas but sulphur a solid?**

Ans. Oxygen exist as a O_2 molecule while sulphur exist as a S_8 molecule due to more molecular mass sulphur is solid.

Q. **Knowing the electron gain enthalpy values for $O \rightarrow O-$ and $O \rightarrow O^{2-}$ as –141 and 702 kJ mol^{-1} respectively, how can you account for the formation of a large number of oxides having O^{2-} species and not O^{-}?**

Ans. Consider lattice energy factor in the formation of compounds.

Q. **Which of the following does not react with oxygen directly? Zn, Ti, Pt, Fe**

Ans. Pt is a noble metal which does not react directly with oxygen.

Q. **Complete the following reactions:**

(i) $C_2H_4 + O_2 \rightarrow$ **(ii) $4Al + 3O_2 \rightarrow$**

Ans. (i) $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$ (ii) $4Al + 3O_2 \rightarrow 2Al_2O_3$

Q. **How is O_3 estimated quantitatively?**

Ans. When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating O_3 gas.

Q. **What happens when sulphur dioxide is passed through an aqueous solution of Fe(III) salt?**

Ans. $2Fe^{+3} + SO_2 + 2H_2O \rightarrow 2Fe^{+2} + SO_4^{-2} + 4H^+$

Q. **How is the presence of SO_2 detected?**

Ans. It has colourless gas with pungent smell and decolourise acidified $KMnO_4$ solution.

Q. **Write the conditions to maximise the yield of H_2SO_4 by Contact process.**

Ans. The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favourable conditions for maximum yield. But the temperature should not be very low otherwise rate of reaction will become slow.

Q. **Why is $K_{a_2} \ll K_{a_1}$ for H_2SO_4 in water?**

Ans. It is difficult to remove H^+ ion from HSO_4^- ion.

HALOGEN FAMILY (GROUP-17)

(A) PHYSICAL PROPERTIES

(i) Fluorine and chlorine are gases, bromine is a liquid whereas iodine is a solid.

(ii) Their melting and boiling points steadily increase with atomic number.

(iii) All halogens are coloured. This is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level. By absorbing different quanta of radiation, they display different colours.

For example, F_2, has yellow, Cl_2, greenish yellow, Br_2, red and I_2, violet colour.

(iv) Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water. But are soluble in organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions.

(v) Except the smaller enthalpy of dissociation of F_2 compared to that of Cl_2. **The X-X bond disassociation enthalpies from chlorine onwards show the expected trend : Cl – Cl > Br – Br > F – F > I – I. The reason for the smaller enthalpy of dissociation of F_2 is the relatively larger electrons-electrons repulsion among the lone pairs in F_2 molecule where they are much closer to each other than in case of Cl_2.**

(B) CHEMICAL PROPERTIES

(i) Oxidation states and trends in chemical reactivity

- All the halogens exhibit –1 oxidation state. However, chlorine, bromine and iodine exhibit + 1, + 3, + 5 and + 7 oxidation states also. The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms e.g., in interhalogens, oxides and oxoacids.
- The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only – 1 oxidation state.
- All the halogens are highly reactive. They react with metals and non-metals to form halides. The reactivity of the halogens decreases down the group.

Standard Reduction Potential (SRP)

$$X_2 + 2e^- \longrightarrow 2X^-$$

$$F_2 + 2e^- \longrightarrow 2F^- \quad E^- = +2.87\ V\ ;\ Cl_2 + 2e^- \longrightarrow 2Cl^- \quad E^- = +1.36\ V$$

$$Br_2 + 2e^- \longrightarrow 2Br^- \quad E^- = +1.09\ V\ ;\ I_2 + 2e^- \longrightarrow 2I^- \quad E^- = +0.54\ V$$

More the value of the SRP, more powerful is the oxidising agent.

Hence the order of oxidising power is $F_2 > Cl_2 > Br_2 > I_2$

Order of reducing behaviour is $I^- > Br^- > Cl^- > F^-$

(ii) Halogen oxides :

- Fluorine forms two oxides OF_2 and O_2F_2. However, only OF_2 is the thermally stable at 298 K. These oxide are essentially oxygen fluorides because of the higher electronegativity of flurorine than oxygen . Both are strong fluorinating agents.
- O_2F_2 oxidises plutonium to PuF_6 and the reaction is used in removing plutonium as PuF_6 from spent nuclear fuel.
- Chlorine, bromine and iodine form oxides in which the oxidation states of these halogen vary from + 1 to + 7. A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens, I > Cl > Br. The higher oxides of halogens tend to be more stable than the lower ones. This is called middle row anamoly.
- Chlorine oxides, Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7 are highly reactive oxidising agents and tend to explode. ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment.
- The bromine oxides, Br_2O, BrO_2, BrO_3 are the least stable halogen oxides and exist only at low temperature. They are very powerful oxidising agents.
- The iodine oxides, I_2O_4, I_2O_5, I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is very good oxidising agent and is used in the estimation of carbon monoxide.

COMPOUNDS OF HALOGEN

CHLORINE GAS (Cl_2)

(a) Preparation :

(i) By heating chloride with concentrated H_2SO_4 in presence of MnO_2.

$$4H^+ + MnO_2 + 2X^- \longrightarrow X_2 + Mn^{+2} + 2H_2O$$

Bromides and iodides also liberate Br_2 and I_2 respectively with concentrated H_2SO_4 and MnO_2.

(ii)
- $CaOCl_2 + 2HCl \longrightarrow CaCl_2 + Cl_2 + H_2O$
- $2KMnO_4 + 16\ HCl \rightarrow 2\ KCl + 2\ MnCl_2 + 5\ Cl_2 + 8\ H_2O$
- $PbO_2 + 4\ HCl \rightarrow PbCl_2, + Cl_2 + 2\ H_2O$

(iii) **Manufacture of chlorine :**

- **Deacon's process :** By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ (catalyst) at 723 K.

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

- **Electrolytic process :** Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution). Chlorine is liberated at anode. It is obtained as a by–product in many chemical industries e.g.; in manufacturing of sodium hydroxide.

$$NaX\ (aq) \longrightarrow Na^+\ (aq) + X^-\ (aq)$$

$$\text{Anode : } 2X^- \longrightarrow X_2 + 2e^-$$

(b) Properties :

(i) It is a greenish–yellow gas with pungent and suffocating odour. It is about 2–5 times heavier than air. It can be liquefied into greenish–yellow liquid which boils at 239K. It is soluble in water.

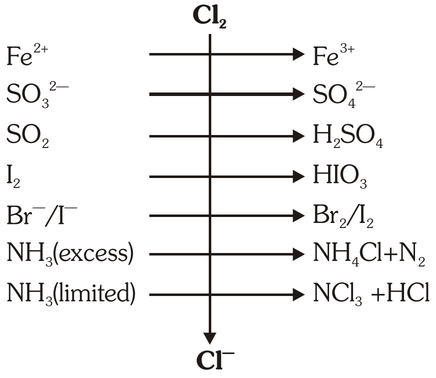
(ii) **Oxidising & bleaching properties :** Chlorine dissolves in water giving HCl and HOCl. Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

It is a powerful bleaching agent ; bleaching action is due to oxidation.

$$Cl_2 + H_2O \longrightarrow 2\ HCl + O$$

Coloured substance + O → Colourless substance

It bleaches vegetable or organic matter in the presence of moisture. Bleaching effect of chlorine is permanent.



HALOGEN ACIDS (HCl)

(a) Preparation :

(i) By heating a halide with concentrated acid :

$$NaCl + H_2SO_4 \xrightarrow{150°C} NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \xrightarrow{550°C} Na_2SO_4 + HCl$$

- Above method is called as salt cake method as it involves the formation of $NaHSO_4$ (salt cake).
- HCl cannot be dried over P_2O_5 (P_4O_{10}) or quick lime since they react with gas chemically.

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$$

$$P_4O_{10} + 3HCl \longrightarrow POCl_3 + 3HPO_3$$

- HCl is, hence dried by passing through concentrated H_2SO_4 .

(b) Properties :

(i) This is colourless, pungent smelling gas with acidic taste.

(ii) This is neither combustible nor supporter of combustion.

(iii) When perfectly dry, HX have no action on litmus, but in presence of moisture, they turn blue litmus red, showing acidic nature. Among HX, HI is the strongest and HF is the weakest acid.

Pseudo halogens and pseudo halides : Some inorganic compounds consisting of two or more atoms of which at least one is N have been found to behave like halogens & they are known as pseudo halogen solids,

Pseudo halogens	Pseudo halides
(i) $(CN)_2$ cyanogen	(i) (CN^-) cyanide ion
(ii) $(SCN)_2$ thiocyanogen	(ii) (SCN^-) thiocyanate ion
(iii) $(SeCN)_2$ selenocyanogen	(iii) $(SeCN)^-$ selenocyanate ion
(iv) $(SCSN_3)_2$ azidocarbondisulphide	(iv) $(OCN)^-$ cyanate ion
	(v) $(NCN)^{2-}$ cyanamide ion
	(vi) $(N_3)^-$ azide ion etc.

INTERHALOGEN COMPOUNDS :

We know that halogen atoms have different electronegativity. Due to this difference in electronegativity the halogen atoms combine with each other and give rise to the formation of binary covalent compounds, which are called interhalogen compounds. These are of four types.

AB	AB_3	AB_5	AB_7 *
ClF	ClF_3	ClF_5	IF_7
BrF	BrF_3	BrF_5	
ICl	ICl_3	IF_5	
IF	IF_3		

* Where A - halogen of smaller size and A is more electro positive than B.

(a) Properties :

(i) These compounds may be gases, liquids or solids.

Gases : ClF, BrF, ClF_3 , IF_7;   Liquids : BrF_3, BrF_5 ;   Solids : ICl, IBr, IF_3, ICl_3.

(ii) Interhalogens containing fluorine are generally colourless but inter halogens consisting of heavier halogens are coloured. The intensity of colour increases with increase in the molecular weight of the compounds.

(iii) All interhalogens are covalent molecules and are diamagnetic in nature since all the valence electrons present as bonding or non-bonding electrons are paired.

(iv) Interhalogen compounds are more reactive than the parent halogens but less reactive than F_2.

$$ICl + 2Na \longrightarrow NaI + NaCl$$

The order of reactivity of some interhalogens is as follows :

$$ClF_3 > BrF_3 > IF_7 > BrF_5 > BrF.$$

(v) These compounds can be used as non aqueous solvents. Interhalogen compounds are very useful fluorinating agents. ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U .

$$U(s) + 3\ ClF_3(\ell) \longrightarrow UF_6\ (g) + 3\ ClF\ (g)$$

TEST OF HALOGENS

F^- = **Itching of glass**

$AgNO_3$ test (Cl^- , Br^-, I^-)

Cl – Salt + $AgNO_3 \rightarrow$ AgCl (White ppt)

Br salt + $AgNO_3 \rightarrow$ AgBr (Pale yellow ppt)

I – salt + $AgNO_3 \rightarrow$ AgI (Yellow ppt)

Test of I_2

I_2 + Starch $\rightarrow$ Navy blue

$I_2 + CCl_4 \rightarrow$ Violet

Layer test (Br^- , I^-)

$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2 \xrightarrow{CCl_4}$ Reddish brown (Halogen displacement reaction)

(**Note :** In case of I^- violet colour is obtained.)

Chromyl chloride test (Test of Cl^-) : see d-block

NCERT QUESTIONS (REASONING)

Q. Covalent radius of fluorine is 64 pm but the bond length is not equal to 128 pm and that is 143 pm and bond energy is found to be comparable to I_2.

Ans. This may be attributed to ℓ.p – ℓ.p repulsions due to small size of F atom.

Q. Electron affinity of chlorine is more than F. Inspite of this F_2 is the better oxidising agent. Why ?

Ans. SRP of F_2 is much higher than that of Cl_2 on account of smaller bond dissociation energy and high hydration energy of F^- ion.

Q. Layer test of Br^- is successful with Cl_2 but not with I_2. Explain?

Ans. Br^- is oxidised by Cl_2 but not by I_2

Q. What is the difference between bleaching action of SO_2 and Cl_2

Ans. The bleaching action of SO_2 is temporary because it takes place through reduction.

$$SO_2 + 2\ H_2O \longrightarrow H_2SO_4 + 2\ H$$

$$SO_3^{2-} + \text{Coloured material} \longrightarrow SO_4^{2-} + \text{Reduced colourless material.}$$

$$\text{Reduced Colourless material} \xrightarrow{O_2 \text{ of air}} \text{Coloured material.}$$

The bleaching action of Cl_2 is permanent because it takes place through oxidation

Q. (a) When HCl reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride. why ?

(b) Chlorine water turns blue litmus red but solution becomes colourless after sometime.

Ans. (a) It forms H_2 gas. $Fe + 2\ HCl \longrightarrow FeCl_2 + H_2$.

Liberation of hydrogen prevents the formation of ferric chloride.

(b) Blue litmus change into red due to acidic nature ($Cl_2 + H_2O \rightarrow HOCl + HCl$) but it is bleaching agent, therefore, it decolourises the red litmus.

ZERO GROUP (GROUP-18)

INTRODUCTION

Group 18 consists of six elements: helium, neon, argon, krypton , xenon and radon . All these are gases and chemically unreactive. They form very few compounds . Because of this they are termed noble gases.

(A) PHYSICAL PROPERTIES

(i) All the noble gases are mono-atomic.

(ii) They are colourless, and tasteless. They are sparingly soluble in water.

(iii) They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces,.

(iv) Helium has the lowest boiling point (4.2K) of any known substance. It has a unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

(B) CHEMICAL PROPERTIES

In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

(i) The noble gases except helium ($1s^2$) have completely filled $ns^2\ np^6$ electronic configuration in their valence shell.

(ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

Neil Bartlett, observed the reaction of a noble gas. First , he prepared a red compound which is formulated as $O_2^+ [PtF_6]^-$. He, then realised that the first ionisation enthalpy of molecular oxygen (1175 kJ mol $^{-1}$) was almost identical with that xenon (1170 kJ mol $^{-1}$). He made efforts to prepare same type of compound with $Xe^+ [PtF_6]^-$ by mixing Pt F_6 and Xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised.

The compounds of krypton are fewer. Only the difluoride (KrF_2) has been studied in detail. Compounds of radon have not been isolated but only identified (e.g., RnF_2) by radiotracer technique. No true compounds of Ar, Ne or He are yet known .

COMPOUNDS OF XENON

Xenon-fluorine compounds

Xenon forms three binary fluorides, XeF_2, XeF_4 and XeF_6 by the direct reaction of elements under appropriate experimental conditions.

$$\underset{\text{(xenon in excess)}}{Xe(g) + F_2(g)} \xrightarrow{\text{673K,1 bar}} XeF_2(s)$$

$$\underset{\text{(1:5 ratio)}}{Xe(g) + 2F_2(g)} \xrightarrow{\text{873K, 7bar}} XeF_4(s)$$

$$\underset{\text{(1:20 ratio)}}{Xe(g) + 3F_2(g)} \xrightarrow{\text{873K, 60–70bar}} XeF_6(s)$$

XeF_6 can also be prepared by the interaction of XeF_4 and O_2F_2 at 143K.

$$XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$$

XeF_2, XeF_4 and XeF_6 are colourless crystalline solids and sublime readily at 298 K. They are powerful fluorinating agents. They are readily hydrolysed even by traces of water. For example, XeF_2 is hydrolysed to give Xe, HF and O_2.

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

Formation of addition compounds : XeF_2 reacts with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.

$$XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^-$$

$$\underset{\text{(lewis acid)}}{IF_5} + XeF_2 \longrightarrow [XeF]^+ [IF_6]^- \;;$$

$$\underset{\text{(lewis acid)}}{2SbF_5} + XeF_2 \longrightarrow [XeF]^+ [SbF_6]^-$$

- $CsF + XeF_6 \longrightarrow \overset{+}{C}s[XeF_7]^-$

[With s-block flourides and alkyl flourides it is F^- acceptor with others it is F^- donor]

USES OF INERT GASES :

(1) He is non-inflammable and light gas, so it is used in filling balloons for meteorological observations.

(2) He is used in gas cooled nuclear reactors.

(3) Liquid He is used as cryogenic agent.

(4) He is used to produce powerful superconducting magnets.

(5) Ne is used in discharge tubes.

(6) Ar is used as inert atmosphere in metallurgical process.

(7) Xenon and Krypton are used in light bulbs designed for special purposes.

IMPORTANT ORDER :

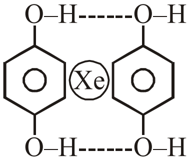
(1) He < Ne < Ar < Kr < Xe	**Atomic radius**
(2) He > Ne > Ar > Kr > Xe	**Ionisation energy**
(3) He < Ne < Ar < Kr < Xe < Rn	**Density**
(4) He < Ne < Ar < Kr < Xe < Rn	**mpt. bpt**

[Atomic mass / size / polarisability / London force] ↑

(5) He < Ne < Ar < Xe < Rn **[solubility in water because of dipole-induced dipole attraction]**

Clatherate Compounds : Larger inert gas atoms are trapped into cavity or crystal structure of some organic compounds and form clatherate compounds. For eg xenondiquinol.

- Force of attraction between noble gas and organic compound is **dipole-induced dipole** attraction.



He, Ne do not form clatherate compounds due to smaller size