The p-Block Elements

7

Nitrogen Family

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] $2s^22p^3$
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] $4f^{14}5d^{10}6s^26p^3$

* 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.

CHEMICAL PROPERTIES :

1. Hydrides :

MH_3 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 : Mg_3N_2, Ca_3P_2, Zn_3As_2, Mg_3Sb_2 and Mg_3Bi_2.

* All hydrides are coloured gases.

* NH_3 is highly soluble other hydrides are less soluble.

* Poisonous nature increases from NH_3 to BiH_3

Ammonia ----------------------------Bismuthine

$\xrightarrow{\text{Basic character decreases}}$

$\xrightarrow{\text{Thermal stability decreases}}$

$\xrightarrow{\text{Reducing nature increases}}$

$\xrightarrow{\text{Dipole moment decreases}}$

$\xrightarrow{\text{Bond angle decreases}}$

2. Oxides :

Elements of VA group form oxides of the type M_2O_3, M_2O_4 and M_2O_5.

Moving from :

$$L \xrightarrow{\text{acidic nature of oxide decreases}} R$$

Moving from

$$T \xrightarrow{\text{acidic nature of oxide increases}} B$$

3. Halides : Trihalides MX_3 and penta halides MX_5

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

Trihalide (MX_3) : All trihalides are stable except NCl_3, NBr_3 and NI_3.

The reason assigned to unstable nature of NCl_3, NBr_3, NI_3 is :

(i) Low polarity of N–X bond

(ii) Large difference in the size of nitrogen and halogen atom.

Penta - Halides (MX_5) :

* PCl_5, $AsCl_5$ and $SbCl_5$ 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^3d 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

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$

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

* PCl_5 acts as an effective chlorinating agent.

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.

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 tetratomic [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≡N bond.

* Nitrogen shows oxidation state from –3 to +5

* Hydride of nitrogen i.e. ammonia is stable and forms H-bonding.

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.

1. Preparation

(a) From ammonia and its compounds

(i) $3CuO + 2NH_3 \xrightarrow{\Delta} N_2 + 3Cu + 3H_2O$

(ii) $CaOCl_2 + 2NH_3 \rightarrow 3CaCl_2 + 3H_2O + N_2$ (bleaching powder)

(iii) $2NH_3 + 3Cl_2 \rightarrow 6HCl + N_2$

(iv) Laboratory method :

(1) $NH_4NO_2(aq) \xrightarrow{\Delta} N_2(g) + 2H_2O\ (1)$

(2) $(NH_4)_2Cr_2O_7 \rightarrow N_2 + 2H_2O + Cr_2O_3$

(b) From air :

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

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

$3Ca + N_2 \xrightarrow{\Delta} Ca_3N_2$

(ii) $N_2 + O_2 \rightleftharpoons 2NO$ (electric arc)

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

(iii) $\underset{\text{calcium carbide}}{CaC_2} + N_2 \xrightarrow{1273K} \underset{\text{calcium cyanamide}}{CaCN_2} + C$

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

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.

OXIDES OF NITROGEN :

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

- **Preparation :**

$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

Resonance :

$:N \equiv \overset{+}{N} - \underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}: \leftrightarrow :\underset{\cdot\cdot}{\overset{-}{N}} = \overset{+}{N} = \ddot{O}:$

- Special features : Oxide is neutral
- It acts as an anaesthetic agent.

2. **Nitric Oxide [NO],** O.S. (+2) colourless gas.

- **Preparation**

$4NH_3 + 5O_2 \xrightarrow{1100K,\ Pt} 4NO + 6H_2O$

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

- **Preparation :**

$NO(g) + NO_2(g) \xrightarrow{<253K} N_2O_3(g)$

4. **Nitrogen dioxide (NO_2),** O.S. (+4) brown gas.
5. **Dinitrogen pentoxide (N_2O_5),** O.S. (+5), colourless gas

OXY-ACIDS OF NITROGEN :

Nitrous acid [HNO_2]

- **Preparation :**

$N_2O_3 + H_2O \rightarrow 2HNO_2$

$NaNO_2 + HCl \rightarrow NaCl + HNO_2$

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.

$3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$

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

$2HNO_2 \rightarrow 2NO + H_2O + [O]$

$H_2S + [O] \rightarrow H_2O + S$

$2KI + H_2S + [O] \rightarrow 2KOH + I_2$

$2FeSO_4 + H_2SO_4 + [O] \rightarrow Fe_2(SO_4)_3 + H_2O$

- **Reducing properties :**

$HNO_2 + [O] \rightarrow HNO_3$

$Br_2 + H_2O + HNO_2 \rightarrow HNO_3 + 2HBr$

$H_2O_2 + HNO_2 \rightarrow HNO_3 + H_2O$

$KMnO_4 \xrightarrow{HNO_2} MnSO_4$

- **Organic reactions :** Urea $\xrightarrow{HNO_2} N_2$

Ethyl amine $\xrightarrow{HNO_2}$ ethyl alcohol

Aniline $\xrightarrow{HNO_2}$ diazonium chloride

AMMONIA [NH_3]

1. **Preparation**

Laboratory method :

$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_4 + 2H_2O$

$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$

* The gas is collected by downward displacement of air.

* The gas is dried by CaO [P_2O_5, H_2SO_4 and $CaCl_2$ react with ammonia]

Manufactures :

Haber Process :

$$N_2 + 3H_2 \xrightarrow[450°C, 250atm]{Fe, Mo} 2NH_3$$

Cyanamide process :

$$CaC_2 + N_2 \xrightarrow{1000°C} CaCN_2 + C$$

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3$$

Serpeck's process :

$$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO$$

$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3$$

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 [$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$]

Chemical : Few of the chemical reaction are :

(i) $NH_3 + HCl \rightarrow NH_4Cl$

(ii) $2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$

(iii) $2NH_3 + 3CuO \rightarrow 3Cu + 3H_2O + N_2$

(iv) $CaCl_2 + 8NH_3 \rightarrow CaCl_2.8NH_3$

(v) With Cl_2

(a) $8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$

(b) $NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$

(vi) Complex formation :

$Ag^+ \xrightarrow{2NH_3} [Ag(NH_3)_2]^+$, $Cu^{+2} \xrightarrow{4NH_3} [Cu(NH_3)_4]^{2+}$

Other Reaction :

(vii) $2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2$

(viii) $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$

(ix) $K_2HgI_4 + NH_3 + 3KOH \rightarrow NH_3 - HgO.HgI\downarrow + 7KI + 2H_2O$ (red brown ppt.)

(x) $FeCl_3 + 3NH_3 + 3H_2O \rightarrow Fe(OH)_3\downarrow + 3NH_4Cl$ (brown ppt.)

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 HNO_3, $(NH_4)_2CO_3$, Na_2CO_3 etc.

PHOSPHORUS :

Occurrence : Five important minerals of phosphorus are :

* Phosphorite $Ca_3(PO_4)_2$

* Fluoropatite $3Ca_3(PO_4)_2.CaF_2$

* Hydroxyapatite $3Ca_3(PO_4)_2.Ca(OH)_2$.

* Chloroapatite $3Ca_3(PO_4)_2.CaCl_2$

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 $Ca_3(PO_4)_2$ with coke and silica in an electric furnace.

$$2Ca_3(PO_4)_2 + 6SiO_2 \xrightarrow{1770 K} 6CaSiO_3 + P_4O_{10}$$

$$P_4O_{10} + 10C \rightarrow P_4 + 10CO$$

PHOSPHORUS PENTOXIDE [P_4O_{10}]

It is formed by burning phosphorus in excess of air : $P_4 + 5O_2 \rightarrow P_4O_{10}$

Note :

Since it is collected as snowy powder hence it is called

Flower of phosphorus.

Dissolution in cold water :

$P_4O_{10} + 2H_2O$ (cold) → $4HPO_3$ metaphosphoric acid

Dissolution in hot water :

$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$ orthosphosphoric acid

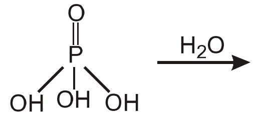
OXY-ACIDS OF PHOSPHORUS :

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.

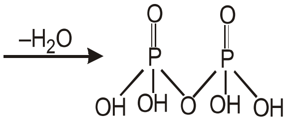


HPO_3 [metaphosphoric acid]

[orthophosporic acid]

- Pyro is used for acid obtained by loss of H_2O molecule form two acid molecules

2 × orthophosphoric acid

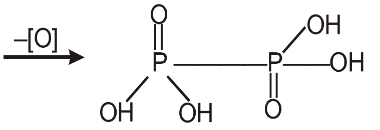


[pyro phosphoric acid]

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

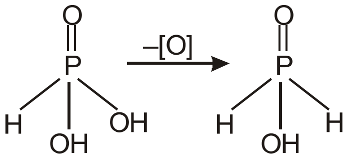
pyrophosphoric acid

[$H_4P_2O_7$]



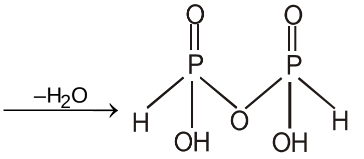
Hypophosphoric acid

Similarly :



[phosphorus acid] [hyposphorus acid]

2 × phosphors acid



(pyrophosphorus acid)

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.

$$H_2S + 2HNO_3 \rightarrow 2H_2O + 2NO_2 + S$$

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)

Oxygen Family

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] $2s^22p^4$
Sulphur [S_{16}]	[Ne] $3s^23p^4$
Selenium [Se_{34}]	[Ar] $3d^{10}4s^24p^4$
Tellurium [Te_{52}]	[Kr] $4d^{10}5s^25p^4$
Polonium [Po_{84}]	[Xe] $4f^{14}\ 5d^{10}\ 6s^26p^4$

* 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 abudnt 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.

HYDRIDES OF GROUP 16 ELEMENTS :

* Form hydrides of the formula H_2X [H_2O, H_2S, H_2Se, H_2Te and H_2Po]

* Bond angle of hydrides decreases from H_2O to H_2Po

* The volatility of hydrides increases from H_2O to H_2S then decrease. High b.p. of H_2O is due to the presence of intermolecular H–bonding.

* The acidic strength increases from H_2O to H_2Te. This is due to increase of size of the anion in the group.

* The thermal stability of hydrides increases in the order : $H_2O > H_2S > H_2Se > H_2Te > H_2Po$.

* The covalent character of hydrides increases in going from O to Po.

* H_2S, H_2Se, H_2Te and H_2Po burn in atmosphere of oxygen with blue flame forming dioxides

e.g., $2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$.

* Except H_2O 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 H_2O (liquid), all hydrides are gases at room temperature.

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 from 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.

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.

1. Preparations :

(i) On heating suitable compounds such as oxides, $Nb(NO_3)_2$, $CaOCl_2$, $KMnO_4$ etc.

$2HgO \xrightarrow{\Delta} 2Hg + O_2$, $2BaO_2 \xrightarrow{\Delta} 2BaO + O_2$,

$2Ag_2O \xrightarrow{\Delta} 4Ag + O_2$,

$3MnO_2 \xrightarrow{\Delta} Mn_3O_4 + O_2$, $2PbO_2 \xrightarrow{\Delta} 2PbO + O_2$,

$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + O_2 + 4NO_2$,

$2CaOCl_2 \xrightarrow{\Delta} 2CaCl_2 + O_2$,

$2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$,

$2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$ (Lab. method)

$4K_2CrO_4 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$

(ii) Reaction of water or acid with certain suitable compounds :

$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$

$4KMnO_4 + 6H_2SO_4 \rightarrow 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2$

$2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$

$2MnO_2 + 2H_2SO_4 \rightarrow 2MnSO_4 + 2H_2O + O_2$

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 :

$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$

At cathode : $2H^+ + 2e \rightleftharpoons H_2$

At anode : $2H_2O + 2SO_4^{2-} \rightarrow 4H^+ + 2SO_4^{2-} + O_2 + 4e$

$NaOH \rightarrow Na^+ + OH^-$

At cathode : $2Na^+ + 2H_2O + 2e \rightarrow 2Na^+ + 2OH^- + H_2$

At anode : $4OH^- \rightarrow 2H_2O + O_2 + 4e$

3. Properties :

(a) Physical characteristic :

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

$_8O^{16} : {}_8O^{17} : {}_8O^{18} :: 10,000 : 1 : 8$

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

Reactions of Na, Ca, Al, Fe are :

$4Na + O_2 \rightarrow 2Na_2O$; $2Ca + O_2 \rightarrow 2CaO$

$4Al + 3O_2 \rightarrow 2Al_2O_3$; $3Fe + 2O_2 \rightarrow Fe_3O_4$

Reactions of C, P_4, S and H_2 :

$C + O_2 \rightarrow CO_2$; $P_4 + 5O_2 \rightarrow 2P_2O_5$

$S + O_2 \rightarrow SO_2$; $2SO_2 + O_2 \xrightarrow{Pt} 2SO_3$

$2H_2 + O_2 \rightarrow 2H_2O$

Reactions of NH_3 and HCl :

$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O$; $4HCl + O_2 \xrightarrow{Cu_2Cl_2} 2H_2O + 2Cl_2$

Reactions of organic compounds :

$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$; $C_2H_2 + 2.5O_2 \rightarrow 2CO_2 + H_2O$

$2CH_3OH + O_2 \rightarrow 2HCHO + 2H_2O$; $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

4. Uses of oxygen :

- It is used in artificial respiration (O_2 + He)
- For the combustion process.
- Liquid oxygen is used as a fuel in the rockets.
- For oxyacetylene (3300ºC) and oxyhydrogen (2800ºC) flames, employed in cutting and welding purposes.
- As an oxidant in several reactions.
- In the preparation of several important oxides.

SULPHUR :

* Constitute about 0.1% earth's crust.

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.

$CaS + H_2O + CO_2 \rightarrow CaCO_3\downarrow + H_2S\uparrow$, $2H_2S + O_2 \rightarrow 2H_2O + S\downarrow$

Spent oxides of coal gas : Contain Fe_2S_3

$2Fe_2S_3 + 3O_2 \rightarrow 2Fe_2O_3 + 6S\downarrow$

Iron pyrites :

$3FeS_2 \xrightarrow{\text{distillation}} Fe_3S_4 + 2S\downarrow$

$3FeS_2 \xrightarrow{\Delta} Fe_3S_4 + 3O_2 + 3S\downarrow$

$FeS + CO_2 \xrightarrow{\Delta} FeO + CO + S\downarrow$

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

2. **Chemical characteristics :**

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

$H_2 + S \rightarrow H_2S$, $Cl_2 + 2S \rightarrow S_2Cl_2$

$C + 2S \rightarrow CS_2$, $2As + 3S \rightarrow As_2S_3$; $Fe + S \rightarrow FeS$

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

$S + HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O$

$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$

$4S + 6NaOH \rightarrow 2Na_2S + Na_2S_2O_3 + 3H_2O$

Reactions with K_2S : $K_2S + 4S \rightarrow K_2S_5$

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.

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.

SULPHUR DIOXIDE SO_2

1. **Methods of preparation :**

Laboratory methods :

$S + 2H_2SO_4 \rightarrow H_2O + 3SO_2\uparrow$

$Cu + 2H_2SO_4\,(conc.) \rightarrow CuSO_4 + 2H_2O + S_2\uparrow$

$2Ag + 2H_2SO_4\,(conc.) \rightarrow Ag_2SO_4 + 2H_2O + SO_2\uparrow$

$Na_2SO_3 + 2HCl\,(dil.) \rightarrow 2NaCl + H_2O + SO_2\uparrow$

$NaHSO_4 + HCl\,(dil.) \rightarrow NaCl + H_2O + SO_2\uparrow$

Industrial method :

$S + O_2 \rightarrow SO_2\uparrow$

$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2\uparrow$

$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2\uparrow$

$2CaSO_4 + C \rightarrow 2CaO + 2SO_2\uparrow + CO_2$

2. **Chemical characteristics :**

* **Aqueous solutions of SO_2 acts as a reducing agent :**

$H_2O + SO_2 \rightarrow H_2SO_3$; $H_2SO_3 + H_2O \rightarrow H_2SO_4 + [H]$ (nascent hydrogen)

$2KMnO_4 + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4$ (colourless) $+ 2H_2SO_4$

$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3$ (green) $+ H_2O$

- Acts as an **oxidising agent :**

  $Mg + SO_2 \rightarrow 2MgO + MgS$

  $4K + \rightarrow 3SO_2 \rightarrow K_2SO_3 + K_2SO_4$

  $2SnCl_2 + SO_2 + 4HCl \rightarrow SnCl_4 + 2H_2O + S$

  $2Hg_2Cl_2 + SO_2 + 4HCl \rightarrow 4HgCl_2 + 2H_2O + S$

- Acts as **bleaching agent** (due to reducing nature)

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

  Coloured matter + H → Colourless matter

- Acidic nature (SO_2) is an acidic oxide)

  $SO_2 + H_2O \rightarrow H_2SO_3$

  $BaO + SO_2 \rightarrow BaSO_3$

- Addition reaction :

  $SO_2 + Cl_2 \rightarrow SO_2Cl_2$ (Sulphurly chloride)

  $PbO_2 + SO_2 \rightarrow PbSO_4$

- Thermal decomposition :

  $3SO_2 \xrightarrow{1200^\circ C} 2SO_3 + S$

- Reaction with burning Mg :

  $3Mg + SO_2 \rightarrow 2MgO + MgS$

4. Uses of SO_2

- Used in the manufacture of H_2SO_4, paper (from wood pulp)
- Used as disinfectant, antechoir, bleaching agent.
- As a refrigerant (liquid SO_2)
- Used in refining petroleum and sugar.

SULPHURIC ACID [H_2SO_4] :

- It is a **king of chemicals**
- It is also known as **oil of vitriol**.
- The three step process for the preparation of H_2SO_4 is described as :

  $S \rightarrow SO_2 \rightarrow SO_3 \rightarrow H_2SO_4$

1. Manufacture : (a) Lead chamber process

(b) Contact process

(a) Lead chamber process : Here oxidation of SO_2 is affected catalytically by means of oxides of nitrogen in the presence of water.

$2SO_2 + O_2(air) + 2H_2O + [NO]$ (catalyst) $\rightarrow 2H_2SO_4 + [NO]$

Mechanism may be described as :

$2NO + O_2 \rightarrow 2NO_2$

$NO_2 + SO_2 + H_2O \rightarrow H_2SO_4 + NO$

The unreacted gases (NO, NO_2, O_2 and N_2) are absorbed in H_2SO_4 and nitrosyl sulphuric acid. The product on decomposition gives H_2SO_4.

$2H_2SO_4 + NO + NO_2 \rightarrow 2NO^+H\ SO_4^- + H_2O$

$2NOHS_4 + H_2O \rightarrow 2H_2SO_4 + NO\uparrow + NO_2\uparrow$

(b) Contact process :

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

  $2SO_2 + O_2 \xrightarrow[\text{Pt or } V_2O_5]{Fe_2O_3 \text{ or}} 2SO_3$

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

  $H_2SO_4 + SO_3 \rightarrow H_2S_2O_7$ (oleum)

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

  $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

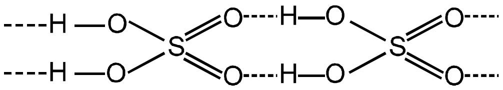
2. Properties :

Physical characteristics :

- H_2SO_4 is colourless, only liquid.
- Freezing point and boiling point are 10.5ºC and 340ºC respectively. Forms constant boiling mixture (at 370ºC) containing 98.33% of the acid.
- Density is 1.84 gm cm^{-3}.
- Forms hydrate with the evolution of heat :

  $H_2SO_4.H_2O$ [monohydrate], $H_2SO_4.2H_2O$ [dihydrate], $H_2SO_4.3H_2O$ [tri hydrate]

- Conductor of heat and electricity
- High b.p. and viscosity of H_2SO_4 is dut to H–bonding.



Chemical characteristics :

- Acid character (dibasic acid)

  $H_2SO_4 \rightarrow H^+ + HSO_4^-$, $HSO_4^- \rightarrow H^+ + SO_4^{2-}$

  Forms two type of salts :

  $NaOH + H_2\ SO_4 \rightarrow NaH\ SO_4 + H_2O$

  $NaHSO_4 + NaOH \rightarrow Na_2SO_4 + H_2O$

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

$C_{12}H_{22}O_{11} \xrightarrow{\text{conc. } H_2SO_4} 12C + 11H_2O$

; $HCOOH \xrightarrow{\text{conc. } H_2SO_4} CO + H_2O$

$3C_2H_5OH \xrightarrow{\text{conc. } H_2SO_4} C_2H_4 + (C_2H_5)_2O$

- * **Acts as an oxidizing agent**

$C + 2H_2SO_4 \rightarrow CO_2\uparrow + 2SO_2\uparrow + 2H_2O$

$2HBr + H_2SO_4 \rightarrow 2H_2O + SO_2\uparrow + Br_2$

$H_2S + H_2SO_4 \rightarrow 2H_2O + SO_2\uparrow + S$

- * **Displaces more volatile acids :**

$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$

$2NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_3$

$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$

$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4$

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

$Zn + H_2SO_4(dil) \rightarrow ZnSO_4 + H_2$

Cu gives SO_2.

$Cu + 2H_2SO_4 \text{ (conc.)} \rightarrow CuSO_4 + 2H_2O + SO_2$

- * **Formation of insoluble sulphates :**

$BaCl_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + 2HCl$

$Pb(NO_3)_2\ H_2SO_4 \rightarrow PbSO_4\downarrow + 2HNO_3$

- * **Reaction with PCl_5 and $KClO_3$:**

$PCl_5 + H_2SO_4 \rightarrow ClSO_2OH + POCl_3 + HCl$

$3KClO_3 + 3H_2SO_4 \rightarrow 3KHSO_4 + HClO_3 + 2ClO_2 + H_2O$

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.

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

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.

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

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 :

$$F_2 \xrightarrow{+H_2O} O_2, O_3$$

$$(Cl_2 \text{ or } Br_2)\ X_2 \xrightarrow[\text{sun light}]{+H_2O} HX, HXO$$

$$I_2 \xrightarrow{+H_2O} \text{no reaction}$$

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

$$CH_4 + 2F_2 \rightarrow C + 4HF$$

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

* I_2 has practically no action on hydrocarbons.

Halogen displacement reaction :

* Fluorine replaces (Cl, Br, I)

* Chlorine replaces (Br, I)

$2NaX + F_2 \rightarrow 2NaF + X_2$ [X = Cl, Br, I]

$2NaX + Cl_2$

$2NaCl + X_2$ [X = Br, I]

$2NaX + Br_2 \rightarrow 2NaBr + X_2$ [X = 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 :

$X_2 + 2NaOH \rightarrow NaX + NaXO + H_2O$

Sodium hypohalite

Hot and concentrated alkali :

$2X_2 + 6NaOH \rightarrow 5NaX + NaXO + H_2O$

Sodium halate

F_2 behaves differently with alkalies :

$F_2 + 2NaOH\ (dil) \rightarrow 2NaF + OF_2 + H_2O$

$2F_2 + 4NaOH \rightarrow 4NaF + O_2 + 2H_2O$

Reaction with hydrogen :

$H_2 + F_2 \xrightarrow{\text{dark}} 2HF$

$H_2 + Cl_2 \xrightarrow{\text{diffused sunlight}} 2HCl$

$H_2 + Br_2 \xrightarrow{\Delta} 2HBr$

$H_2 + I_2 \rightleftharpoons 2HI$ (catalyst)

OXY-ACIDS OF HALOGENS :

* F forms only one oxy acid HOF (hypfluorous 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.

Example : HOCl > HOBr > HOI

$HClO_3 > HBrO_3 > HIO_3$

$HClO_4 > HBrO_4 > HIO_4$

Oxidising power :

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

Example : $HOCl > HClO_2 > HClO_3 > HClO_4$

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

follows the order :

$ClO_4 < BrO_4^- < IO_4^-$

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

$HOCl < HClO_2 < HClO_3 < HClO_4$

Stability of conjugate bases :

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

Conjugate bases $[HX + H_2O \rightleftharpoons H_3O^+ + A^-]$

The stability of conjugate bases of oxy acids increases with the increase in the number of oxygen atoms in the anion thus : $ClO^- < ClO_2^- < ClO_3^- < ClO_4^-$

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 [$NaHF_2$ and Na_2F_2]

* AgF is soluble in water while AgCl, AgBr and AgI are insoluble.

* Fluorine form two series of salts [$NaHF_2$ and Na_2F_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.
- * [F_2 + H_2O] gives oxone while other halogens do not give oxone.
- * F^- has more complex forming tendency as compared to other halides ions. $[(AlF_6]^{3-}$, $[FeF_6]^{3-}$]
- * Fluorine does not form poly halide ion like I_3^-, Br_3^- etc.

FLUORINE :

1. Occurrence :

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

- * Fluorspar [CaF_2]
- * Cryolite [Na_3AlF_6]
- * Fluorapatite [$CaF_2 . 3Ca_3 (PO_4)_2$]

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

2. Reaction of F_2 are :

Directly combines with metals and non metals

$2Na + F_2 \rightarrow 2NaF_2$ $\quad$ $2B + 3F_2 \rightarrow 2BF_3$

$Mg + F_2 \rightarrow MgF_2$ $\quad$ $C + 2F_2 \rightarrow CF_4$

$2Ag + F_2 \rightarrow 2AgF$ $\quad$ $P_4 + 10F_2 \rightarrow 4PF_5$

Reaction with H_2, O_2 :

$H_2 + F_2 \rightarrow H_2F_2$ (expoldes even in dark)

$O_2 + F_2 \rightarrow O_2F_2$ (explodes in presence of silent electric discharge)

Reaction with HCl, H_2S and NH_3 :

$2HCl + F_2 \rightarrow 2HF + Cl_2$

$H_2S + 4F_2 \rightarrow 2HF + SF_6$

$2NH_3 + 3F_2 \rightarrow 6HF + N_2$

Reaction with NaOH :

$2F_2 + 2NaOH$ (dil) $\rightarrow 2NaF + OF_2 + H_2O$

$2F_2 + NaOH$ (conc.) $\rightarrow 4NaF + O_2 + 2H_2O$

Reaction with halides :

$2NaX + F_2 \rightarrow 2NaF + X_2$

[$X = Cl^-, Br^-, I^-$] $\quad$ [$X_2 = Cl_2, Br_2, I_2$]

- * Reacts with water to give O_2 and O_3
- * Reacts with other halogens to form inter halogen compounds [ClF, ClF_3, IF_3, IF_7 etc.]
- * Reacts with CH_4 explosively to give CH_3, F, CH_2F_2, CHF_3 and CF_4.

3. Uses :

(i) Fluorides are used as insecticides (CaF_2 is added to tooth paste)

(ii) Sodium and antimony fluorides are used as mordants in dyeing industry.

(iii) Freons (poly chloro fluoro alkanes) are used in refrigeration and air conditioning.

(iv) Br_2 and HF are used as catalyst in petroleum industry.

(v) CuF_2 is used in ceramic industry.

(vi) Teflon (C_2F_4) is polymer used as insulting material in cables.

(vii) For the separation of U^{235} from natural uranium, UF_6 is used.

(viii) Na_3 AlF_6 and CaF_2 are used for the extraction of aluminium.

(ix) Sodium fluoro acetate is used as rat poison.

CHLORINE :

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 [$KCl.MgCl_2.6H_2O$]
- * Horn silver [AgCl]

2. Preparation :

(1) By the oxidation of HCl by MnO_2, $K_2Cr_2O_7$, PbO_2, $KMnO_4$, $CaOCl_2$, NaClO etc.

$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$ (Lab. method)

$NaClO + 2HCl \rightarrow NaCl + H_2O + Cl_2$

$CaOCl_2 + 2HCl \rightarrow CaCl_2 + H_2O + Cl_2$

$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 3CrCl_3 + 7H_2O + 3Cl_2$

(2) Commercial methods :

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

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

(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)

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.

$2Na + Cl_2 \rightarrow 2NaCl$ $\quad$ $2P + 5Cl_2 \rightarrow 2PCl_5$

$Ca + Cl_2 \rightarrow CaCl_2$ $\quad$ $2S + Cl_2 \rightarrow S_2Cl_2$

Reaction with SO_2, CO and NO

$SO_2 + Cl_2 \rightarrow SO_2Cl_2$ (sulphuryl chloride)

$CO + Cl_2 \rightarrow COCl_2$

$2NO + Cl_2 \rightarrow 2NOCl$

Reaction with NH_3 :

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

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

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

$Cl_2 + 2NaOH$ (cold dil.) $\rightarrow 2NaClO + H_2O$

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

$Cl_2 + Ca(OH)_2 \rightarrow CaOCl_2 + H_2O$

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

ClF, BrCl and ICl_3

Reaction with organic compounds :

$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$

$C_2H_4 + Cl_2 \rightarrow ClCH_2\text{–}CH_2Cl$

Oxidizing and bleaching action of Cl_2 :

[Cl_2 on reaction with water liberates nascent oxygen. Hence it is a powerful oxidant.]

$Cl_2 + H_2O \rightarrow 2HCl + [O]$

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

$SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$

$Na_2SO_3 + H_2O + Cl_2 \rightarrow Na_2SO_4 + 2HCl$

$Na_2SO_3 + H_2O + Cl_2 \rightarrow Na_2SO_4 + 2HCl + S$

Liberation of Br_2 and I_2 from KBr and KI

$2KBr + Cl_2 \rightarrow 2KCl + Br_2$

$2KI + Cl_2 \rightarrow 2KCl + I_2$

4. Uses of chlorine :

(i) Used in the manufacture of bleaching powder, hydrochloric acid, hypochlorites, chlorates, $CHCl_3$, CCl_4, DDT, Phosgene, mustard gas etc.

(ii) Used in the purification of drinking water.

(iii) Used in extraction of Au and Pt.

(iv) Used as a bleaching agent for cotton fabrics, paper and rayon.

(v) Used as a germicide and disinfectant.

(vi) Used as an oxidant.

BROMINE

1. Occurrence :

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

Carnalite :

Mother liquor of carnallite contains bromo carnallite $KBr\ MgBr_2 . 6H_2O$.

Sea water and mineral springs : Contain NaBr, $MgBr_2$

Bromargyrite : AgBr

2. Preparation

Laboratory method :

Reactants : KBr, MnO_2 and conc. H_2SO_4.

$2KBr + MnO_2 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + Br_2 + 2H_2O$

Liberation of Br_2 Using Cl_2 gas :

Reactants : (KBr, Cl_2) or ($MgBr_2$, Cl_2)

$2KBr + Cl_2 \rightarrow 2KCl + Br_2$; $MgBr_2 + Cl_2 \rightarrow MgCl_2 + Br_2$

Commercial method :

(a) From carnallite [$KCl . MgCl_2 . 6H_2O$]

Mother liquor left after the separation of crystals of KCl and $MgCl_2$ contains 0.25% $MgBr_2$ (bittern). This on treating with Cl_2 gas Br_2 is liberated.

(b) From sea water :

Sea water contains 0.006% (by weight) of bromine as $MgBr_2$. Here also Br_2 can be obtained by passing chlorine gas.

3. Properties : Physical characteristics

* It is dark–red, poisonous liquid gives brown–red fumes.

* Boiling point is 59.5ºC, Freezing point is –7.2ºC.

* Sparingly soluble in water and is soluble in CCl_4, CS_2, $CHCl_3$ etc.

Chemical characteristics :

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

e.g. $SO_2 + Br_2 + 2H_2O \rightarrow 2HBr + H_2SO_4$; $H_2S + Br_2 \rightarrow 2HBr + S$

Reaction with NH_3 :

With cold and dil. NaOH :

$2NaOH + Br_2 \rightarrow NaBr + NaBrO + H_2O$

With hot and conc. NaOH :

$6NaOH + Br_2 \rightarrow 5NaBr + NaBrO_3 + 3H_2O$

4. Uses of bromine :

(i) Used in the form of AgBr as coating on photographic plates, films etc.

(ii) Used in the manufacture of KBr, NaBr (used as a sedative in medicine).

(iii) Used to prepare 1, 2 dibromoethane which is employed with TEL as an antiknock compound in gasoline.

(iv) Used as an oxidant in organic synthesis.

IODINE

1. Occurrences : Chief sources of iodine are :

(i) Sea Weeds : Contain 0.5% of iodine in the form of iodies.

(ii) Caliche or crude chile saltpetre : Contains 0.2% of sodium iodate.

2. Preparation :

Laboratory method :

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

Liberation of I_2 using Cl_2 gas :

Reactants : KI and Cl_2

$2KI + Cl_2 \rightarrow 2KCl + I_2$

Commercial methods :

From sea weeds : Dry weeds are carefully burnt in shallow pits. The residue called **kelp** is treated with conc. H_2SO_4 and MnO_2

$2NaI + MnO_2 + 3H_2SO_4 \rightarrow 2NHSO_4 + MnSO_4 + I_2$

From caliche or crude chile salt peter : It contains 0.2% sodium iodate ($NaIO_3$). After removal of $NaNO_3$ from caliche, the mother liquor contains $NaIO_3$. It is treated with calculated quantity of sodium bisulphate to obtain iodine.

$2NIO_3 + 5NaHSO_3 \rightarrow 2Na_2SO_4 + 3NaHSO_4 + H_2O + I_2$

3. Properties : Physical characteristics :

* Iodine is a dark violet shining solid.

* Sublimes below its melting point (114ºC) giving violet vapours.

* Iodine is sparingly soluble in water. In presence of KI, the solubility of iodine increases due to the formagtion of tri iodide ion $I^- + I_2 \rightleftharpoons I_3^-$.

* Iodine is soluble in organic solvents such as $CHCl_3$, CCl_4, CS_2 etc.

* Its vapours are pungent and poisonous to inhale.

* At high temperature the equilibrium is mainted between molecular and atomic form

$$I_2 \xrightleftharpoons{1700^\circ C} I + I .$$

Chemical characteristics : Less reactive as compared to Cl_2 and Br_2.

Reaction with H_2 and non–metals :

$$H_2 + I_2 \xrightarrow[pt]{\Delta} 2HI$$

$2K + I_2 \rightarrow 2KI$ $2P + 3I_2 \rightarrow 2PI_3$

Reaction with NaOH : Iodine with cold and dil. NaOH gives sodium hypo iodite (NaOI). With concentrated NaOH iodide (NaI) and idodate ($NaIO_3$) are formed.

Reaction with sodium thisulphate :

$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$ (Sodium tetrahionate)

Reactions showing oxidising properties (It is a weak oxidant)

$Na_3AsO_3 + H_2O + I_2 \rightarrow Na_3AsO_4 + 2HI$

$H_2S + I_2 \rightarrow 2HI + S$

$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI$

Reaction showing basic character : It shows basic properties and forms I^+ and I^{3+} ions.

Formation of ICl, ICN, INO_2 etc. shows the presence of I^+

$ICI \rightleftharpoons I^+ + Cl^-$

$ICN \rightleftharpoons I^+ + CN^-$

Formation of $I(CH_3COO)_3$ and IPO_4 etc show the presence of I^{3+}.

Reaction with $KClO_3$ and $KBrO_3$:

$2KClO_3 + I_2 \rightarrow 2KIO_3 + Cl_2$

$2KBrO_3 + I_2 \rightarrow 2KIO_3 + Br_2$

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

Reaction with strong oxidants :

$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$

$I_2 + 5Cl_2 + 6H_2O \rightarrow 2HIO_3 + 10HCl$

$I_2 + H_2O + 5O_3 \rightarrow 2HIO_3 + 5O_2$

Reaction with starch : Iodine turns starch solution blue.

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.

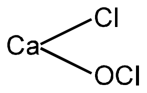
(iv) Solution of I_2 in KI is used in the treatment of goitre.

(v) Used in making photosensitive papers, films etc.

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 $Ca(OCl)_2\ 4H_2O$ and basic calcium chloride $CaCl_2.Ca(OH)_2\ H_2O$

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 $[Ca(OH)_2$ is treated with chlorine at 40ºC results in the formation of bleaching powder.

$2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$

$CaCl_2 + Ca(OH)_2 + H_2O \rightarrow CaCl_2.Ca(OH)_2.H_2O$

$2Cl_2 + 3Ca(OH)_2 \rightarrow Ca(OCl)_2 + CaCl_2.Ca(OH)_2.H_2O + H_2$

Bleaching powder is : $[Ca(OCl)_2 + CaCl_2.Ca(OH)_2.H_2O]$

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 $Ca(OH)_2$.

* It is ionises as : $CaOCl_2 \rightarrow Ca^{2+} + Cl^- + OCl^-$

Chemical characteristics :

Oxidizing and bleaching action :

It loses its oxygen when treated with dilute acid.

$2CaOCl_2 + H_2SO_4 \rightarrow CaCl_2 + CaSO_4 + 2HClO$

$HClO \rightarrow HCl + [O]$ nascent oxygen

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

Oxidizing action :

$COCl_2 + 2KI + 2HCl \rightarrow CaCl_2 + 2KCl + H_2O + I_2$

$Na_3AsO_3 + CaOCl_2 \rightarrow CaCl_2 + Na_3AsO_4$

$CaOCl_2 + H_2S \rightarrow CaCl_2 + H_2O + S$

$3CaOCl_2 + 2NH_3 \rightarrow 3CaCl_2 + 3H_2O + N_2$

Bleaching action :

Coloured matter + [O] → Colourless matter

Reaction with ethylalcohol and acetone :

C_2H_5OH or $CH_3COCH_3 \xrightarrow{CaOCl_2.H_2O} CHCl_3$

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 :

$COCl_2 + 2HCl \rightarrow CaCl_2 + H_2O + Cl_2$

$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$

$CaOCl_2 + CO_2 \rightarrow CaCO_3 + Cl_2$

Reaction in presence of $CoCl_2$

$2CaOCl_2 \longrightarrow 2CaCl_2 + O_2$

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.

EXAMPLE :

(1) Evidence for the existence of unipositive ion I^+ is :

Molten iodine monochloride conducts electricity

(2) Reaction : $4KClO_3 \rightarrow KCl + 3KClO_4$ 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 ($NaHF_2$ and NaF)

(5) In the reaction : $Ca(OH)_2 + Cl_2 \rightarrow$ ---------- + H_2O the unknown compound is :

Bleaching powder ($CaOCl_2$)

(6) The stability oxy halide anion is :

$ClO^- < ClO_2^- < ClO_3^- < ClO_4^-$

(7) The oxidising power of oxy acids is :

$HClO > HClO_2 > HClO_3 > HClO_4$

(8) I_2 is liberated from HI by the halogens :

F_2, Cl_2 and Br_2

$2HI + F_2 (Cl_2, Br_2) \rightarrow 2HF (HCl, HBr) + I_2$

(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.

Nobel Gases (zero group)

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 dins integration 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]	Is^2
Neon [Ne_{10}]	[He] $2s^2$, $2p^6$
Argon [Ar_{18}]	[Ne] $3s^2$, $3p^6$
Krypton [Kr_{36}]	[Ar] $3d^{10}$, $4s^2$, $4p^6$
Xenon [Xe_{54}]	[Kr] $3d^{10}$, $5s^2$, $5p^6$
Radon [Rn_{86}]	[Xe] $4f^{14}$, $5d^{10}$, $6s^2$ $6p^6$

- These element 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.

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.

$2Cu + O_2 \rightarrow 2CuO$ $3Mg + N_2 \rightarrow Mg_3N_2$

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 fo 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 dis integration product of radium.

$_{86}Ra^{226} \rightarrow {}_{86}Rn^{222} + {}_2He^4$

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

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

$CaC_2 + N_2 \rightarrow CaCN_2 + C$

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

$2Cu + O_2 \rightarrow 2Cu$

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.

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 O_2 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 (–269ºC)

Neon :

(i) Neon lamps are used in green houses as it is effective in the growth of chlorophyll.

(ii) Neon lamps ar used in botanical gardens.

(iii) Neon lights are visible in fog and mist and there fore 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.

EXAMPLES

(1) Who obtained an inactive gas by heating the mineral clavate with dil. H_2SO_4.

Hilledbrand

(2) ow 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 where 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) $Xe + O_2F_2 \xrightarrow{-178^\circ C} \text{.............} + O_2$

the unknown product is : $\mathbf{XeF_2}$

(6) Formula of xenonoxy – tetra fluoride is $\mathbf{XeOF_4}$