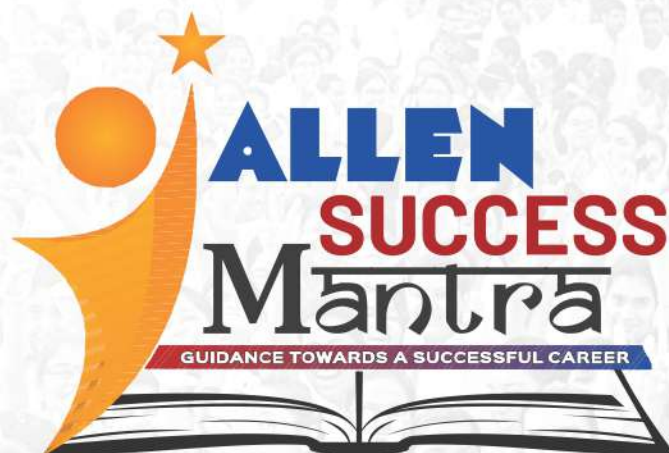


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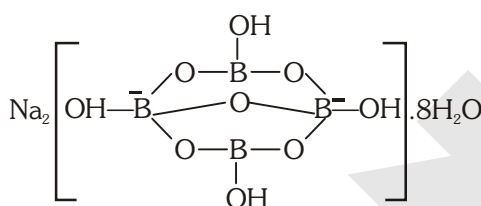
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p-Block

13th-GROUP

- Some important ores of Boron are given as under.
- | | | |
|---|--|--|
| (i) Boric acid, H_3BO_3 | (ii) Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ | (iii) Colemanite, $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ |
|---|--|--|
- Some important minerals of aluminium are given as under.
- | | | |
|---|---|---|
| (i) Corundum, Al_2O_3 | (ii) Bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ | (iii) Cryolite, Na_3AlF_6 |
| (iv) Feldspar, KAlSi_3O_8 | | |

BORAX $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$



Properties :

- (i) It is a white crystalline solid of formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. In fact it contains the tetranuclear units $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ and correct formula; therefore, is $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$.
- (ii) Hydrolysis

$$\text{Na}_2\text{B}_4\text{O}_7 + 7\text{H}_2\text{O} \rightarrow 2\text{NaOH} + 4\text{H}_3\text{BO}_3$$
- (iii) Heating

$$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \xrightarrow{\Delta} \underset{\text{Swells up}}{\text{Na}_2\text{B}_4\text{O}_7} \xrightarrow{\Delta} 2\text{NaBO}_2 + \text{B}_2\text{O}_3$$

Sodium metaborate Boric anhydride
- (iv) When borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured $\text{Co}(\text{BO}_2)_2$ bead is formed.

DIBORANE, B_2H_6

Preparation :

- (i) $3\text{LiAlH}_4 + 4\text{BF}_3 \longrightarrow 3\text{LiF} + 3\text{AlF}_3 + 2\text{B}_2\text{H}_6$
or LiBH_4 or $3(\text{BF}_3)$
- (ii) **Laboratory method :**

$$2\text{NaBH}_4 + \text{I}_2 \rightarrow \text{B}_2\text{H}_6 + 2\text{NaI} + \text{H}_2$$
- (iii) **Industrial scale :**

$$2\text{BF}_3 + 6\text{NaH} \xrightarrow{450\text{K}} \text{B}_2\text{H}_6 + 6\text{NaF}$$

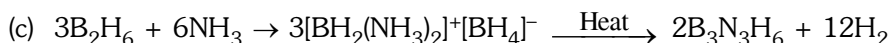
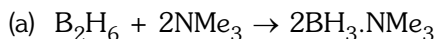
Properties :

- (i) Diborane is a colourless, highly toxic gas with a b.p. of 180 K.
- (ii) Diborane catches fire spontaneously upon exposure to air.
- (iii) Reaction with Oxygen :

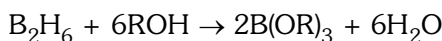
$$\text{B}_2\text{H}_6 + 3\text{O}_2 \rightarrow \text{B}_2\text{O}_3 + 3\text{H}_2\text{O} ; \Delta_c H^\ominus = -1976 \text{ kJ mol}^{-1}$$
- (iv) Hydrolysis :

$$\text{B}_2\text{H}_6(\text{g}) + 6\text{H}_2\text{O}(\ell) \text{ (Cold is enough)} \rightarrow 2\text{B}(\text{OH})_3(\text{aq}) + 6\text{H}_2(\text{g})$$
- $$\text{B}_2\text{H}_6 + \text{HCl (dry)} \xrightarrow[\text{AlCl}_3]{\text{anh.}} \text{B}_2\text{H}_5\text{Cl} + \text{H}_2$$

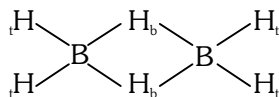
(v) Reaction with Lewis Bases



(vi) Reaction with ROH :



Diborane, B_2H_6

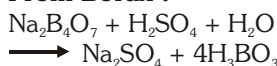


dimer due to formation of
3 centre-2e-bond

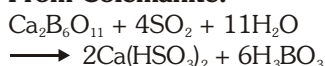
Inorganic benzene

ORTHOBORIC ACID [H_3BO_3 or $B(OH)_3$]

From Borax :



From Colemanite:

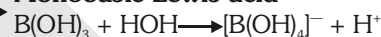


MOP

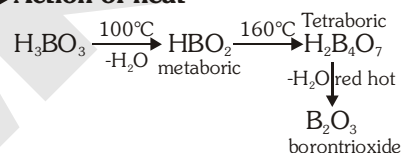


Properties

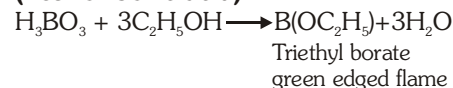
Monobasic Lewis acid



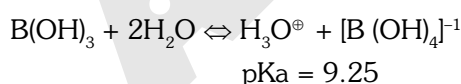
Action of heat



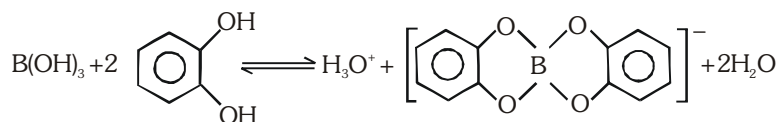
**Reaction with alcohol
(Test of boric acid)**



➤ Boric acid is a weak monobasic acid



➤ It is difficult to titrate boric acid against NaOH solutions and the end point cannot be located correctly. However, it can be successfully titrated in the presence of polyhydroxy alcohols (e.g. Glycerol, mannitol, catechol or sugar). The presence of these compounds greatly increase the acidity of boric acid.

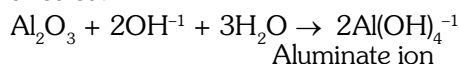


Boron is complexed by these compounds. These complex ions cannot interact with H^+ ions as boron atom has already acquired its maximum covalency of four. Consequently, boric acid in presence of polyhydroxy alcohols can be titrated against NaOH to a definite end point.

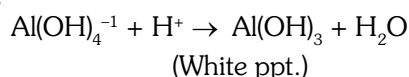
EXTRACTION OF ALUMINIUM

Al is usually extracted from Bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. First, bauxite is purified from the impurities (Red bauxite contains Fe_2O_3 as impurity while white bauxite contains silica as impurity). Red bauxite can be purified by Baeyer's process or Hall's process while white bauxite is purified by Serpeck's process.

- **Baeyer's process**, involves the roasting of the ore to convert FeO to Fe_2O_3 and then digested at 423K with conc. NaOH solution for a few hours when Al_2O_3 gets dissolved to give a solution of $[\text{Al}(\text{OH})_4]^{-1}$. The basic oxide impurities such as Fe_2O_3 are not affected.

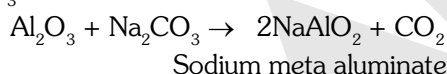


Fe_2O_3 left undissolved is filtered off. The treatment of $[\text{Al}(\text{OH})_4]^{-1}$ solution with a weak acid precipitate pure $\text{Al}(\text{OH})_3$.

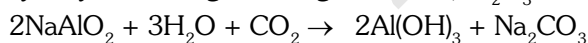


The $\text{Al}(\text{OH})_3$ precipitate is removed by filtration and ignited to get alumina, Al_2O_3 .

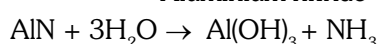
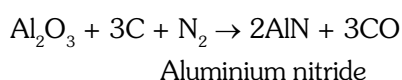
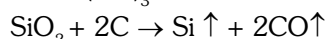
- **Hall's process**, Involves the fusion of the ore with Na_2CO_3 when soluble sodium meta aluminate, NaAlO_2 is produced. This is extracted with water when Fe_2O_3 is left as a residue.



The water extract is heated upto 333K and CO_2 is passed through it. $\text{Al}(\text{OH})_3$ is precipitated due to hydrolysis and is ignited to get alumina, Al_2O_3 .



- **Serpeck's process** involves the heating of bauxite with coke in a current of N_2 at 2075K. The SiO_2 present in the ore is reduced to silicon which volatilizes off and alumina gives aluminium nitride. This can be hydrolysed to $\text{Al}(\text{OH})_3$ which on fusion gives alumina.



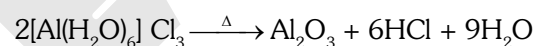
Electrolysis of Al_2O_3 to form aluminium. Pure alumina is dissolved in fused cryolite, Na_3AlF_6 at 1225 K by current of 100 amperes and 6–7 volts to get Al. The Al obtained is purified by Hoopes's process.

ALUMINIUM TRIFLUORIDE

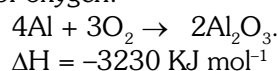
- **Aluminium trifluoride** (AlF_3) is different from other trihalides of Al in being insoluble and nonvolatile. In AlF_3 each Al is surrounded by a distorted octahedron of 6F atoms and 1 : 3 stoichiometry is achieved by the sharing of corner fluorine atoms between two octahedra.

ALUMINIUM CHLORIDE

- Aluminium chloride (AlCl_3) in the pure and anhydrous state is a white solid but commercial samples are yellowish due to the impurity of FeCl_3 .
- Anhydrous AlCl_3 , in the crystalline state possesses a closely packed layer structure with six coordinated aluminium octahedral arrangement.
- Anhydrous AlCl_3 has a very high affinity for water. On treating AlCl_3 with water the Cl^{-} ions go outside the coordination sphere to form $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$ with enthalpy of solution -330 KJ mol^{-1} . Due to this strong Al–O linkage hydrate cannot be dehydrated on heating to form AlCl_3 .



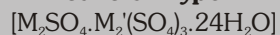
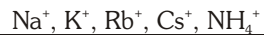
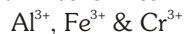
- Aluminium chloride, is a polymeric solid which exists as a dimer Al_2Cl_6 between 200–400°C and then monomer up to 800°C.
- **Thermite welding**, Aluminium has got a very high affinity for oxygen.



It, therefore, displaces metals less electropositive than itself from oxides. The large amount of heat produced is used in welding rails or heavy machinery without removing them from their position. This is called thermite welding or Gold Schmidt's aluminothermic process. In this process, a mixture of Ferric oxide (3 parts) and aluminium powder (1 part) called thermite is used.

- **Boron nitride** (BN), has a structure similar to that of graphite.
- Green edged flame test for borate (BO_3^{3-}) ion. A mixture of $\text{C}_2\text{H}_5\text{OH}$ and BO_3^{3-} salt with conc. H_2SO_4 burns with green edge flame due to the formation of ethyl borate.
- $$\text{H}_3\text{BO}_3 + 3\text{C}_2\text{H}_5\text{OH} \rightarrow \text{B}(\text{OC}_2\text{H}_5)_3 + 3\text{H}_2\text{O}$$
- Ethyl borate

- **Charcoal cavity test for aluminium.** On heating with Na_2CO_3 and a drop of cobalt nitrate solution a blue coloured residue to **cobalt metaaluminate** (Thenard's blue) is obtained.

ALUMS $[M_2SO_4 \cdot M_2'(SO_4)_3 \cdot 24H_2O]$
Alums are the double salts of Type

M : Monovalent Cation:

M' : Trivalent cation :

Soda alum

Potash alum

Ammonium alum

 example **Alum** properties

- aq. solution acidic
- Coagulant
- Mordant for dyeing
- Tanning of leather

Pseudo alums are double sulphates of a divalent and a trivalent metals which crystallize with twenty four water molecules of crystallization, for example.



They are not isomorphous with true alums.

IMPORTANT NOTES

GROUP 14 ELEMENTS

- The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states.
- Tin forms compounds in both oxidation states (Sn in +2 state is a reducing agent).
- Lead compounds in +2 state are stable and in +4 state are strong oxidising agents.
- SiO only exists at high temperature.
- The dioxides — CO₂, SiO₂ and GeO₂ are acidic, whereas SnO₂ and PbO₂ are amphoteric in nature. Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.
- Tin decomposes steam to form dioxide and dihydrogen gas.
- All halide of 14th group are covalent. Exceptions are SnF₄ and PbF₄, which are ionic in nature.
- Stability of dihalides increases down the group.
- The order of catenation is C > Si > Ge ≈ Sn. Lead does not show catenation.

➤ **Catenation** is the unique tendency of 14 group elements to form long chains of different sizes and shapes. The tendency to show catenation is directly related to the strength of bond. The bond energies of 14 group elements decrease as under :

	C-C	Si-Si	Ge-Ge	Sn-Sn	Pb-Pb
Bond energy (KJ mole ⁻¹)	348	222	167	155	—

This is the reason why carbon forms many chains, Si, a few and Ge and Sn form practically no chains.

- CO₂ is a gas while SiO₂ is a solid at room temperature.
- SiO only exists at high temperature
- CO₂, SiO₂, GeO₂, GeO are acidic, PbO, PbO₂ is SnO and SnO₂ are amphoteric and CO is neutral
- ⇒ Among 14th group element only Sn reacts with steam to produce H₂ gas.
- ⇒ Tetrahalide of 14th group element are covalent except SnF₄ and PbF₄

Stability of oxidation state

- ⇒ C⁺⁴ > ————— > Pb⁺⁴ (Stability)
- C⁺² < ————— < Pb⁺² (Stability)
- ⇒ Pb⁺⁴ compounds are strong oxidizing agent.
- ⇒ PbI₄ does not exist.

- Trimethylamine (CH₃)₃N is pyramidal while Trisilylamine N(SiH₃)₃ is planar due to back bonding.

SILICONES (ORGANO SILICONE POLYMER)

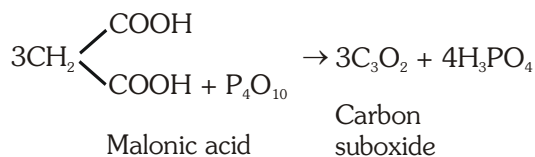
- Silicones are polymeric organosilicon compounds containing Si-O-Si linkage. They have high thermal stability of Si-O-Si chains and are also called high temperature polymers.

General formula : (R₂SiO)_n. Where R = -CH₃, -C₂H₅, -C₆H₅

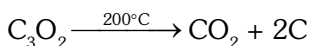
- (i) $R_2SiCl_2 + 2H_2O \xrightarrow{-2HCl} R_2Si(OH)_2 \xrightarrow[-H_2O]{\Delta} \text{Linear Silicones/Cyclic Silicones}$
- (ii) $R_3SiCl + H_2O \xrightarrow{HCl} R_3Si(OH) \xrightarrow[-H_2O]{\Delta} \text{Dimer Silicones}$
- (iii) $RSiCl_3 + 3H_2O \xrightarrow{-3HCl} RSi(OH)_3 \xrightarrow[-H_2O]{\Delta} \text{Crossed Linked Silicones}$

CARBON SUBOXIDE

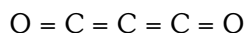
- Carbon suboxide (C_3O_2) is an foul smelling gas which can be prepared by the dehydration of malonic acid with P_4O_{10} .



On heating upto $200^\circ C$, it decomposes into CO_2 and carbon.



The molecule is thought to have a linear structure.



OXIDE OF LEAD

- $PbO \xrightleftharpoons[\text{Litharge}]{\text{massicot}} PbO$
- **Red lead (Pb_3O_4)** is considered to be mixture of lead monoxide and lead dioxide and it is written as $(PbO)_2 \cdot 2PbO_2$.
- **Lead dioxide (PbO_2)**. It is a brown powder obtained by the treatment of red lead with HNO_3 .
 $Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$
 It is used as an active material of the positive plate in storage cells and finds use in match industry as an oxidizing agent.

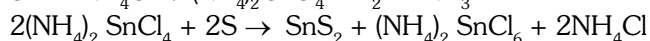
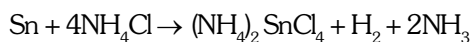
REACTION OF LEAD OXIDES

Oxide	ex NaOH	HCl	H_2SO_4	HNO_3
PbO	Na_2PbO_2	$PbCl_2$	$PbSO_4$	$Pb(NO_3)_2$
PbO_2	Na_2PbO_3	$PbCl_2 + Cl_2$	$PbSO_4 + O_2$	$Pb(NO_3)_2$
Pb_2O_3	$Na_2PbO_2 + NaPbO_3$	$PbCl_2 + Cl_2$	$PbSO_4 + O_2$	$Pb(NO_3)_2 + PbO_2$
Pb_3O_4	$Na_2PbO_2 + Na_2PbO_3$	$PbCl_2 + Cl_2$	$PbSO_4 + O_2$	$Pb(NO_3)_2 + PbO_2$

TIN & ITS COMPOUNDS

- **Action of conc. HNO_3 on tin**
- (a) Dilute HNO_3
 $4Sn + 10HNO_3 \rightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$
- (b) Hot conc. HNO_3
 $Sn + 4HNO_3 \rightarrow H_2SnO_3 + 4NO_2 + H_2O$
 Metastannic acid
- Action of conc. NaOH on tin** $\Rightarrow Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2 \uparrow$
- $SnCl_2$**
- $SnCl_2 \cdot 2H_2O$ on heating undergoes to form it's basic chloride $Sn(OH) \cdot Cl$. The anhydrous salt, therefore, be obtained by heating the hydrated salt in the presence of HCl vapour.
- Stannous chloride reduces mercuric chloride ($HgCl_2$) to a white precipitate of mercurous chloride (Hg_2Cl_2) which finally turns to metallic mercury (dark grey or black).
 $2Hg^{2+} + 3Cl^- + Sn^{2+} \rightarrow Hg_2Cl_2 + Sn^{4+}$
 Mercurous chloride
- $Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg \downarrow + SnCl_4$
 Black

- **Mosaic gold** (SnS_2). Stannic sulphide exists in yellow glistening scales which is used for decorative purposes under and the name mosaic gold. It is prepared by heating mixture of tin fillings, sulphur and NH_4Cl in a retort.



- **Tin Cry**. Tin metal when bent produces a cracking noise due to rubbing of metal crystals over one another.

CARBON MONOXIDE [CO]

Colorless odourless, tasteless, neutral, poisonous gas

$\text{C} \equiv \text{O}$

CO properties

By dehydration of formic acid and oxalic acid

$$\text{HCOOH} \xrightarrow[\text{H}_2\text{SO}_4]{\text{Conc.}} \text{CO} + \text{H}_2\text{O}$$

$$\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array} \xrightarrow[\text{H}_2\text{SO}_4]{\text{Conc.}} \text{CO} + \text{CO}_2 + \text{H}_2\text{O}$$

By incomplete combustion

$$\text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}$$

By passing air on red hot coke

dry air $\rightarrow \text{CO} + \text{N}_2$ Producer gas

moist air $\rightarrow \text{CO} + \text{N}_2 + \text{H}_2$ semi water gas

water vapour $\rightarrow \text{CO} + \text{H}_2$ water gas or synthesis gas

Complexing agent

$$\text{Ni} + 4\text{CO} \rightarrow [\text{Ni}(\text{CO})_4]$$

Reducing agent

$$\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2$$

$$\text{ZnO} + \text{CO} \rightarrow \text{Zn} + \text{CO}_2$$

Combustion

$$\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$$

blue flame

CARBIDES

Binary compounds of carbon with other elements (except hydrogen) are known as carbides

CARBIDES

Ionic Carbide

C + higher electropositive element
(IA, IIA & Al)

Eg. Be_2C , Mg_2C_3 , Al_4C_3 , CaC_2

Covalent Carbide

C + Non-metals
(like B & Si)

Eg. B_4C , SiC

Interstitial Carbides

C + transition metals

Eg. : TiC , WC

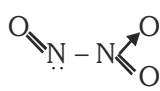
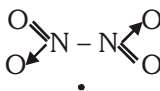
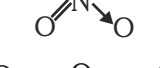
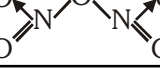
GROUP 15 ELEMENTS

NITROGEN FAMILY

1. Nitrogen and phosphorus are **non-metals**, arsenic and antimony **metalloids** and bismuth is a **typical metal**.
2. Except nitrogen all the elements show allotropy.
3. Bismuth hardly forms any compound in -3 oxidation state.
4. The only well characterised Bi (V) compound is BiF_5 .
5. In the case of nitrogen, all oxidation states from $+1$ to $+4$ tend to disproportionate in acid solution. For example,
(i) $3\text{HNO}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}$
6. In case of phosphorus nearly all intermediate oxidation states disproportionate into $+5$ and -3 both in alkali and acid.
7. 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 predominantly basic.
8. In case of nitrogen, only NF_3 is known to be stable.
9. Trihalides except BiF_3 are predominantly covalent in nature.
 - \Rightarrow The only well characterised Bi (V) compound is BiF_5
 - \Rightarrow All the oxidation states from $+1$ to $+4$ tend to disproportionate in acidic solution :
exp: $3\text{HNO}_2 \longrightarrow \text{HNO}_3 + 2\text{NO}$
 - \Rightarrow All the intermediate oxidation states disproportionate into $+5$ and -3
 $4\text{H}_3\text{PO}_3 \xrightarrow{\Delta} 3\text{H}_3\text{PO}_4 + \text{PH}_3$
 $\text{H}_3\text{PO}_2 \xrightarrow{\Delta} \text{H}_3\text{PO}_4 + \text{PH}_3$
 - \Rightarrow Hydride of 15th group elements :

$\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$	Basic character
$\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$	Stability
$\text{PH}_3 < \text{AsH}_3 < \text{NH}_3 < \text{SbH}_3 < \text{BiH}_3$	Boiling Point
$\text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{NH}_3$	Melting Point
$\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$	Bond Energy
 - \Rightarrow Penta oxide of 15th group element is acidic. N_2O_3 , P_2O_3 are acidic, As_2O_3 , Sb_2O_3 are amphoteric with Bi_2O_3 is basic.
 - \Rightarrow Trihalide of 15th group elements are covalent except BiF_3

STRUCTURE OF OXIDES OF NITROGEN AND PHOSPHORUS NITROGEN

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

Oxides of Nitrogen

Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen oxide]	N ₂ O	+1	$\text{NH}_4\text{NO}_3 \xrightarrow{\text{Heat}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$	Colourless gas, neutral
Nitrogen monoxide [Nitrogen (II) oxide]	NO	+2	$2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O} + 2\text{NO}$	Colourless gas, neutral
Dinitrogen trioxide [Nitrogen (III) oxide]	N ₂ O ₃	+3	$2\text{NO} + \text{N}_2\text{O}_4 \xrightarrow{250\text{K}} 2\text{N}_2\text{O}_3$	Blue solid, acidic blue liquid (–30°C)
Nitrogen dioxide [Nitrogen (IV) oxide]	NO ₂	+4	$2\text{Pb}(\text{NO}_3)_2 \xrightarrow{673\text{K}} 4\text{NO}_2 + 2\text{PbO} + \text{O}_2$	brown gas, acidic
Dinitrogen tetroxide [Nitrogen (IV) oxide]	N ₂ O ₄	+4	$2\text{NO}_2 \xrightleftharpoons[\text{Heat}]{\text{Cool}} \text{N}_2\text{O}_4$	Colourless solid/liquid, acidic
Dinitrogen pentaoxide [Nitrogen(V) oxide]	N ₂ O ₅	+5	$4\text{HNO}_3 + \text{P}_4\text{O}_{10} \rightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$	colourless solid, acidic

COMPOUNDS OF NITROGEN FAMILY

AMMONIA (NH₃)

Colorless, Pungent Smell, basic in nature liquified easily, uses as coolant

Preparation

(i) $2\text{NH}_4\text{Cl} + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCl}_2 + 2\text{NH}_3 + 2\text{H}_2\text{O}$

(ii) $\text{Mg}_3\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Mg}(\text{OH})_2 + 2\text{NH}_3$

Manufacturing Haber Process

$$\text{N}_2 + 3\text{H}_2 \xrightleftharpoons[200-300\text{atm}]{\text{Fe+Mo, 750K}} 2\text{NH}_3 + 24\text{KCal}$$

MOP **NH₃** properties

$4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}$
 $4\text{NH}_3 + 5\text{O}_2 \xrightarrow[1100\text{K}]{\text{Pt/Rh}} 4\text{NO} + 6\text{H}_2\text{O}$
 $8\text{NH}_3 + 3\text{Cl}_2 \xrightarrow{\text{excess}} 6\text{NH}_4\text{Cl} + \text{N}_2$
 $\text{NH}_3 + 3\text{Cl}_2 \xrightarrow{\text{excess}} \text{NCl}_3 + 3\text{HCl}$

Ostwald's process

NITRIC ACID (HNO₃)

Preparation :

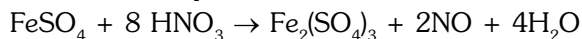
Ostwald's process :

- (i) $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \xrightarrow[500\text{K, 9bar}]{\text{Pt/Rh-gauge catalyst (From air)}} 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
- (ii) $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
- (iii) $3\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{HNO}_3(\text{aq}) + \text{NO}(\text{g})$

Properties :

HNO₃, nitric acid was earlier called as aqua fortis (meaning strong water). It usually acquires yellow colour. due to its decomposition by sunlight into NO₂. It acts as a strong oxidising agent.

Reaction with FeSO₄ :

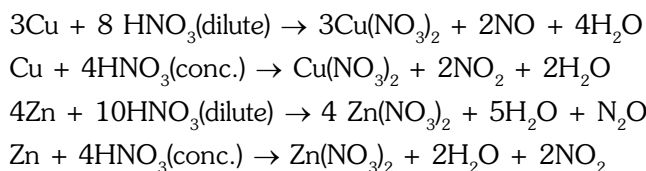


Reaction with non-metals :

Non-metals converted into highest oxyacids by hot and conc.

HNO₃. NO₂ gas is evolved (S to H₂SO₄; P to H₃PO₄; C to H₂CO₃; I₂ to HIO₃; As to H₃AsO₄; Sb to H₃SbO₄ and Sn to H₂SnO₃). Most of the metals except noble metals are attacked by HNO₃. It plays double role in action on metals, i.e., it acts as an acids as well as an oxidising agent.

Reaction with metals :



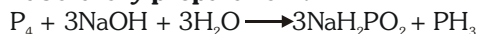
Concentration of nitric acid	Metal	Main products
Very Dilute HNO_3	Mg, Mn	H_2 + metal nitrate
	Fe, Zn, Sn	NH_4NO_3 + metal nitrate
	Cu, Ag, Hg	No reaction
Dilute HNO_3	Fe, Zn	N_2O + metal nitrate
	Pb, Cu, Ag	NO + metal nitrate
Conc. HNO_3	Sn	NO_2 + H_2SnO_3 (Metastannic acid)
Conc. HNO_3	Fe, Co, Ni,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

PHOSPHINE (PH_3)

Preparation :



Laboratory preparation :



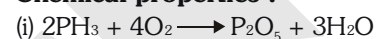
Uses :

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

Physical properties :

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

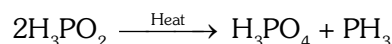
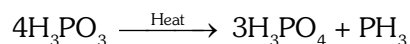
Chemical properties :



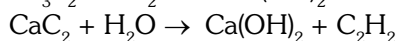
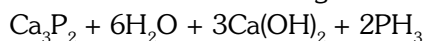
Oxoacids of Phosphorus

Name	Formula	Oxidation state of Phosphorus	Characteristic bonds and their number	Preparation
Hypophosphorus (Phosphinic)	H_3PO_2	+ 1	One P — OH Two P — H One P = O	white P_4 + alkali
Orthophosphorous (Phosphonic)	H_3PO_3	+ 3	Two P — OH One P — H One P = O	P_2O_3 + H_2O
Pyrophosphorous	$\text{H}_4\text{P}_2\text{O}_5$	+ 3	Two P — OH Two P — H Two P = O	PCl_3 + H_3PO_3
Hypophosphoric	$\text{H}_4\text{P}_2\text{O}_6$	+ 4	Four P — OH Two P = O One P — P	red P_4 + alkali
Orthophosphoric	H_3PO_4	+ 5	Three P — OH One P = O	P_4O_{10} + H_2O
Pyrophosphoric	$\text{H}_4\text{P}_2\text{O}_7$	+ 5	Four P — OH Two P = O One P — O — P	heat phosphoric acid
Metaphosphoric*	$(\text{HPO}_3)_n$	+ 5	Three P — OH Three P = O Three P — O — P	phosphorous acid + Br_2 , heat in a sealed tube

- Acidity of oxides and the solubility of 15 group oxides decreases from N to Bi. For example, N_2O_3 , N_2O_5 , P_4O_6 , P_4O_{10} , As_4O_6 and As_4O_{10} are acidic and dissolve water forming acids. Sb_4O_6 and Sb_4O_{10} are weakly acidic and insoluble in water Bi_2O_3 is a basic oxide and is insoluble in water.
- On heating, phosphorus acid, H_3PO_3 decomposes into phosphine (PH_3) and phosphoric acid (H_3PO_4).

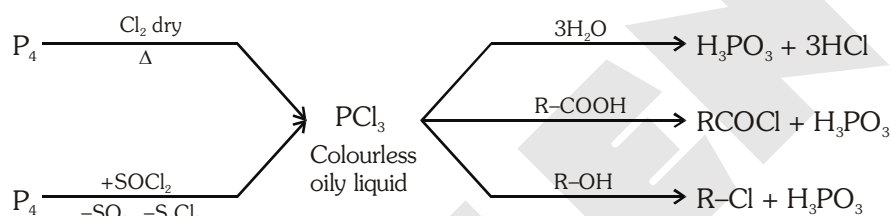


- **Holme's signals.** A mixture of Ca_3P_2 and CaC_2 on treatment with H_2O forms PH_3 and P_2H_4 along with C_2H_2 . The mixture burns with a bright luminous flame and it acts as a signal for approaching ships.

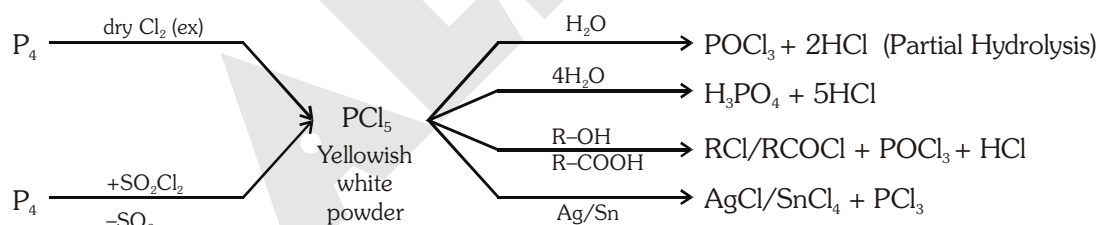


- **Smoke screens,** involve the use of calcium phosphide, Ca_3P_2 . The PH_3 gas obtained from Ca_3P_2 catches fire to give the needed smoke.
- **Phosphatic slag or Thomas slag or Basic slag** is obtained as a biproduct in the manufacture of steel and is probably a double salt of tricalcium phosphate and calcium silicate.

PCl_3



PCl_5



GROUP 16 ELEMENTS

OXYGEN FAMILY

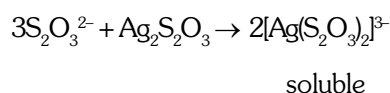
- Oxygen is the most abundant of all the elements on earth crust.
 - Oxygen and sulphur are non-metals, selenium and tellurium metalloids, whereas polonium is a metal.
 - Polonium hardly shows -2 oxidation state.
 - Reducing property of dioxide decreases from SO_2 to TeO_2 ; SO_2 is reducing while TeO_2 is an oxidising agent.
 - Sulphur hexafluoride, SF_6 is exceptionally stable for steric reasons.
 - 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 below : $2\text{Se}_2\text{Cl}_2 \rightarrow \text{SeCl}_4 + 3\text{Se}$
- ☐ The weakening of M-H bond with the increase in the size of M (not the electronegativity) explains the increasing acidic character of hydrides down the group.
- ☐ **Halides** : All these elements form a number of halides. The halides of oxygen are not very stable. Selenium does not form dihalides.
e.g. OF_2 , Cl_2O_6 , I_2O_5 , etc.

SODIUM THIOSULPHATE $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

Preparation :

- (a) $\text{Na}_2\text{SO}_3 + \text{S} \xrightarrow{\text{Boil}} \text{Na}_2\text{S}_2\text{O}_3$
- (b) $4\text{S} + 6\text{NaOH} \xrightarrow{\text{Boil}} \text{Na}_2\text{S}_2\text{O}_3 + 2\text{Na}_2\text{S} + 3\text{H}_2\text{O}$
- (c) $2\text{Na}_2\text{S} + 3\text{SO}_2 \xrightarrow{\text{Boil}} 2\text{Na}_2\text{S}_2\text{O}_3 + \text{S}$
- (d) Spring's reaction
- $$\text{Na}_2\text{S} + \text{Na}_2\text{SO}_3 + \text{I}_2 \xrightarrow{\text{Heat}} \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaI}$$

Concentrated $\text{Na}_2\text{S}_2\text{O}_3$ does not give a white ppt. with AgNO_3 . This is because silver thiosulphate formed is readily soluble in excess of sodium thiosulphate forming soluble complex.



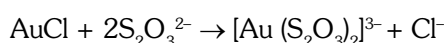
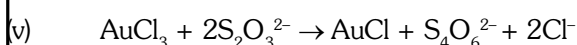
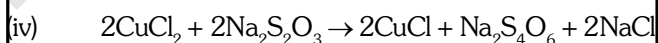
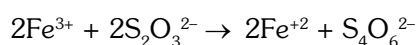
Reaction with oxidizing agent :

- (i) $\text{Na}_2\text{S}_2\text{O}_3 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl} + \text{S}$
- (ii) $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$
- Sodium tetrathionate
- This reaction forms the basis of iodometric estimation of $\text{Cr}_2\text{O}_7^{2-}$ and Cu^{2+} salts.



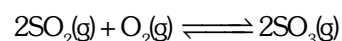
Violet

The violet colour disappears quickly due to the reduction of ferric chloride by $\text{S}_2\text{O}_3^{2-}$ ions,

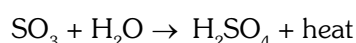


Sulphur trioxides (SO_3) is a white crystalline solid with melting point 290K and boiling point 318K.

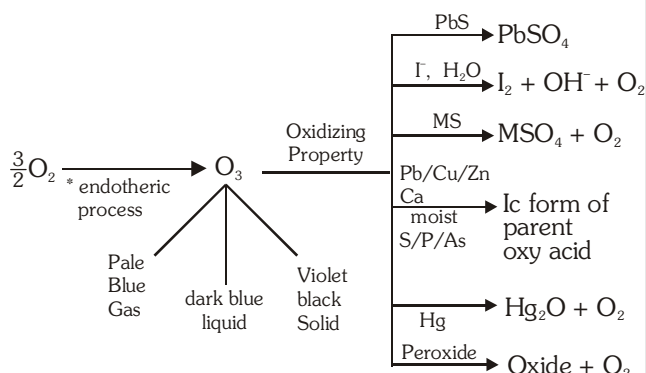
SO_3 is prepared by the direct oxidation of SO_2 with atmospheric oxygen in presence of finally divided Pt or V_2O_5 at a pressure of 2 bar. and temperature 720K.



SO_3 reacts with water to produce H_2SO_4 and large amount of heat is evolved.



OZONE



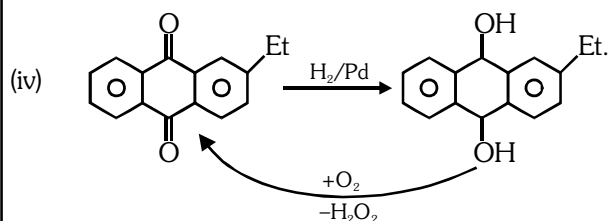
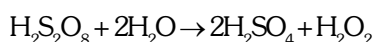
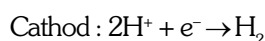
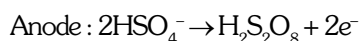
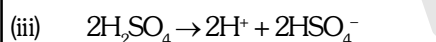
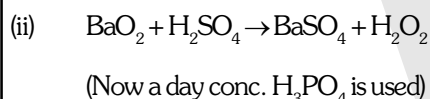
* Fishy odour, Highly toxic.

Gases Absorbent

O_3	Turpentine Oil/Oil of cinnamon.
NO	$FeSO_4$
SO_2	NaOH
CO	Cu_2Cl_2
O_2	Pyrogallol

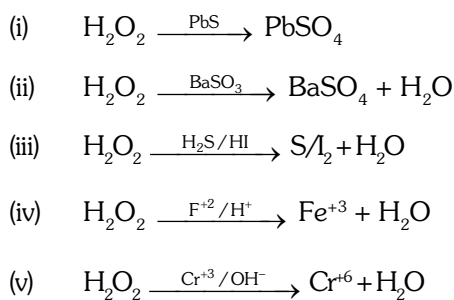
HYDROGEN PEROXIDE

Preparation :

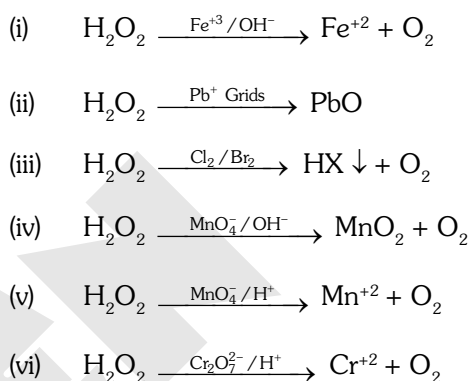


Properties :

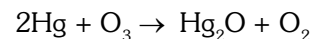
Oxidizing property :



Reducing property :



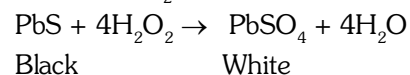
➤ Tailing of mercury is due to the formation of mercury oxide when Hg reacts with ozone.



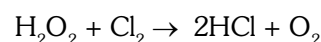
As a result of it, mercury loses its meniscus and starts sticking to the glass.

➤ The bleaching action of ozone and H_2O_2 is permanent and is due to oxidation while that of SO_2 is temporary and is due to reduction.

➤ H_2O_2 is used to restore the colour of old lead paintings which have been blackened due to the formation of PbS by the action of H_2S present in the air.



➤ Antichlor action of H_2O_2 is due to its tendency to reduce the excess of chlorine from bleaching powder to HCl.



$\Rightarrow NH_2.NH_2 + H_2O_2$ as rocket propellant.

\Rightarrow Storage :

SULPHURIC ACID (H₂SO₄)

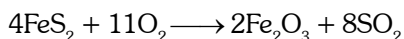
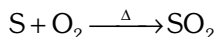
It is also known as oil of vitriol and king of chemicals.

Manufacture of sulphuric acid :

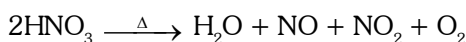
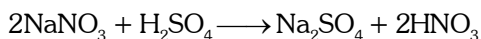
Lead chamber process :

The various steps involved are :

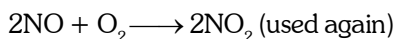
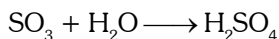
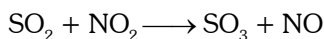
- (a) Production of SO₂ : By burning S or iron pyrites.



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



- (c) Reaction in lead chamber

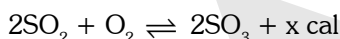


Contact process :

The steps involved are :

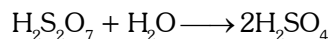
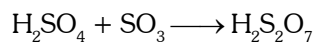
- (a) **Production of SO₂** : It is produced by burning sulphur or iron pyrites and purified by treating with steam to remove dust particles.

- (b) **Conversion of SO₂ to SO₃** : It is done in container or catalyst chamber after being pre-heated to 450°C.



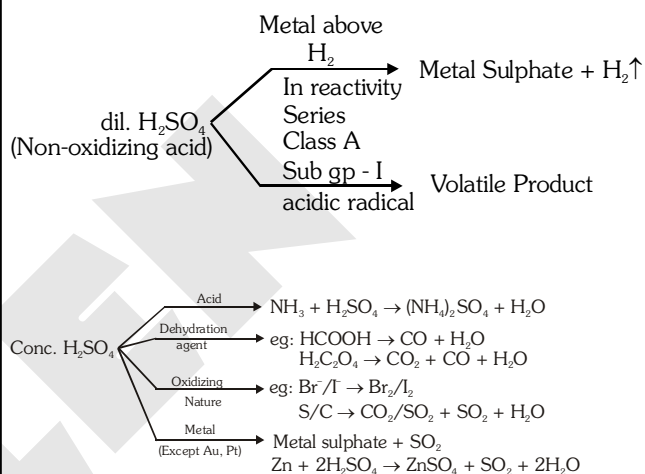
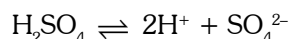
Catalyst : Formerly, platinised asbestos was used which is costly and easily poisoned. These days V₂O₅ is used.

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



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

It is strong dibasic acid.



Uses :

In lead storage batteries.

In manufacture of paints and pigments.

In metallurgy for electrolytic refining of metals.

GROUP 17 ELEMENTS

- The electron affinity values (in KJ mol⁻¹) for 17 group element are given below :

F	Cl	Br	I
333	349	325	296
 - All halogens are coloured. For example, F₂ has yellow gas, Cl₂ greenish yellow gas, Br₂ red liquid and I₂ violet coloured solid.
 - They react with metals and non-metals to form halides and the reactivity of the halogens decreases down the group. i.e. the order is F₂ > Cl₂ > Br₂ > I₂
 - In general, a halogen oxidises halide ions of higher atomic number.

$$\text{F}_2 + 2\text{X}^- \rightarrow 2\text{F}^- + \text{X}_2 \quad (\text{X} = \text{Cl}, \text{Br} \text{ or } \text{I})$$

$$\text{Cl}_2 + 2\text{X}^- \rightarrow 2\text{Cl}^- + \text{X}_2 \quad (\text{X} = \text{Br} \text{ or } \text{I})$$

$$\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$$
 - Reaction with water :**

$$2\text{F}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 4\text{H}^+(\text{aq}) + 4\text{F}^-(\text{aq}) + \text{O}_2(\text{g})$$

$$\text{X}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HX}(\text{aq}) + \text{HOX}(\text{aq})$$
 (where X = Cl or Br)

$$4\text{I}^-(\text{aq}) + 4\text{H}^+(\text{aq}) + \text{O}_2(\text{g}) \rightarrow 2\text{I}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l})$$
 - Halogens form many oxides with oxygen but most of them are unstable.
 - Fluorine forms two oxides OF₂ and O₂F₂. However, only OF₂ is thermally stable at 298 K. These oxides are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents.
 - O₂F₂ oxidises plutonium to PuF₆ and the reaction is used in removing plutonium as PuF₆ from spent nuclear fuel.
 - A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens, I > Cl > Br.
 - I₂O₅ is a very good oxidising agent and is used in the estimation of carbon monoxide.
- ☐ **Reactivity :** All halogens are chemically very reactive elements. This is due to their low dissociation energy and high EN. Fluorine is the most reactive and iodine is the least reactive halogen.

INTERHALOGEN COMPOUNDS

- ☐ These compounds are regarded as halides of more electropositive (i.e. less electronegative) halogens.
- ☐ Types of interhalogen compound :
 AB type : ClF, BrF, BrCl, ICl, IBr
 AB₃ type : ClF₃, BrF₃, ICl₃
 AB₅ type : BrF₅, IF₅
 AB₇ type : IF₇

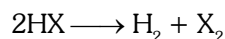
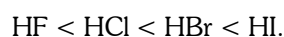
HYDROGEN HALIDES

Bond strength, bond length and thermal stability :

- Since size of halogen atom increases from F to I down the group, bond length of H – X bond increases down the group.
 ∴ reactivity and acidic character ↑.
 HF < HCl < HBr < HI.
- Bond strength is inversely, proportional to bond length i.e., larger the bond length, lower the bond strength is
 HF > HCl > HBr > HI.
- Higher the bond dissociation energy, greater will be thermal stability. Thus, thermal stability follows the order.
 HF > HCl > HBr > HI.

REDUCING CHARACTER :

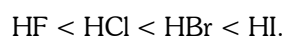
The reducing character of hydrogen halides increases down the group as



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

ACIDIC STRENGTH :

The acidic strength of these acids increases down the group and hence follows the order.

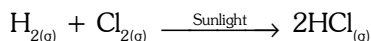


Since H–I bond is weakest, it can be easily dissociated into H⁺ and I[–] ions while HF with greater bond dissociation energy can be dissociated with maximum difficulty.

HYDROCHLORIC ACID, (HCl)

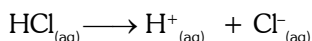
Preparation : By dissolving hydrogen chloride gas in water. Hydrogen chloride gas required in turn can be prepared by the following methods:

By the direct combination of hydrogen and chlorine.



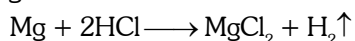
Hydrogen chloride gas can also be obtained by burning hydrogen in chlorine.

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

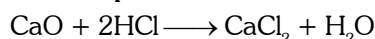


Thus anhydrous HCl does not show acidic properties. Only aqueous HCl or in presence of moisture, HCl behaves as an acid.

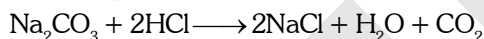
Metal + Hydrochloric acid \longrightarrow Metal chloride + Hydrogen



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



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



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



Reducing property :

HCl is a strong reducing agent.



Uses :

In the production of dyes, paints, photographic chemicals, etc.

Used in the preparation of chlorides, chlorine, aqua-regia, etc.

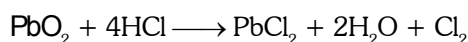
Used as a laboratory reagent.

PSEUDO HALIDES

Pseudo halides are uninegative groups which show certain characteristics of halide ions. For example Cyanide (CN⁻), Cyanate (OCN⁻), Thiocyanate (SCN⁻), Selenocyanate (SeCN⁻), Azide (N₃⁻), Aziothio carbonate (SCSN₃⁻) and isocyanate (ONC⁻).

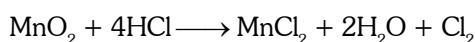
CHLORINE (Cl₂)

Preparation : By oxidation of conc. HCl.

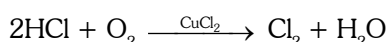


Manufacture :

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

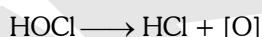
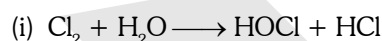


Deacon process :



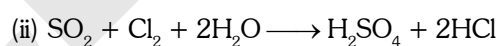
Properties : It is a yellowish green gas, poisonous in nature, soluble in water. Its aqueous solution is known as chlorine water which on careful cooling gives chlorine hydrate Cl₂·8H₂O.

Bleaching action and oxidising property

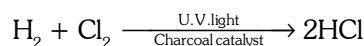


Coloured matter + nascent [O] \rightarrow Colourless matter

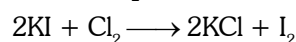
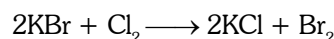
The bleaching action of chlorine is permanent and is due to its oxidising nature.



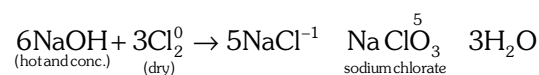
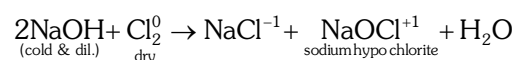
Action of hydrogen :



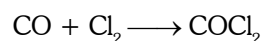
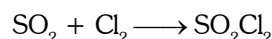
Displacement reactions :



Action of NaOH :



Addition reactions :

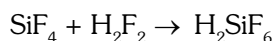
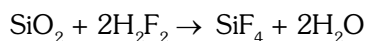


Test for chlorine :

- It is a greenish yellow gas with irritating smell.
- It turns starch iodide paper blue.
- It bleaches litmus paper and indigo solution.

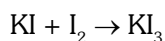
NOTE

- **Action of silica and glass** : Strong solution of HF attacks glass readily forming silicon fluoride which gives complex fluosilicic acid, H_2SiF_6 with excess HF.



This is called etching of glass.

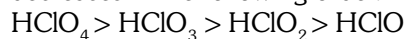
- Iodine is slightly soluble in water but much more soluble in KI due to the formation of KI_3 .



The solution behaves as a simple mixture of KI and I_2 .

OXY-ACID

- The acidic strength of the oxoacids of halogen decreases in the following order.



- The chlorine oxyanion in which the central atoms has highest oxidation number will have maximum number of oxygen atoms for participation in the extension of the π -bond. Thereby the charge on the ion is delocalized which greatly stabilizes the ion and thus decreases its tendency to accept a proton i.e., causes the ion to be very weak base with the result that the strength of the acid increases.

- The acidity of oxoacids of different halogens having the same oxidation number decreases with the increases in atomic numbers of the halogen

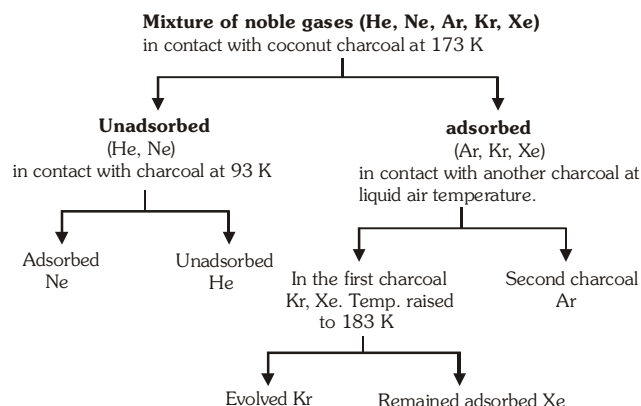


GROUP 18 ELEMENTS

- Relative Abundance:
 $\text{Ar} > \text{Ne} > \text{Kr} > \text{He} > \text{Xe} > \text{Rn}$
- Melting and Boiling point:
 $\text{Rn} > \text{Xe} > \text{Kr} > \text{Ar} > \text{Ne} > \text{He}$
- He has the lowest boiling point among all element
- Noble gases are monoatomic, colourless, odourless, sparingly soluble in water and diffusing through most commonly used laboratory materials.
- $\text{O}_2[\text{PtF}_6]$ is the first noble gas compound.
- Ar, Kr and Xe form clathrate compound when pass in ice with high pressure.
 $\text{A} \cdot 6\text{H}_2\text{O}$ (A = Ar/Kr/Xe)

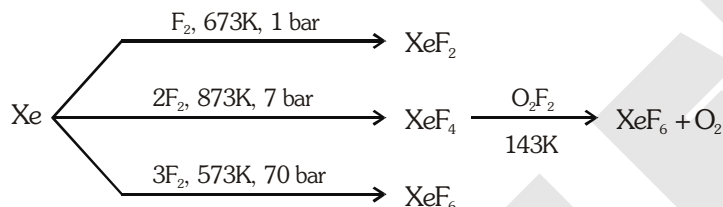
NOBLE GAS

- In Dewar's method, the separation of noble gases is summarized below

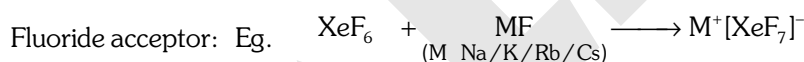
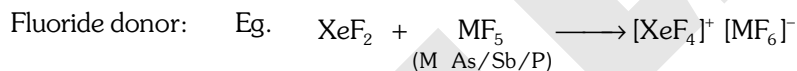


- The viscosity of He is extremely low, about $1/100^{\text{th}}$ of hydrogen gas.

Preparation of Xe-Fluoride:



Properties:



Hydrolysis:

