

p - Block Elements

Boron Family

1. ELECTRONIC CONFIGURATION :

The general outer electronic configuration is ns^2np^1 . Hence these elements belong to p-block.

| Elements | Configuration |
|-------------------------------|--|
| Boron [B ₅] | [He] 2s ² 2p ¹ |
| Aluminium [Al ₁₃] | [Ne] 3s ² , 3p ¹ |
| Gallium [Ga ₃₁] | [Ar] 3d ¹⁰ , 4s ² 4p ¹ |
| Indium [In ₄₉] | [Kr] 4d ¹⁰ , 5s ² , sp ¹ |
| Thallium [Tl ₈₁] | [Xe] 4f ¹⁴ , 5d ¹⁰ , 6s ² 6p ¹ |

- B is nonmetal due to its small size, high I.E. and high E.N.
- Al, Ga, In, Tl show typical metallic properties.
- Al is third most abundant element [7.4%]
- Tl is highly toxic.
- Compounds of Al are Al₂O₃, AlCl₃.6H₂O, alums, LiAlH₄, ultramarine etc.

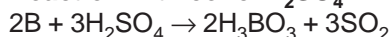
2. CHEMICAL CHARACTERISTICS :

Boron

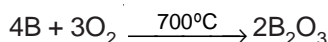
Oxidation state : [+3]

B₂O₃, BCl₃, H₃BO₃, Na₂B₄O₇
[Boron also shows (-3) O.S. in metal borides]

Reaction with conc. H₂SO₄ :



Reaction with O₂.

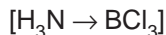


Formation of chlorides :

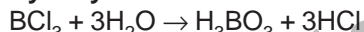


Nature of Chlorides

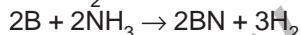
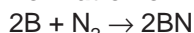
Lewis acids :



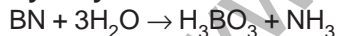
Hydrolysis :



Formation of nitrides :



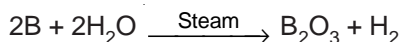
Hydrolysis of nitride :



Reducing character :

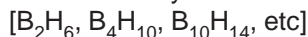


Treatment with steam :



Nonmetal

Boron forms hydrides



B₂O₃ is acidic;

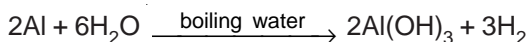
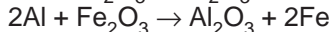
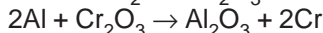
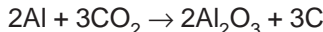
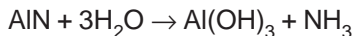
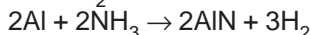
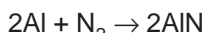
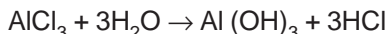
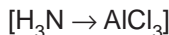
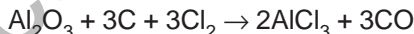
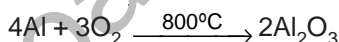
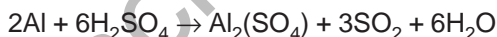


Borates are stable

Aluminium

[+3]

Al₂O₃, AlCl₃, Al(OH)₃
NaAlO₂

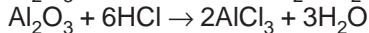
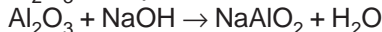


Metal

Forms complex hydride :

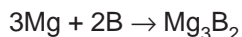


Al₂O₃ is amphoteric

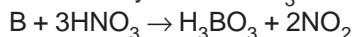


Aluminates are less stable

Forms borides with other metals



Attacked by conc. HNO_3



Orthoboric acid

Maximum covalency of four is observed in the compound $\text{K}[\text{BF}_4]$

$\text{B}(\text{OH})_3$ is acidic

It forms covalent compounds only

Forms of covalent carbide B_4C

Halides exist in monomeric form BX_3

It dissolves in fused alkalis

Al forms alloys with other metals

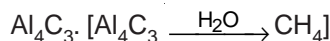
Becomes passive with conc. HNO_3 due to the formation of oxide layer Al_2O_3

Maximum covalency of six is observed in $\text{Na}_3[\text{AlF}_6]$

$\text{Al}(\text{OH})_3$ is basic

It forms both covalent and electrovalent compounds

Forms an ionic carbide

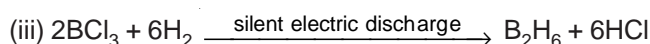
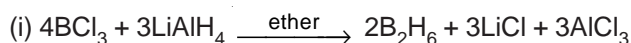


AlCl_3 and AlBr_3 exist as dimer

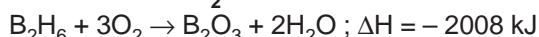
It dissolves in hot alkalis.

3. DIBORANE (B_2H_6)

3.1 Preparations



Reaction with O_2 :

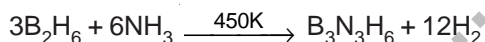


[Thus boranes are useful as high energy fuels]

Reaction with water :



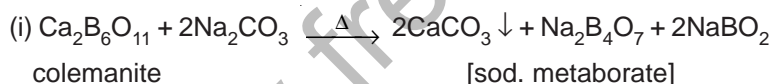
Reaction with ammonia :



[(borazol) inorganic benzene]

4. BORAX [$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$]

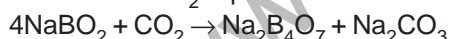
4.1 Preparation :



colemanite

[sod. metaborate]

A current of CO_2 is passed in the mother liquor, sodium metaborate is converted to borax.



4.2 Properties :

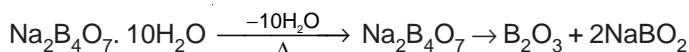
Sparingly soluble in cold water.

Soluble in hot water.

Solution is alkaline



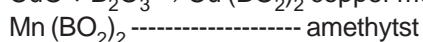
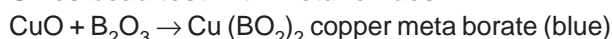
Action of heat :



boric anhydride sod. metaborate

□□□□□□□□□□
transparent bead

Gives bead test with metal oxides :



4.3 Uses :

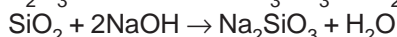
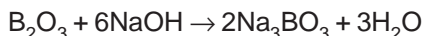
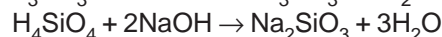
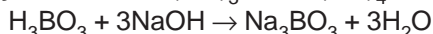
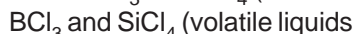
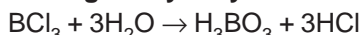
- (i) In borax bead test
- (ii) Preservation for food stuffs
- (iii) In making heat and shock resistance glass
- (iv) Welding, soldering and in metallurgy
- (v) Used in match and leather industries

5. DIAGONAL RELATIONSHIP BETWEEN BORON AND SILICON :**Common characteristics :**

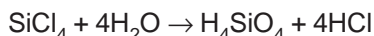
- B and Si do not occur in free state
- B and Si are non metals
- B and Si act as semi conductors
- B and Si show two allotropic forms (crystalline and amorphous)

Hydrides : Both form hydrides :

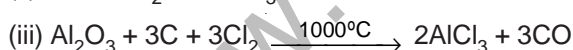
| | [B] | [Si] |
|-------------|------------------|--------------------|
| B_2H_6 | diborane – 6 | SiH_4 silane |
| B_4H_{10} | tetraborane – 10 | Si_2H_6 disilene |

Oxides : Oxides of both the elements are acidic in nature :**Hydroxides :** B(OH)₃ and Si(OH)₄ are weak acids**Halides :** BF₃ and SiF₄ (colourless gases)**Undergoes hydrolysis :**

boric acid

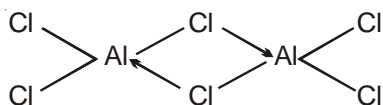


silicic acid

Carbides : B₄C and SiC are very hard substances and are used as abrasive.**6. ALUMINIUM CHLORIDE :****6.1 Preparation :****Anhydrous AlCl₃****Hydrated aluminium chloride [AlCl₃ . 6H₂O]****6.2 Properties**

- * AlCl₃ (anhydrous) is white, hygroscopic substance.
- * Sublimes at 183° C under normal pressure. (at 100° C in vacuum)
- * V.D. corresponds to Al₂Cl₆ (at 350° C) and AlCl₃ (at 750° C)
- * Soluble in organic solvents (C₆H₆, CS₂ etc)
- * **Addition compounds :**
Forms addition compounds with NH₃, PH₃, COCl₂ etc. [e.g. AlCl₃ . 6NH₃]
- * **Hydrolysis :** It is highly soluble in water and undergoes hydrolysis .
AlCl₃ + 3H₂O → Al(OH)₃ + 3HCl
- * **Action of heat :** Hydrated form on heating gives Al₂O₃.
AlCl₃ . 6H₂O → Al(OH)₃ + 3HCl + 3H₂O
2Al(OH)₃ → Al₂O₃ + 3H₂O

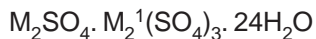
* **Structure** : (Halogen bridge dimer):



6.3 Uses : (i) Catalyst in the manufacture of petrol by cracking and in Friedel Crafts reactions. (ii) Reagent in the manufacture of dyes, drugs and perfumes.

7. ALUMS :

General formula :



M = monovalent cation : Na⁺, K⁺, Rb⁺ etc.

M₁ = Trivalent cation : Al³⁺, Fe³⁺, Mn³⁺ etc.

Examples : M₂SO₄ · M₂¹(SO₄)₃ · 24H₂O

| M | M ¹ | Name of the alum |
|------------------------------|------------------|------------------|
| K ⁺ | Al ³⁺ | Potash alum |
| NH ₄ ⁺ | Al ³⁺ | Ammonium alum |
| K ⁺ | Cr ³⁺ | Chrome alum |
| NH ₄ ⁺ | Fe ³⁺ | Ferric alum |

7.1 Preparation :

Hot solution of equimolar amount of the constituent sulphates are mixed and the solution is left for crystallization.

- * Alums are fairly soluble in cold water but soluble in hot water.
- * Solutions of alums are acidic
- * Alums are isomorphous and form mixed crystal
- * Lose water of crystallization when heated and swells up (burnt alum)
- * Solutions give the properties of ions of the constituent salts

7.2 Uses :

- (i) Used as a mordant in dyeing and printing
- (ii) In purification of water
- (iii) In leather tanning
- (iv) As antiseptic and in stopping bleeding from cuts.

1. ELECTRONIC CONFIGURATION :

The general outer electronic configuration of elements of IV A group is ns^2np^2 . Hence these elements belong to p-block.

| Elements | Configuration |
|-------------------------------|--|
| Carbon [C ₆] | [He] 2s ² 2p ² |
| Silicon [Si ₁₄] | [Ne] 3s ² 3p ² |
| Germanium [Ge ₃₂] | [Ar] 3d ¹⁰ , 4s ² 4p ² |
| Tin [Sn ₅₀] | [Kr] 4d ¹⁰ , 5s ² 5p ² |
| Lead [Pb ₈₂] | [Xe] 4f ¹⁴ , 5d ¹⁰ , 6s ² 6p ² |

- * C and Si are non metals.
- * C occurs in free state as coal, diamond and graphite. In combined state it is found in tissues of plant and animal kingdom.
- * Ge is metalloid.
- * Sn and Pb are metals. Pb is the end product of the heavier radioactive elements.
- * C is the 17th and Si is the 2nd most abundant element by mass in earth's crust.

2. CHEMICAL CHARACTERISTICS :

Oxides :

Group 14 elements form two types of oxides viz monoxide and dioxide.

2.1 Monoxide [MO]

CO, SiO, GeO, SnO, PbO

SiO (unstable) CO → neutral

GeO → basic

SnO, PbO → amphoteric

Carbon monoxide : It is a colour less toxic gas. It has the highest bond energy amongst monoxide of other members [1070 kJ mol⁻¹]. It forms carbonyls with transition metals Ni(CO)₄, Fe(CO)₅, Cr(CO)₆. These coordination compounds are also called organometallics. CO is found in exhaust fumes of automobiles.

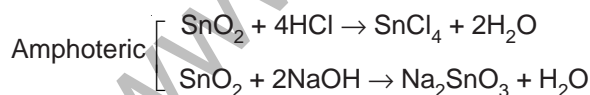
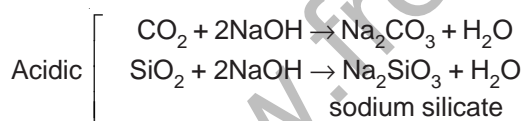
2.2 Dioxides [MO₂]

CO₂, SiO₂, GeO₂, SnO₂ and PbO₂

CO₂, SiO₂ → acidic

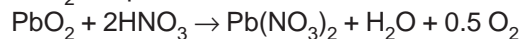
GeO₂, SnO₂, PbO₂ → amphoteric

Reactions of CO₂, SiO₂ and SnO₂



2.3 Oxidizing character of PbO₂ :

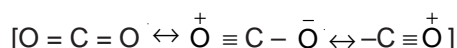
PbO₂ is a powerful oxidant. The reaction with HNO₃ can be written as :



2.4 CO₂ and SiO₂

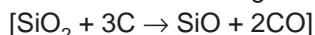
CO₂ :

- * It is a gas at room temperature
- * Solid CO₂ is called dry ice. It sublimates at -78°C and at 1 atmospheric pressure.
- * It is a linear, monomeric and nonpolar molecule.
- * It is soluble in water and is used as fire extinguisher.
- * On reduction with coke gives CO [CO₂ + C → 2CO]
- * It is a resonance hybrid of three non-equivalent structures.



SiO₂ ;

- * It is a solid at room temperature.
- * It has a three dimensional net work solid.
- * High m.p. (187 K) does not boil.
- * Gives silicate when fused with NaOH.
- * It is soluble in water.
- * On reduction with coke gives SiC.

**3. CARBIDES :**

Carbides are binary compounds of carbon with the elements of lower or about equal electronegativity.

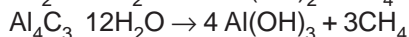
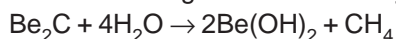
Carbides

**Electrovalent carbides :**

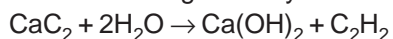
They are formed by strong electropositive elements (I, IIA, IIIA group members) Zn, Cd etc.

(i) Methanides (contain C⁴⁻ ion)

- * These carbides give methane on hydrolysis :

**(ii) Acetylides [contain [C≡C]²⁻ ion]**

- * These carbides give acetylene on hydrolysis.

**(iii) Allylide : [contain C₃⁴⁻ ion]**

- * These carbides give propyne or allylene on hydrolysis.

**3.2 Covalent carbides :**

B₄C and SiC are covalent carbides.

SiC (carborundum) : It is extremely hard, non-fusible, thermally stable and chemically inert solid.

- * The structure of SiC is similar to that of diamond.
- * It has a better thermal conductivity at high temperature. Resistant to abrasion and corrosion.
- * B₄C exhibit similarity with silicon carbide in properties.

3.3 Interstitial carbides (metallic carbides) :

- * Transition metals when combine with carbon or reduction of metallic oxide with carbon produces interstitial carbides.
- * Carbon atom being small occupy positions in the interstices of metal lattices. Formula of these carbides depend on the ratio of the number of metal atoms to the number of interstitial holes filled by carbon.
- * These carbides [M₃C, where M = Fe, Co, Ni etc] are easily hydrolysed by water and dilute acids to give a mixture of hydrocarbons and hydrogen.

4. ANOMALOUS BEHAVIOUR OF CARBON :**Because of :**

- * Small size
- * High electronegativity
- * High ionization energy
- * Non-availability of empty d-orbital carbon differs from the rest of the elements of group.

Points of differences :

- (1) Carbon is hard. Diamond (allotropic form) is the hardest substance known with highest melting point. Other members of this group are relatively soft (Sn and Pb have low m.p.)
- (2) Carbon form multiple bonds (pπ - pπ bonding) with itself and with N, O and S. Other members have very less tendency to form multiple bonds.
- (3) Carbon cannot expand its covalency beyond 4 due to absence of d-orbitals. Thus do not form complexes.
- (4) CO₂ is a gas a room temperature while dioxides of other elements are solids.
- (5) Carbon exhibit the unique character of catenation while other members (except Si) do not show this character.
- (6) CCl₄ does not hydrolyse while SiCl₄ undergoes hydrolysis.

5. SILICON :

Occurrence :

- * 26% of silicon is found in earth's crust.
- * As SiO_2 is found in sand, quartz etc.
- * As silicates it is found in felspar ($\text{K Al Si}_2 \text{O}_3$), mica $\text{KH}_2\text{Al}(\text{SiO}_4)_3$, clays etc.

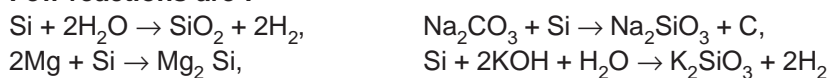
5.1 Preparations



5.2 Properties :

- * It is a hard and brittle solid with a very high m.p. (1410°C)
- * **Allotropic forms are :** (i) Brown amorphous powder (ii) Grey crystalline mass. Amorphous silicon is more active than crystalline variety.

Few reactions are :



6. GLASS :

- * 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.
- * Being amorphous solid it has no sharp melting point and melts at high temperature
- * Glass has no definite chemical formula, however it may be represented as :
 $x \text{M}_2\text{O} \cdot y \text{M}'\text{O} \cdot 6 \text{SiO}_2$
 where M = alkali metals Na, K.
 M' = bivalent metals Ca, Pb, Zn etc.
 x and y are integers.

Raw materials needed to manufacture glass are :

(a) Silica (SiO_2) (b) Alkali metal salts (Na_2CO_3 , NaNO_3 , Na_2SO_4 , NaNO_3 , K_2CO_3 , KNO_3) (c) Heavy metal oxides (PbO , Pb_3O_4) (d) Alkaline earth metal salts (CaCO_3 , BaCO_3 , CaO)

6.2 Soft or soda or window glass :

It is ordinary glass-obtained by the fusion of the following material :

(i) Na_2CO_3 (ii) CaCO_3 (iii) Silica SiO_2 (sand or quartz)

Solid mixture after fusion should be cooled slowly. The process is known as annealing.

1. **Soft glass :** It is a common glass. The raw materials are SiO_2 , CaCO_3 and Na_2CO_3 .
2. **Hard glass :** It is a potash glass. The raw material are SiO_2 , CaCO_3 and K_2CO_3 .
3. **Flint glass :** It is a lead potash glass. The raw materials are SiO_2 , red Pb, K_2CO_3 . It is used in making prism, lenses and optical glass.
4. **Crook's glass :** It is a optical glass containing CeO_2 which prevents the entry of UV rays.
5. **Pyrex 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.
6. **Silica or quartz glass :** It is made by pure silica. It does not break even when put in water in red hot state.
7. **Ground glass :** Soft glass is grounded by turpentine oil and emery.
8. **Reinforced glass :** It has a network of wires embedded in the glass itself. Hence it resists shocks and does not shatter easily.
9. **Laminated safety glass :** A layer of transparent plastic (vinyl acetate resin) between two layers of glass with the aid of suitable adhesive. It is used in making wind screen of automobiles. It breaks when subjected to heavy impact but particles are not harmful as they are plastic coated.

7. CEMENT :

- * J. Aspdin introduced cement for the first time in England.
- * It resembles with the famous Portland rock in England hence the name Portland cement was given.
- * Composition of Portland cement Lime, $\text{CaO} = 50-60\%$, Silica, $\text{SiO}_2 = 20-25\%$, Alumina, $\text{Al}_2\text{O}_3 = 5-10\%$, Ferric oxide, $\text{Fe}_2\text{O}_3 = 1-2\%$, Sulphur trioxide, $\text{SO}_3 = 1-2\%$, Magnesia $\text{MgO} = 2-3\%$ Sodium oxide $\text{Na}_2\text{O} = 1\%$, Potassium oxide $\text{K}_2\text{O} = 1\%$
- * For a good quality cement the ratio of the oxide should be maintained as : $[\% \text{SiO}_2] : [\% \text{Al}_2\text{O}_3] = 2.5 - 4.0$
 $[\% \text{CaO}] : [\% \text{SiO}_2 + \% \text{Al}_2\text{O}_3 + \% \text{Fe}_2\text{O}_3] = 1.9 - 2.1$

* **Raw materials :**

1. Lime stone [CaCO_3] \rightarrow it supplies CaO
2. Clay [$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$] \rightarrow it supplies SiO_2 , Al_2O_3 .
3. Gypsum, [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$] \rightarrow it decreases the setting time of cement.

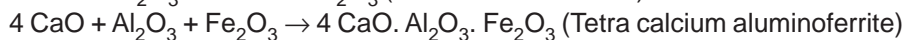
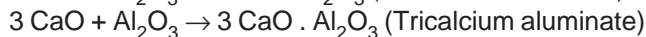
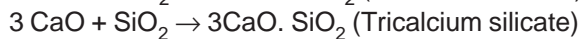
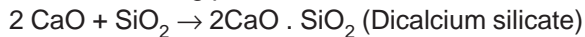
7.1 Preparation of Slurry :

* **Dry process :** When the raw materials i.e., lime stone and clay are hard dry process is used.

* **Wet process :** When the raw materials i.e., lime stone and clay are soft wet process is used.

* Burning of slurry in rotary kiln the maximum temperature zone is $1000\text{--}1500^\circ\text{C}$.

Reactions taking place in the kiln are :



The resulting product of kiln is known as cement clinker it is collected in the cooler part. Obviously the composition of cement clinker is : $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{Al}_2\text{O}_3$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$.

Mixing of cement clinker with gypsum :

Clinker is powdered and 2 – 3% gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is added to slow down the setting of cement. It assumes the form : $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ calcium sulphoaluminate.

Mortar : A mixture of Cement, sand [1 : 3] in water, used in binding bricks and plastering.

1. ELECTRONIC CONFIGURATION

The general outer electronic configuration of elements of VA group is ns^2np^3 . Hence these elements belong to p-block.

| Elements | Configuration |
|-------------------------------|--|
| Nitrogen [N ₇] | [He] 2s ² 2p ³ |
| Phosphorus [P ₁₅] | [Ne] 3s ² 3p ² |
| Arsenic [As ₃₃] | [Ar] 3d ¹⁰ 4s ² 4p ³ |
| Antimony [Sb ₅₁] | [Kr] 4d ¹⁰ 5s ² 5p ³ |
| Bismuth [Bi ₈₃] | [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ³ |

- * N and P are non metals.
- * As and Sb are metalloids. Bi is of -course metal.
- * Nitrogen constitutes about 78% by volume of the atmosphere (essential constituent of fertilizers, explosives and proteins)
- * Phosphorus occurs in bones, phosphate rocks. It is used as fertilizers.
- * As, Sb, Bi occur mostly as sulphides.
- * Bi is the end product of (4n + 1) radioactive series.
- * Elements of this group are called pnicogens.

2. CHEMICAL PROPERTIES :

2.1 Hydrides :

MH₃ type of hydride is formed :

| | | | | |
|-----------------|-----------------|------------------|------------------|------------------|
| NH ₃ | PH ₃ | AsH ₃ | SbH ₃ | BiH ₃ |
| Ammonia | Phosphine | Arsine | Stibine | Bismuthine |

- * Hydrides are formed by the action of water of dilute acids on compounds : Mg₃N₂, Ca₃P₂, Zn₃As₂, Mg₃Sb₂ and Mg₃Bi₂.
- * All hydrides are coloured gases.
- * NH₃ is highly soluble other hydrides are less soluble.
- * Poisonous nature increases from NH₃ to BiH₃

Ammonia ----- Bismuthine

| | |
|-----------------------------|---|
| Basic character decreases | → |
| Thermal stability decreases | → |
| Reducing nature increases | → |
| Dipole moment decreases | → |
| Bond angle decreases | → |

2.2 Oxides :

Elements of VA group form oxides of the type M₂O₃, M₂O₄ and M₂O₅.

Moving from :

L acidic nature of oxide decreases → R

Moving from

T acidic nature of oxide increases → B

2.3 Halides : Trihalides MX₃ and penta halides MX₅

Nitrogen does not form pentahalides due to absence of d-orbital.

Trihalide (MX₃) : All trihalides are stable except NCl₃, NBr₃ and NI₃.

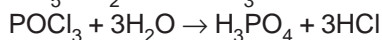
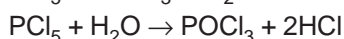
The reason assigned to unstable nature of NCl₃, NBr₃, NI₃ is :

- (i) Low polarity of N–X bond
- (ii) Large difference in the size of nitrogen and halogen atom.

Penta - Halides (MX₅) :

- * PCl₅, AsCl₅ and SbCl₅ are well known
- * Bi does not form penta halide due to inert pair effect.

- * The hybridized state of the central atom in liquid and gaseous state is $sp^3 d$ showing trigonal bipyramidal geometry.
- * X-ray analysis have shown that PCl_5 and PBr_5 exist as ionic compounds $[PCl_4]^+ [PCl_6]^-$ and $[PBr_4]^+ Br^-$.
- * PCl_5 undergoes thermal decomposition and also hydrolysed by water



- * PCl_5 acts as an effective chlorinating agent.

3. ANOMALOUS BEHAVIOUR OF NITROGEN :

The anomalous behaviour of nitrogen is due to :

- * Small size
- * High E.N. and high I.E.
- * Non availability of vacant d-orbital
- * Tendency to form multiple bond.

4. NITROGEN DIFFERS FROM OTHER ELEMENTS OF ITS OWN GROUP :

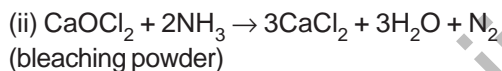
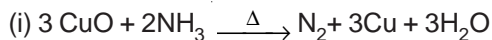
- * Nitrogen is a gas while other elements are solids
- * Nitrogen is diatomic, while other elements are tetraatomic [P_4 , As_4 , Sb_4]
- * Nitrogen can form N_3^- ion (due to small size and high E.N.)
- * Nitrogen is chemically inert under ordinary condition due to high dissociation energy of $N \equiv N$ bond.
- * Nitrogen shows oxidation state from -3 to $+5$
- * Hydride of nitrogen i.e. ammonia is stable and forms H-bonding.

5. NITROGEN :

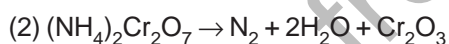
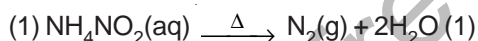
- * Nitrogen was discovered by Daniel Rutherford.
- * It occurs in the atmosphere to the extent of 78% by volume.
- * Nitrogen occurs in the combined form in various compounds KNO_3 , $NaNO_3$, NH_4Cl , $(NH_4)_2SO_4$ etc.

5.1. Preparation

(a) From ammonia and its compounds



(iv) Laboratory method :



(b) From air :

Nitrogen is prepared commercially from air by liquefaction and fractional distillation .

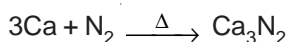
5.2 Properties :

Physical

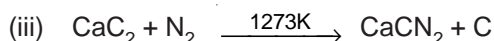
- * It is colourless, tasteless and odourless gas
- * It is highly soluble in water
- * Its m.p. is 63.2 K and b.p. is 77.2 K
- * It is absorbed by charcoal

Chemical : Few reactions of N_2 are

(i) Li, Mg, Ca, Al form nitrides



This reaction forms the basis for the manufacture of HNO_3 by **Birk land and Eyde process**.



calcium carbide calcium cyanamide

Since $CaCN_2$ gives ammonia when reacts with water. Therefore $[CaCN_2 + C]$ called nitrolium and it is used as fertilizer.

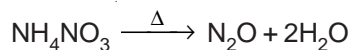
5.3 Uses :

- * Used for the manufacture of NH_3 , HNO_3 , CaCN_2 etc.
- * To provide inert atmosphere N_2 gas is used in metallurgical processes.
- * It is used in filling electric bulbs.

6. OXIDES OF NITROGEN :

(1) **Nitrous oxides [N_2O]**, O.S. (+1), laughing gas, colourless.

* **Preparation :**

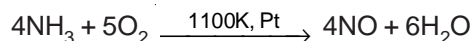


Resonance :



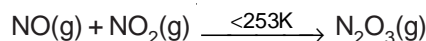
- * Special features : Oxide is neutral
 - * It acts as an anaesthetic agent.
- (2) **Nitric Oxide [NO]**, O.S. (+2) colourless gas.

* **Preparation**



(3) **Dinitrogen trioxide (N_2O_3)**, O.S. (+3), blue liquid (<253K)

* **Preparation :**



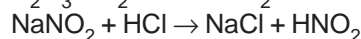
(4) **Nitrogen dioxide (NO_2)**, O.S. (+4) brown gas.

(5) **Dinitrogen pentoxide (N_2O_5)**, O.S. (+5), colourless gas

7. OXY-ACIDS OF NITROGEN :

Nitrous acid [HNO_2]

* **Preparation :**

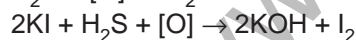
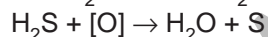


Properties

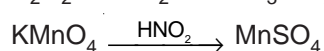
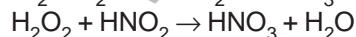
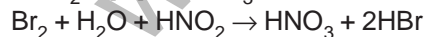
- * It is a weak acid and does not exist in free liquid state. In aqueous solution it is unstable and changes to HNO_3 .
 $3\text{HNO}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}$

- * It acts both as an oxidizing as well as reducing agent.

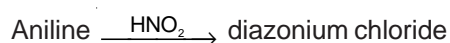
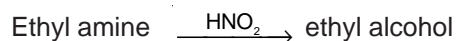
- * **Oxidizing properties :**



- * **Reducing properties :**



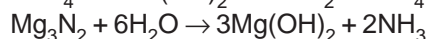
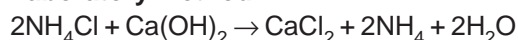
- * **Organic reactions :** Urea $\xrightarrow{\text{HNO}_2}$ N_2



8. AMMONIA [NH₃]

8.1 Preparation

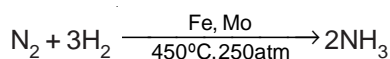
Laboratory method :



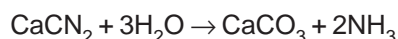
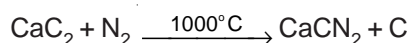
- * The gas is collected by downward displacement of air.
- * The gas is dried by CaO [P₂O₅, H₂SO₄ and CaCl₂ react with ammonia]

Manufactures :

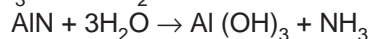
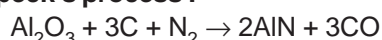
Haber Process :



Cyanamide process :



Serpeck's process :

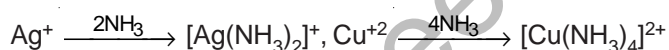
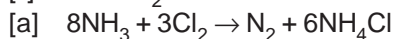
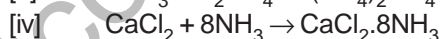
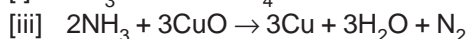
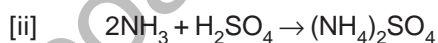
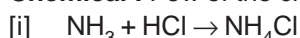


8.2 Properties :

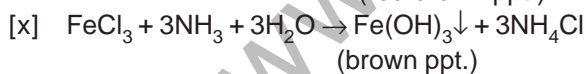
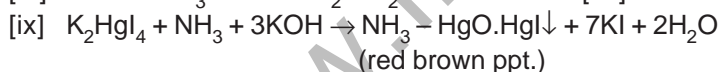
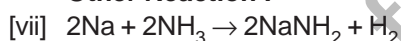
Physical

- * Lighter than air
- * Easily liquefied by cooling or compression
- * Highly soluble in water. The solution is alkaline
- * Forms H-bonding with water.
- * Turns litmus to blue [NH₃ + H₂O → NH₄⁺ + OH⁻]

Chemical : Few of the chemical reaction are :



Other Reaction :



8.3 Uses :

- * Due to lone pair of electrons it acts as a lewis base.
- * Preparation of fertilizers.
- * In making artificial silk.
- * As a laboratory reagent.
- * In refrigeration.
- * In making HNO₃, (NH₄)₂CO₃, Na₂CO₃ etc.

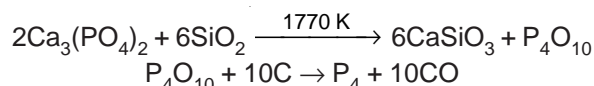
9. PHOSPHORUS :

Occurrence : Five important minerals of phosphorus are :

- * Phosphorite Ca₃(PO₄)₂
- * Fluorapatite 3Ca₃(PO₄)₂·CaF₂
- * Hydroxyapatite 3Ca₃(PO₄)₂·Ca(OH)₂
- * Chloroapatite 3Ca₃(PO₄)₂·CaCl₂

It is mainly present in bones and teeth which constituent about 58% calcium phosphate and also in animal cells (DNA).

Isolation : It is isolated by heating $\text{Ca}_3(\text{PO}_4)_2$ with coke and silica in an electric furnace.



10. PHOSPHORUS PENTOXIDE [P_4O_{10}]

It is formed by burning phosphorus in excess of air : $\text{P}_4 + 5\text{O}_2 \rightarrow \text{P}_4\text{O}_{10}$

Note : Since it is collected as snowy powder hence it is called

Flower of phosphorus.

Dissolution in cold water :



Dissolution in hot water :



11. OXY-ACIDS OF PHOSPHORUS :

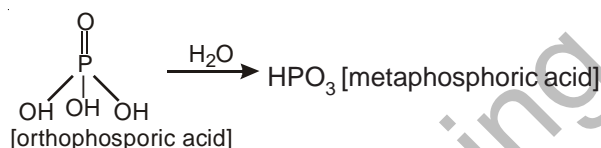
There are two series of oxyacids of phosphorus.

* Phosphorus acid series.

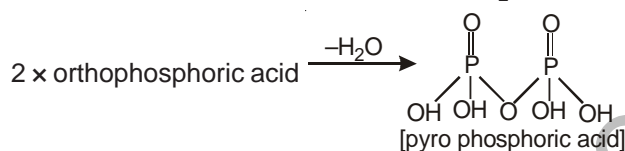
* Phosphoric acid series.

Three prefixes meta, pyro and hypo is used while naming the oxy acids of phosphorus.

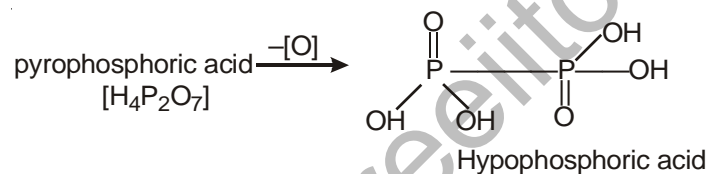
* Meta is used for acid obtained by loss of H_2O molecule from one acid molecule.



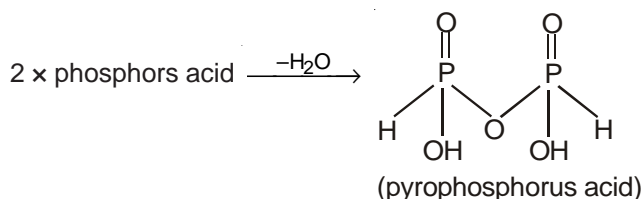
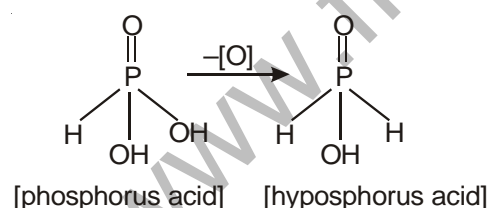
* Pyro is used for acid obtained by loss of H_2O molecule from two acid molecules



* Hypo is used for the acid having lower oxygen content than the parent acid.



Similarly :



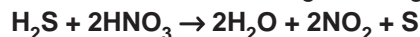
12. TYPICAL EXAMPLES :

[1] Three series of salts of H_3PO_4 are **NaH_2PO_4 , Na_2HPO_4 and Na_3PO_4 .**

[2] What is glacial phosphoric acid.

Metaphosphoric acid HPO_3

[3] Give one reaction showing oxidising property of HNO_3 .



[4] Thermally most stable oxide of nitrogen is :

NO

[5] Nature of oxides on moving from P to Bi

P_2O_6 (acidic), As_4O_6 and Sb_4O_6 (amphoteric) Bi_2O_3 (basic)

1. ELECTRONIC CONFIGURATION :

The general outer electronic configuration of VI A group is ns^2np^4 . Hence these elements belong to p-block

| Element | Configuration |
|-------------------------------|--|
| Oxygen [O ₈] | [He] 2s ² 2p ⁴ |
| Sulphur [S ₁₆] | [Ne] 3s ² 3p ⁴ |
| Selenium [Se ₃₄] | [Ar] 3d ¹⁰ 4s ² 4p ⁴ |
| Tellurium [Te ₅₂] | [Kr] 4d ¹⁰ 5s ² 5p ⁴ |
| Polonium [Po ₈₄] | [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴ |

- * O, S, Se, Te element are collectively called **chalcogens** (ore forming). Most of the metal ores are oxides or sulphides.
- * O, S, Se are non metals, Te is metalloid and Po is metal.
- * O resembles N and F. It forms strong $p\pi-p\pi$ bond. It also forms H-bond like N and F.
- * Oxygen, the most abundant element (21% is present in atmosphere, constitute 46.6% of earth's crust).
- * Sulphur constitute about 0.05% of earth's crust.
- * S, Se, Te can make use of d-orbital and show a covalency of six and can exhibit an octahedral geometry.
- * Polonium, the most metallic element is radioactive.

2. HYDRIDES OF GROUP 16 ELEMENTS :

- * Form hydrides of the formula H₂X [H₂O, H₂S, H₂Se, H₂Te and H₂Po]
- * Bond angle of hydrides decreases from H₂O to H₂Po
- * The volatility of hydrides increases from H₂O to H₂S then decrease. High b.p. of H₂O is due to the presence of intermolecular H-bonding.
- * The acidic strength increases from H₂O to H₂Te. This is due to increase of size of the anion in the group.
- * The thermal stability of hydrides increases in the order : H₂O > H₂S > H₂Se > H₂Te > H₂Po.
- * The covalent character of hydrides increases in going from O to Po.
- * H₂S, H₂Se, H₂Te and H₂Po burn in atmosphere of oxygen with blue flame forming dioxides e.g., $2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$
- * Except H₂O all hydrides of this group are reductant. This is due to weakening of M-H bond the bond length increase with increases of size of M-atom.
- * Except H₂O (liquid), all hydrides are gases at room temperature.

3. ANOMALOUS BEHAVIOUR OF OXYGEN :

The anomalous behaviour of oxygen is due to :

(a) Small size (b) High electronegativity and (c) absence of d-orbitals.

Point of difference are :

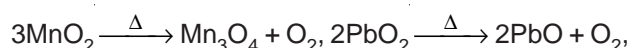
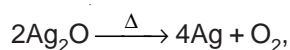
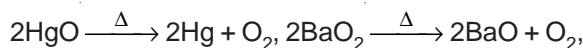
- [1] Oxygen is a gas while other elements are solids at ordinary temperature.
- [2] Oxygen is diatomic molecule while others are polyatomic (S, Se etc. are octaatomic ||).
- [3] Compounds of oxygen are more ionic than those of other elements.
- [4] Oxygen forms strong hydrogen bonds whereas other elements of this group form no H-bonding.
- [5] Oxygen is paramagnetic (molecular orbital theory) while other elements are diamagnetic.
- [6] Oxygen generally shows O.S. of -2, while other members exhibit o.s. of +2, +4, +6 in addition to -2.

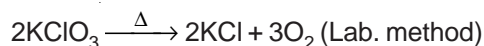
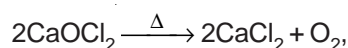
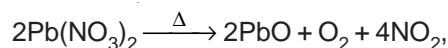
4. OXYGEN [PRIESTLY AND SCHEELE] :

- * Oxygen constitutes 21% by volume of the atmosphere (23% by mass)
- * It's abundance in earth's crust is 46%.
- * It is present to the extent of 89% by weight in water.

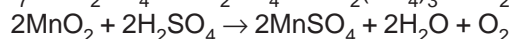
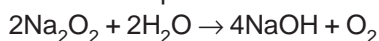
4.1 Preparations :

- [1] On heating suitable compounds such as oxides, Nb(NO₃)₂, CaOCl₂, KMnO₄ etc.





[2] Reaction of water or acid with certain suitable compounds :



4.2 Manufacture :

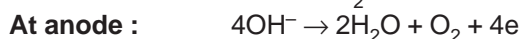
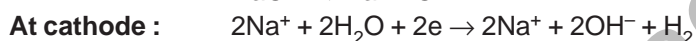
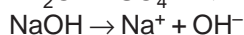
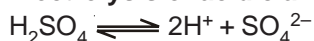
Oxygen is obtained on commercial scale by following methods.

[a] By Brin's process.

[b] From liquid air by fractional distillation (Claude's process)

[c] By electrolysis of acidic or alkaline water.

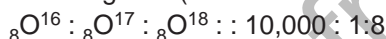
Electrolysis of acidic and alkaline water :



4.3 Properties :

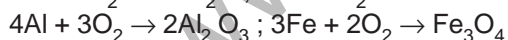
(a) Physical characteristic :

- * It is colourless, odourless and tasteless gas.
- * Slightly heavier than air.
- * Slightly soluble in water.
- * Boiling point is -183°C and Freezing point is -219°C .
- * Liquid oxygen is pale blue in colour.
- * Paramagnetic (on the basis of molecular orbital theory).

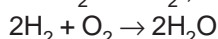


(b) Chemical characteristics : Important chemical properties of oxygen are given below :

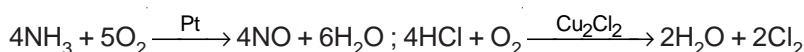
Reactions of Na, Ca, Al, Fe are :



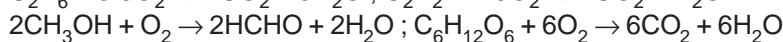
Reactions of C, P₄, S and H₂ :



Reactions of NH₃ and HCl :



Reactions of organic compounds :



4.4 Uses of oxygen :

- * It is used in artificial respiration ($\text{O}_2 + \text{He}$)
- * For the combustion process.
- * Liquid oxygen is used as a fuel in the rockets.

- * For oxyacetylene (3300°C) and oxyhydrogen (2800°C) flames, employed in cutting and welding purposes.
- * As an oxidant in several reactions.
- * In the preparation of several important oxides.

5. SULPHUR :

- * Constitute about 0.1% earth's crust.

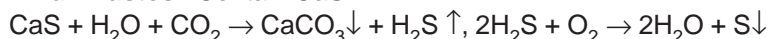
5.1 Extraction :

[a] Main source of sulphur are : Sicily and Louisiana the processes employed are called :

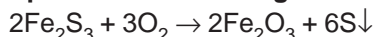
Sicilian process and Louisiana (or Frasch) process :

[b] Sulphur from alkali wastes, spent oxides of coal gas and iron pyrites :

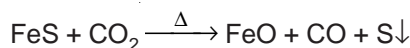
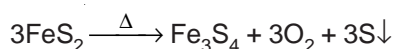
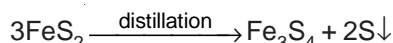
Alkali wastes : Contain CaS.



Spent oxides of coal gas : Contain Fe_2S_3



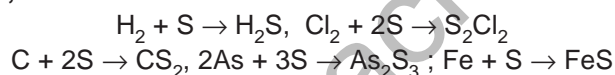
Iron pyrites :



Flowers of sulphur : In the purification process, vapours of boiling sulphur (444°C) are condensed on the cold walls of the vessel as a light yellow powder called flowers of sulphur.

5.2 Chemical characteristics :

Reactions with H_2 , Cl_2 , C, As the Fe :



Reaction with conc.. HNO_3 , conc. H_2SO_4 and NaOH



Reactions with K_2S : $\text{K}_2\text{S} + 4\text{S} \rightarrow \text{K}_2\text{S}_5$

5.3 Uses of sulphur :

- * In the manufacturer of SO_2 , H_2SO_4 , CS_2 , matches, gun powder.
- * Used for destroying bacteria, fungi, insects, etc.
- * Used for Vulcanizing rubber and in the manufacture of sulphur dyes.
- * Used in medicines.

6. OXIDES OF SULPHUR :

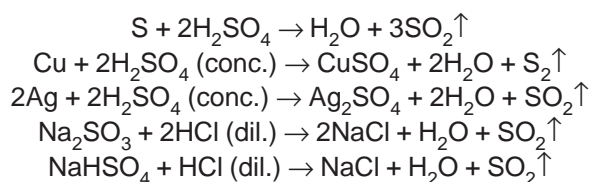
| Name | Formula | Nature |
|---------------------|------------------------|-------------------------|
| Sulphur suboxide | S_2O | Colourless gas |
| Sulphur monoxide | SO | Colourless gas |
| Sulphur sesquioxide | S_2O_3 | Green crystalline solid |
| Sulphur dioxide | SO_2 | Colourless gas |
| Sulphur trioxide | SO_3 | Volatile liquid |
| Sulphur heptoxide | S_2O_7 | Liquid |
| Sulphur tetroxide | SO_4 | White solid. |

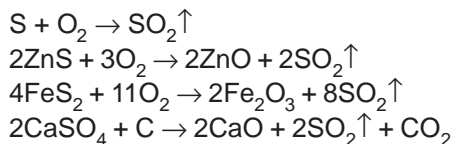
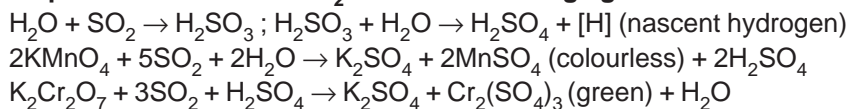
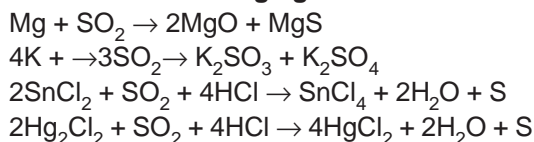
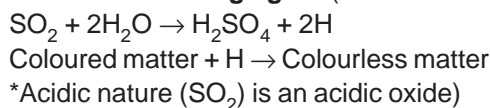
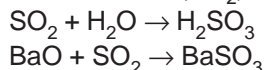
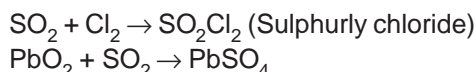
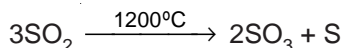
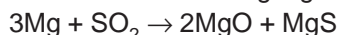
Here we shall discuss SO_2 and SO_3 being common and important.

7. SULPHUR DIOXIDE SO_2

7.1 Methods of preparation :

Laboratory methods :



Industrial method :**7.2 Chemical characteristics :*****Aqueous solutions of SO₂ acts as a reducing agent :*****Acts as an oxidising agent :***** Acts as bleaching agent (due to reducing nature)*****Acidic nature (SO₂) is an acidic oxide)*****Addition reaction :*****Thermal decomposition :*****Reaction with burning Mg :****7.4 Uses of SO₂**

- * Used in the manufacture of H₂SO₄, paper (from wood pulp)
- * Used as disinfectant, antechair, bleaching agent.
- * As a refrigerant (liquid SO₂)
- * Used in refining petroleum and sugar.

8. SULPHURIC ACID [H₂SO₄] :

- * It is a **king of chemicals**
- * It is also known as **oil of vitriol**.
- * The three step process for the preparation of H₂SO₄ is described as :

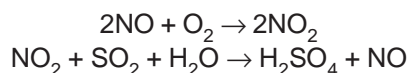
$$\text{S} \rightarrow \text{SO}_2 \rightarrow \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$$

8.1 Manufacture : [a] Lead chamber process [b] Contact process

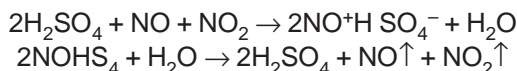
[a] Lead chamber process : Here oxidation of SO₂ is affected catalytically by means of oxides of nitrogen in the presence of water.



Mechanism may be described as :

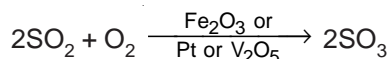


The unreacted gases (NO, NO₂, O₂ and N₂) are absorbed in H₂SO₄ and nitrosyl sulphuric acid. The product on decomposition gives H₂SO₄.

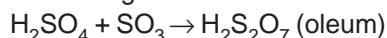


[b] Contact process :

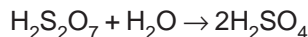
- * It involves the oxidation of SO_2 by air in presence of a catalyst



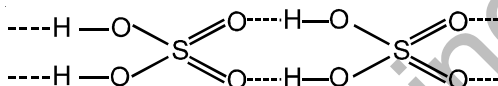
- * SO_3 is dissolved in 98% sulphuric acid resulting in the formation of oleum.



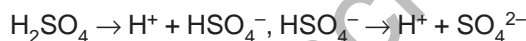
- * On dilution, H_2SO_4 of required concentration can be obtained.

**8.2 Properties :****Physical characteristics :**

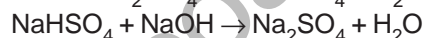
- * H_2SO_4 is colourless, only liquid.
- * Freezing point and boiling point are 10.5°C and 340°C respectively. Forms constant boiling mixture (at 370°C) containing 98.33% of the acid.
- * Density is 1.84 gm cm^{-3} .
- * Forms hydrate with the evolution of heat :
 $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ [monohydrate], $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ [dihydrate], $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ [tri hydrate]
- * Conductor of heat and electricity
- * High b.p. and viscosity of H_2SO_4 is due to H-bonding.

**Chemical characteristics :**

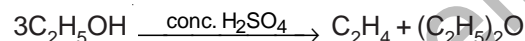
- * Acid character (dibasic acid)



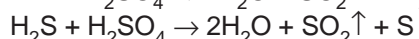
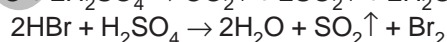
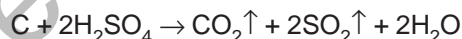
Forms two type of salts :



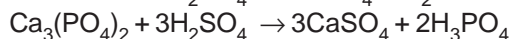
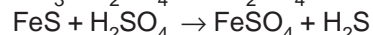
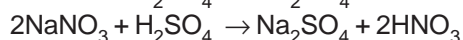
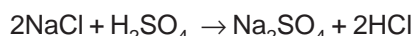
- * Dehydrating agent [due to high affinity for water]



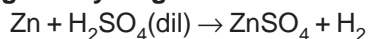
- * Acts as an oxidizing agent



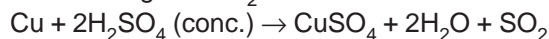
- * Displaces more volatile acids :



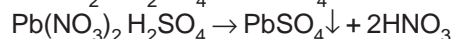
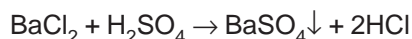
- * Reaction with metals : Zn, Mg, Fe gives hydrogen :



Cu gives SO_2 .



- * Formation of insoluble sulphates :



- * Reaction with PCl_5 and KClO_3 :



8.3 Uses of H_2SO_4 :

- * Used as a laboratory reagent.
- * Used in the manufacture of acids (HNO_3 , HCl , H_3PO_4), dyes, drugs, disinfectants, alum, ferrous sulfate for ink etc.
- * Used as a dehydrating and oxidizing agents.
- * Used in the textile, paper and dyeing industries.
- * Used in leather industry for tanning.
- * Used in the refining of petroleum.
- * Used in the manufacture of explosives such as nitroglycerine gun coating, TNT, picric acid acid.
- * Used in lead storage batteries.
- * Used for cleansing metals before electroplating, enameling, galvanizing etc.

9. TYPICAL EXAMPLE :

[i] Number of water of crystallization associated with $Na_2S_2O_3$ are :

Five

[ii] Catalyst used in lead chamber process for the manufacture of H_2SO_4 is :

NO

[iii] Of the two processes for the manufacture of H_2SO_4 which one is cheaper.

Contact process

[iv] Give two example of amphoteric oxide **Al_2O_3 , ZnO** .

Halogen Family

1. ELECTRONIC CONFIGURATION :

The general outer electronic configuration of elements of VII group is ns^2np^5 . Hence these elements belong to p-block.

| Element | Configuration |
|------------------------------|-------------------------------|
| Fluorine [F ₉] | [He] $2s^22p^5$ |
| Chlorine [Cl ₁₇] | [Ne] $3s^23p^5$ |
| Bromine [Br ₃₅] | [Ar] $3d^{10}4s^24p^5$ |
| Iodine [I ₅₃] | [Kr] $4d^{10}5s^25p^5$ |
| Astatine [At ₈₅] | [Xe] $4f^{14}5d^{10}6s^26p^5$ |

- * First four member F, Cl, Br and I are called halogens as their salts are present in sea water.
- * At is radioactive, artificially prepared and unstable.
- * Strong tendency to accept one electron to acquire stable inert gas configuration. Hence exhibit nonmetallic behaviour.
- * High electronegativity makes them very reactive and here they are not available in free state.
- * Except At, the members are found in combined state in suitable quantities in nature.

2. GENERAL PHYSICAL PROPERTIES :

[a] Physical state :

| F | Cl | Br | I |
|-----|-----|---------------|----------------|
| Gas | Gas | Fuming liquid | Volatile solid |

[b] Colour : Halogens are coloured

| F | Cl | Br | I |
|-------------|-----------------|---------------|-------------|
| Pale yellow | Greenish yellow | Reddish brown | Deep violet |

The molecules absorb visible region of light for excitation of outer electrons to higher energy levels.

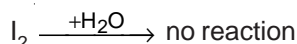
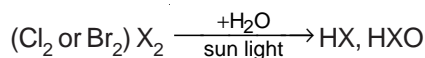
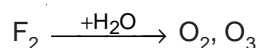
| | | | | |
|----------|---|------------------------|---|---------------------|
| Fluorine | – | [Absorbs violet light] | → | Appears pale yellow |
| Iodine | – | [Absorbs yellow light] | ⇒ | Appears violet |

3. CHEMICAL CHARACTERISTICS :

Halogens are most reactive due to :

- [i] Low bond dissociation energy.
- [ii] High electron affinities

In halogen F_2 is the most reactive I_2 is least reactive Reaction with water :



Reaction with metals and nonmetals :

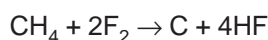
- * F_2 combines with metals to give fluorides.
- * Cl_2 , combines with large number of metals. The reaction is slow.
- * Br_2 and F_2 do not react with noble and less active metals.

Examples : CuF_2 , NaF , KI , $NaCl$, $NaBr$, $MgCl_2$

- * X_2 combines with nonmetals like S, P, As etc.

Reaction with hydrocarbons :

- * F_2 decomposes hydrocarbons

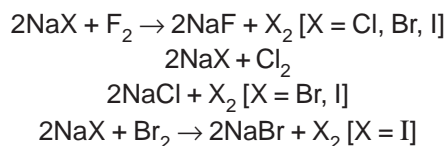


Cl_2 and Br_2 gives substitution reaction. $CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl, CH_2Cl_2, CHCl_3, CCl_4$

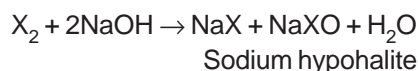
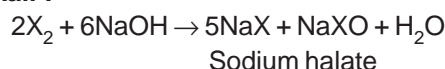
- * I_2 has practically no action on hydrocarbons.

Halogen displacement reaction :

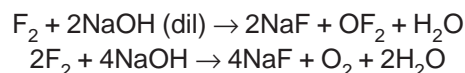
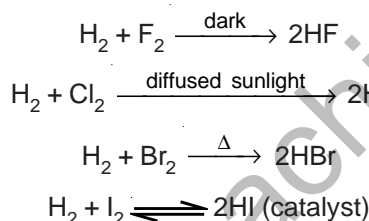
- * Fluorine replaces (Cl, Br, I)
- * Chlorine replaces (Br, I)

**Reaction with alkalines :**

Cl_2 , Br_2 and I_2 behave similarly when treated with alkali (It is a disproportionation reaction)

Cold and dilute alkali :**Hot and concentrated alkali :**

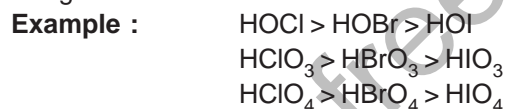
F_2 behaves differently with alkalis :

**Reaction with hydrogen :****4. OXY-ACIDS OF HALOGENS :**

- * F forms only one oxy acid HOF (hypofluorous acid)
- * Cl, Br and I form four series of acids.

Acid-character :

- * The acid – character of the oxy acids of same halogen increases with the increase in the oxidation number of the halogen.

**Oxidising power :**

Oxidizing power of the oxy acids of same halogen decreases with the increase of O.S. of halogen.

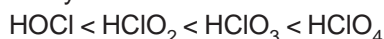


The order of oxidizing power of perhalic acid (or their salts)

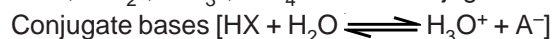
follows the order :



Thermal stability : Thermal stability of oxyacid of chlorine follows the order :

**Stability of conjugate bases :**

ClO^- , ClO_2^- , ClO_3^- , ClO_4^- are the conjugate bases of the acids HClO , HClO_2 , HClO_3 and HClO_4 .



The stability of conjugate bases of oxy acids increases with the increase in the number of oxygen atoms in the anion thus : $\text{ClO}^- < \text{ClO}_2^- < \text{ClO}_3^- < \text{ClO}_4^-$

5. ANOMALOUS BEHAVIOUR OF FLUORINE :

Anomalous behaviour of Fluorine is due to :

- Small size, – high electronegativity
- Non – availability of d-orbital, –low dissociation energy
- Highest positive reduction potential.

Main points of differences are :

- * Fluorine shows only -1 oxidation state.
- * Fluorine exhibits one as its covalency.
- * Fluorine forms inter and intramolecular H-bonding.
- * HF is weak acid as compared to HCl, HBr and HI.
- * Fluorine forms two series of salts $[\text{NaHF}_2 \text{ and } \text{Na}_2\text{F}_2]$
- * AgF is soluble in water while AgCl, AgBr and AgI are insoluble.
- * Fluorine form two series of salts $[\text{NaHF}_2 \text{ and } \text{Na}_2\text{F}_2]$
- * AgF is soluble in water while AgCl, AgBr and AgI are insoluble.
- * Fluorine does not forms oxy acids while oxy acids of other halogens are well known (HClO_3 , HBrO , HiO_4 etc.)
- * Fluorine is most reactive amongst halogens (due to low F-F energy).
- * Fluorine forms SF_6 whereas no other halogens forms SX_6 .
- * CaF_2 is insoluble in water whereas CaCl_2 , CaBr_2 and CaI_2 are soluble.
- * Fluorides are more stable than other halides UF_6 is more stable than UCl_6 . NF_3 is stable while NCl_3 is unstable and explosive. SF_6 is stable SCl_6 is unstable.
- * Fluorine directly combines with carbon whereas other halogens do not.
- * $[\text{F}_2 + \text{H}_2\text{O}]$ gives oxone while other halogens do not give oxone.
- * F^- has more complex forming tendency as compared to other halides ions. $[(\text{AlF}_6)^{3-}, (\text{FeF}_6)^{3-}]$
- * Fluorine does not form poly halide ion like I_3^- , Br_3^- etc.

6. FLUORINE :

6.1 Occurrence :

Fluorine is very reactive and hence it does not occur in free state. In combined state it occurs as :

- * Fluorspar $[\text{CaF}_2]$
- * Cryolite $[\text{Na}_3\text{AlF}_6]$
- * Fluorapatite $[\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2]$

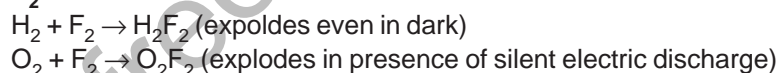
Fluorine occurs in small quantities in plant, teeth, bones, sea water etc.

6.2 Reaction of F_2 are :

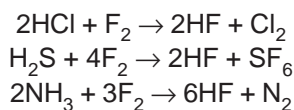
Directly combines with metals and non metals



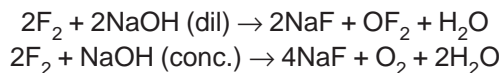
Reaction with H_2 , O_2 :



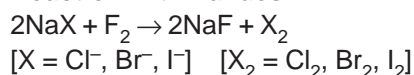
Reaction with HCl, H_2S and NH_3 :



Reaction with NaOH :



Reaction with halides :



- * Reacts with water to give O_2 and O_3
- * Reacts with other halogens to form inter halogen compounds $[\text{ClF}, \text{ClF}_3, \text{IF}_3, \text{IF}_7 \text{ etc.}]$
- * Reacts with CH_4 explosively to give CH_3F , F , CH_2F_2 , CHF_3 and CF_4 .

6.3 Uses :

- [1] Fluorides are used as insecticides (CaF_2 is added to tooth paste)
- [2] Sodium and antimony fluorides are used as mordants in dyeing industry.
- [3] Freons (poly chloro fluoro alkanes) are used in refrigeration and air conditioning.
- [4] Br_2 and HF are used as catalyst in petroleum industry.
- [5] CuF_2 is used in ceramic industry.

- [6] Teflon (C_2F_4) is polymer used as insulating material in cables.
 [7] For the separation of U^{235} from natural uranium, UF_6 is used.
 [8] Na_3AlF_6 and CaF_2 are used for the extraction of aluminium.
 [9] Sodium fluoro acetate is used as rat poison.

7. CHLORINE :

7.1 Occurrence :

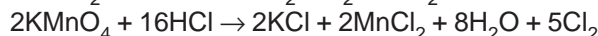
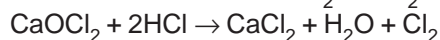
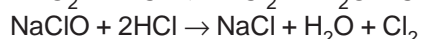
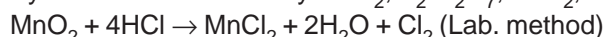
It is widely distributed in the form of chlorides. NaCl is the most important chloride occurs in sea water, lakes and in rocks.

Chloride mineral are :

- * Rock salt [NaCl] . Sylvine (KCl)
- * Carnallite [$KCl \cdot MgCl_2 \cdot 6H_2O$]
- * Horn silver [AgCl]

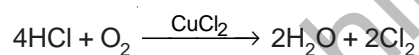
7.2 Preparation :

- [1] By the oxidation of HCl by MnO_2 , $K_2Cr_2O_7$, PbO_2 , $KMnO_4$, $CaOCl_2$, NaClO etc.



- [2] Commercial methods :

- [a] [Decon's process] Air oxidation of hydrochloric acid in presence of copper (II) chloride catalyst.



- [b] By the electrolysis of aqueous NaCl solution :

At anode Cl_2 is liberated

At cathode H_2 is liberated

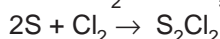
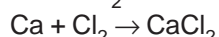
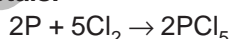
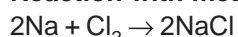
(Caster – Kellner and Nelson cell)

7.3 Properties : Physical characteristics :

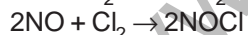
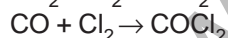
- * Cl_2 is greenish yellow gas.
- * Cl_2 is poisonous having a suffocating odour.
- * Cl_2 is soluble in water and carbon disulphide.
- * Cl_2 is 2.5 times heavier than air.

Chemical characteristics :

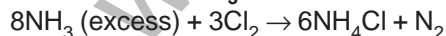
Reaction with metals and nonmetals.



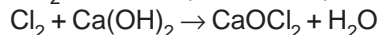
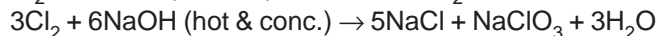
Reaction with SO_2 , CO and NO



Reaction with NH_3 :



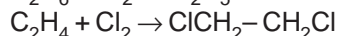
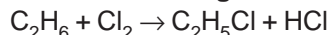
Reaction with NaOH and $Ca(OH)_2$:



Reaction of F_2 , Br_2 , and I_2 : The compounds obtained are :

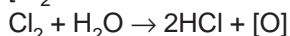
ClF , $BrCl$ and ICl_3

Reaction with organic compounds :

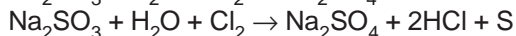
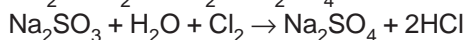
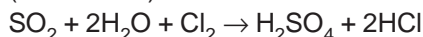
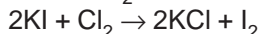
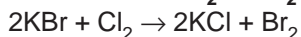


Oxidizing and bleaching action of Cl₂ :

[Cl₂ on reaction with water liberates nascent oxygen. Hence it is a powerful oxidant.]



(Permanent) Coloured substance + [O] → Colourless substance other reactions :

**Liberation of Br₂ and I₂ from KBr and KI****7.4 Uses of chlorine :**

- [1] Used in the manufacture of bleaching powder, hydrochloric acid, hypochlorites, chlorates, CHCl₃, CCl₄, DDT, Phosgene, mustard gas etc.
- [2] Used in the purification of drinking water.
- [3] Used in extraction of Au and Pt.
- [4] Used as a bleaching agent for cotton fabrics, paper and rayon.
- [5] Used as a germicide and disinfectant.
- [6] Used as an oxidant.

8. BROMINE**8.1 Occurrence :**

Bromine occurs in the combined state as bromides of Na, K and Mg. It was discovered by Ballard (1826). It is present in :

Carnalite :

Mother liquor of carnallite contains bromo carnallite KBr·MgBr₂·6H₂O.

Sea water and mineral springs : Contain NaBr, MgBr₂

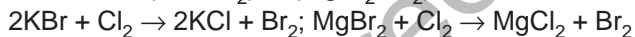
Bromargyrite : AgBr

8.2 Preparation**Laboratory method :**

Reactants : KBr, MnO₂ and conc. H₂SO₄.

**Liberation of Br₂ Using Cl₂ gas :**

Reactants : (KBr, Cl₂) or (MgBr₂, Cl₂)

**Commercial method :****[a] From carnallite [KCl·MgCl₂·6H₂O]**

Mother liquor left after the separation of crystals of KCl and MgCl₂ contains 0.25% MgBr₂ (bittern). This on treating with Cl₂ gas Br₂ is liberated.

[b] From sea water :

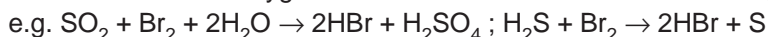
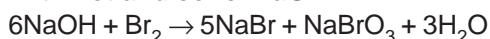
Sea water contains 0.006% (by weight) of bromine as MgBr₂. Here also Br₂ can be obtained by passing chlorine gas.

8.3 Properties : Physical characteristics

- * It is dark-red, poisonous liquid gives brown-red fumes.
- * Boiling point is 59.5°C, Freezing point is -7.2°C.
- * Sparingly soluble in water and is soluble in CCl₄, CS₂, CHCl₃ etc.

Chemical characteristics :

Due to liberation of oxygen it can act as an oxidant and **bleaching agent**.

**Reaction with NH₃ :****With cold and dil. NaOH :****With hot and conc. NaOH :**

8.4 Uses of bromine :

- [1] Used in the form of AgBr as coating on photographic plates, films etc.
- [2] Used in the manufacture of KBr, NaBr (used as a sedative in medicine).
- [3] Used to prepare 1, 2 dibromoethane which is employed with TEL as an antiknock compound in gasoline.
- [4] Used as an oxidant in organic synthesis.

9. IODINE

9.1 Occurrences : Chief sources of iodine are :

- [i] **Sea Weeds :** Contain 0.5% of iodine in the form of iodides.
- [ii] **Caliche or crude chile saltpetre :** Contains 0.2% of sodium iodate.

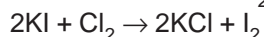
9.2 Preparation :

Laboratory method :

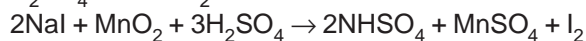
Reactants : KI, MnO₂ and conc. H₂SO₄, $2KI + MnO_2 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2$

Liberation of I₂ using Cl₂ gas :

Reactants : KI and Cl₂

**Commercial methods :**

From sea weeds : Dry weeds are carefully burnt in shallow pits. The residue called **kelp** is treated with conc. H₂SO₄ and MnO₂

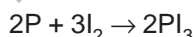
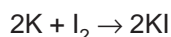
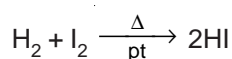


From caliche or crude chile salt peter : It contains 0.2% sodium iodate (NaIO₃). After removal of NaNO₃ from caliche, the mother liquor contains NaIO₃. It is treated with calculated quantity of sodium bisulphate to obtain iodine.

**9.3 Properties : Physical characteristics :**

- * Iodine is a dark violet shining solid.
- * Sublimes below its melting point (114°C) giving violet vapours.
- * Iodine is sparingly soluble in water. In presence of KI, the solubility of iodine increases due to the formation of triiodide ion $I^- + I_2 \rightleftharpoons I_3^-$.
- * Iodine is soluble in organic solvents such as CHCl₃, CCl₄, CS₂ etc.
- * Its vapours are pungent and poisonous to inhale.
- * At high temperature the equilibrium is maintained between molecular and atomic form $I_2 \xrightleftharpoons[1700^\circ C]{} I + I$.

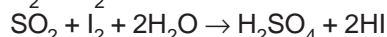
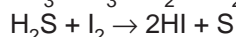
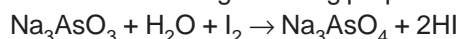
Chemical characteristics : Less reactive as compared to Cl₂ and Br₂.

Reaction with H₂ and non-metals :

Reaction with NaOH : Iodine with cold and dil. NaOH gives sodium hypoiodite (NaOI). With concentrated NaOH iodide (NaI) and iodate (NaIO₃) are formed.

Reaction with sodium tetrathionate :

Reactions showing oxidising properties (It is a weak oxidant)

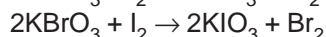
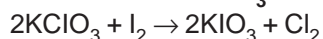


Reaction showing basic character : It shows basic properties and forms I⁻ and I³⁺ ions.

Formation of ICl, ICN, INO₂ etc. shows the presence of I⁺

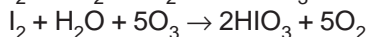
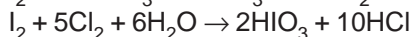


Formation of I(CH₃COO)₃ and IPO₄ etc show the presence of I³⁺.

Reaction with KClO₃ and KBrO₃ :

Iodine does not liberate Cl_2 and Br_2 from the corresponding chloride and bromide respectively.

Reaction with strong oxidants :



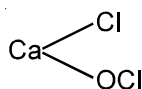
Reaction with starch : Iodine turns starch solution blue.

9.4 Uses of iodine :

- [i] Used in the preparation of iodoform, iodides, dyes etc.
- [ii] Used as a laboratory reagent.
- [iii] Used in making medicines such as iodex, tincture iodine.
- [iv] Solution of I_2 in KI is used in the treatment of goitre.
- [v] Used in making photosensitive papers, films etc.

10. BLEACHING POWDER [CaCOCl_2] :

- * It is a mixed salt called calcium chloro hypochlorite.
- * Proton of HCl and HOCl are cumulatively replaced by calcium [2H^+ by one Ca^{2+}]

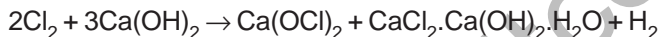
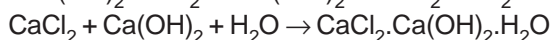
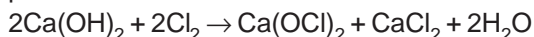


- * In fact, bleaching power is a mixture of calcium hypochlorite $\text{Ca}(\text{OCl})_2 \cdot 4\text{H}_2\text{O}$ and basic calcium chloride $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$

10.1 Manufacture :

There are two plants used in the manufacture of bleaching powder. **Hasenclever's plant and Backmann's Plant (Modern process)**

Basic reaction : When slaked lime [$\text{Ca}(\text{OH})_2$] is treated with chlorine at 40°C results in the formation of bleaching powder.



Bleaching powder is : $[\text{Ca}(\text{OCl})_2 + \text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}]$

10.2 Properties :

Physical characteristics :

- * Bleaching powder is a pale yellow in colour having a strong odour of chlorine.
- * Soluble in water but clear solution cannot be obtained due to the presence of $\text{Ca}(\text{OH})_2$.
- * It ionises as : $\text{CaOCl}_2 \rightarrow \text{Ca}^{2+} + \text{Cl}^- + \text{OCl}^-$

Chemical characteristics :

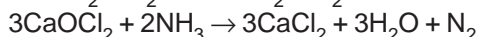
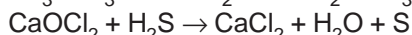
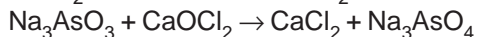
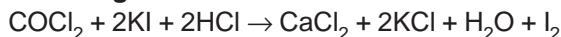
Oxidizing and bleaching action :

It loses its oxygen when treated with dilute acid.



The oxidizing and bleaching action of bleaching powder is due to the formation of nascent oxygen.

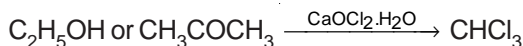
Oxidizing action :



Bleaching action :

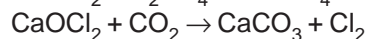
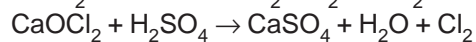
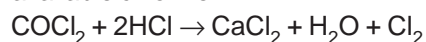
Coloured matter + $[\text{O}] \rightarrow$ Colourless matter

Reaction with ethylalcohol and acetone :

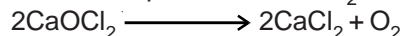


Reaction with dilute acids or acids or CO_2 (available chlorine) :

The chlorine obtained from a sample of bleaching powder by treatment with excess of dilute acids or CO_2 is called available chlorine :



Reaction in presence of CaCl_2



10.3 Uses of bleaching powder :

- [i] Used in the sterilization of drinking water (disinfectant and germicide)
- [ii] Used as bleaching agent for cotton, linen and wood pulp.
- [iii] Used for the commercial preparation of chloroform.
- [iv] Used as an oxidizing agent in industry.

11. EXAMPLE :

- [1] Evidence for the existence of unipositive ion I^+ is :

Molten iodine monochloride conducts electricity

- [2] Reaction : $4\text{KClO}_3 \rightarrow \text{KCl} + 3\text{KClO}_4$ represents :

Disproportionation

- [3] Shapes of chlorate (ClO_3^-) and perchlorate (ClO_4^-) ions respectively are :

Pyramidal and tetrahedral

- [4] which hydracid of halogens forms two series of salts.

HF (NaHF₂ and NaF)

- [5] In the reaction : $\text{Ca}(\text{OH})_2 + \text{Cl}_2 \rightarrow \text{-----} + \text{H}_2\text{O}$ the unknown compound is :

Bleaching powder (CaOCl₂)

- [6] The stability oxy halide anion is :

$\text{ClO}^- < \text{ClO}_2^- < \text{ClO}_3^- < \text{ClO}_4^-$

- [7] The oxidising power of oxy acids is :

$\text{HClO} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$

- [8] I_2 is liberated from HI by the halogens :

F_2, Cl_2 and Br_2

$2\text{HI} + \text{F}_2 (\text{Cl}_2, \text{Br}_2) \rightarrow 2\text{HF} (\text{HCl}, \text{HBr}) + \text{I}_2$

- [9] Which silver halide is insoluble in ammonia

AgI

- [10] HBr and HI cannot be prepared by treating corresponding bromide and iodide with H_2SO_4 .

HBr and HI are strong reductants and reduce H_2SO_4 to SO_2 and get themselves oxidized to Br_2 and I_2 respectively.

Noble Gases (zero group)

1. PRELUDE :

- * Zero group of group-18 contains six gaseous elements He, Ne, Ar, Kr, Xe and Rn.
- * First five elements are present in small quantities in atmosphere and as such called rare gas.
- * Radon is obtained by the disintegration of radium and is radioactive.
- * Due to stable outer configuration of s^2p^6 (octet) these gases exhibit inert character and are called inert gases.
- * Under specific conditions, these gases can form compounds [XeF_2 , XeF_4 etc.]. These gases are referred as noble gases,

Electronic configuration of noble gases :

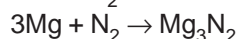
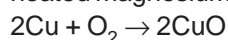
| Element | Electronic Configuration |
|------------------------------|--|
| Helium [He_2] | $1s^2$ |
| Neon [Ne_{10}] | $[\text{He}] 2s^2, 2p^6$ |
| Argon [Ar_{18}] | $[\text{Ne}] 3s^2, 3p^6$ |
| Krypton [Kr_{36}] | $[\text{Ar}] 3d^{10}, 4s^2, 4p^6$ |
| Xenon [Xe_{54}] | $[\text{Kr}] 3d^{10}, 5s^2, 5p^6$ |
| Radon [Rn_{86}] | $[\text{Xe}] 4f^{14}, 5d^{10}, 6s^2, 6p^6$ |

- * These elements occupy position between most electronegative (halogens) and the most electropositive (alkali metals) elements. Thus zero group elements are neither electropositive nor electronegative in nature.
- * Helium has stable s^2 (duplex) configuration. Because of duplex and octet configuration they show zero valency.

2. DISCOVERY OF NOBLE GASES :

* Ramsay and Rayleigh [1894] [Argon] :

It was found that the density of atmospheric nitrogen was 0.5% higher than that obtained by chemical methods. They isolated this gas from air by passing over heated copper to remove oxygen and then nitrogen by passing over heated magnesium.



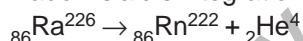
The vapour density and atomic weight of the gas was found to be 20 and 40 respectively. The gas was named Argon.

* Ramsay and Travers [1898] [Helium, Neon, Krypton and Xenon]

They carried out fractional distillation of liquid argon under reduced pressure. From the first fraction they isolated **Helium** and **Neon**. By further fractional distillation they had isolated **Krypton** and **Xenon**.

* Dorn [1900] [Radon]

Radon is a disintegration product of radium.



- * **Jansen** ascertained the presence of helium in the sun by spectroscopic analysis.

3. ISOLATION :

There are two methods employed to isolate noble gases commercially.

[1] Fractional distillation of liquid air :

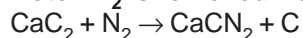
Since the noble gases have the boiling points quite far apart. Hence fractional distillation is easily employed.

Claude's apparatus : This is used for the manufacture of liquid O_2 and N_2 where noble gases are obtained as by-products.

First fraction : [He, N_2]

The mixture of gases is passed through a spiral cooled in liquid nitrogen. In this process most of the nitrogen condenses while He and Ne passes out. This mixture is cooled in a rectifying column (low temperature containing liquid H_2) where neon solidifies. Helium still remains in the gaseous state escapes out.

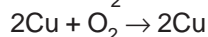
Note : N_2 is removed from He by CaC_2



Second fraction : [Ar, O_2]

Mixture of Ar and O_2 is passed through spiral tube cooled by liquid nitrogen. In this process most of the oxygen is liquefied and argon with a little bit of oxygen escapes out.

Note : O_2 is removed from Ar by heated Cu



Third fraction [Kr, Xe]

This fraction is evaporated whereby the residual liquid becomes richer in Kr and Xe. The separation of Kr and Xe is then becomes easier as they have wide difference in their boiling points.

4. USES OF NOBLE GASES :**Helium :**

- [i] Used in balloons and airships as it is light and non-inflammable.
- [ii] Used in creating inert atmosphere in metallurgy and welding metals.
- [iii] Used in filling tungsten lamps required for signaling.
- [iv] A mixture of He and O₂ is used for respiration by divers in deep sea. Since He is much less soluble in the blood than nitrogen at high pressure.
- [v] Used for filling vacuum tubes and radio tubes.
- [vi] Used for producing low temperature (–269°C)

Neon :

- [i] Neon lamps are used in green houses as it is effective in the growth of chlorophyll.
- [ii] Neon lamps are used in botanical gardens.
- [iii] Neon lights are visible in fog and mist and therefore neon lights are used for making signals in night for pilots.
- [iv] Neon is also used in discharge tubes required for decorative and advertising purpose.

Argon :

- [i] Used for creating inert atmosphere for welding.
- [ii] Ar plus He mixture is used for signal electrical device.
- [iii] Ar plus Ne are used in filling fluorescent tubes, radio-valves etc.
- [iv] Used in bulbs to enhance the life of filament.

Krypton and Xenon : Used in filling up bulbs containing incandescent filaments.

Radon : [i] Used in radio therapy of cancer.

[ii] Used to check the defects in steel sheets.

5. EXAMPLES :

- [1] Who obtained an inactive gas by heating the mineral clayate with dil. H₂SO₄.

Hilbrand

- [2] How the discovery of rare gases has affected the theoretical development of chemistry give two evidences.

[i] **Periodic table** [Rare gases have been placed between alkali metals (most electronegative).

[ii] **Discovery of isotopes** : Neon isotopes were first to be separated.

- [3] Asthma patient use for respiration a mixture of :

Helium + Oxygen

- [4] Maximum heat of vaporizations associated with inert gas

Xenon

- [5] $\text{Xe} + \text{O}_2\text{F}_2 \xrightarrow{-178^\circ\text{C}} \dots\dots\dots + \text{O}_2$

the unknown product is : **XeF₂**

- [6] Formula of xenon oxy – tetra fluoride is

XeOF₄

P-block

ns²-np⁶

18

He
2

13

14

15

16

17

B
5

C
6

N
7

O
8

F
9

Ne
10

Al
13

Si
14

P
15

S
16

Cl
17

Ar
18

Ga

Ge

As

Se

Br
35

Kr

In

Sn

Sb

Te

I
53

Xe

Tl

Pb
82

Bi

Po

At

Rn