p-BLOCK

BORON FAMILY

1. EXTRACTION OF BORON

Amorphous boron of low purity (called moissan boron) is obtained by reducing B_2O_3 with Mg or Na at a high temperature. It is 95–98% pure (being contaminated with metal borides), and is black in colour.

$$Na_2[B_4O_5(OH)_4].8H_2O \xrightarrow{\text{acid}} H_3BO_3 \xrightarrow{\text{heat}} B_2O_3 \xrightarrow{\text{Mg or Na}} 2B + 3\,MgO$$

It is difficult to obtain pure crystalline boron, as it has a very high melting point (2180°C) and the liquid is corrosive. Small amounts of crystalline boron may be obtained :

(a) By reducing BCl_3 with H_2. This is done on the kilogram scale.

(b) Pyrolysis of BI_3 (Van Arkel method).

(c) Thermal decomposition of diborane or other boron hydrides.

$$2BCl_3 + 3H_2 \xrightarrow{\text{red hot W or Ta filament}} 2B + 6HCl$$

$$2BI_3 \xrightarrow[\text{Van Arkel}]{\text{red hot W or Ta filament}} 2B + 3I_2$$

$$B_2H_6 \xrightarrow{\text{heat}} 2B + 3H_2$$

Property of Boron

(a) Burning in air

$$4B + 3O_2 \longrightarrow 2B_2O_3$$

(b) Reaction with water

$$B + H_2O \xrightarrow{\text{cold \& hot}} \text{No reaction}$$

$$2B + 3H_2O \xrightarrow{\text{Red hot}} B_2O_3 + H_2$$

(c) $B + HCl \longrightarrow \text{No reaction}$

$$B + H_2SO_4 \xrightarrow{\text{dil.}} \text{No reaction}$$

$$2B + 3H_2SO_4 \xrightarrow{\text{conc.}} 2H_3BO_3 + 3SO_2$$

$$B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$$

(d) $2B + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2$

(e) $2B + N_2 \longrightarrow 2NB$

$$4B + C \longrightarrow B_4C$$

(f) $3Mg + 2B \longrightarrow Mg_3B_2$

2. BORANES

Boranes are boron hydrogen compounds with general molecular formula B_nH_{n+4} or $B_n\ H_{n+6}$.They are electron deficient compounds. The lighter boranes (upto B_5) spontaneously react with air whereas remaining compound are air stable. The physical properties of boranes are given as under :

Formula	Name	Melting point °C	Boiling point °C
B_2H_6	Diborane	– 165.6	– 92.5
B_4H_{10}	Tetraborane	– 120	18
B_5H_9	Pentaborane -9	– 46.6	48
B_5H_{11}	Pentaborane -11	– 123	63
B_6H_{10}	Hexaborane -10	– 62.5	110
B_6H_{12}	Hexaborane -12	– 82.3	80-90
B_8H_{12}	Octaborane -12	– 20	—
B_8H_{14}	Octaborane -14	– 20	—
B_9H_{15}	Enneborane	2.6	—
$B_{10}H_{14}$	Decaborane	99.7	213
$B_{20}H_{16}$	Isosaborane-16	196.2	—

PREPARATION of Diborane

(a) $Mg_3B_2 + \underset{(10\%)}{HCl} \longrightarrow B_2H_6 + B_4H_{10} + B_5H_9$ etc.

(b) $B_4H_{10} \xrightarrow[100°\,C]{\Delta} B_2H_6 + H_2 +$ higher borane

(c) $2\,BCl_3\ (\text{or } B\,Br_3) + 6\,H_2 \xrightarrow[\text{discharge at low pressure}]{\text{Electric}} B_2H_6 + 6HCl$

(d) $3Li\,AlH_4\,/LiBH_4 + 4BF_3 \longrightarrow 3LiF/3BF_3 + 3\,AlF_3 + 2\,B_2H_6$

CHEMICAL PROPERTIES

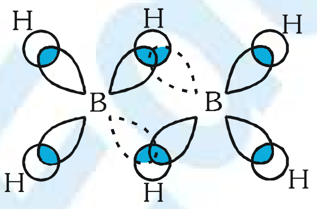
(a) $B_2\,H_6 + O_2 \xrightarrow[\text{air spontaneously}]{\text{burns in}} B_2O_3 + H_2O$

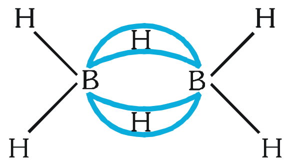
(b) $B_2H_6 + H_2O \xrightarrow{\text{cold is enough}} H_3BO_3 + 6H_2$

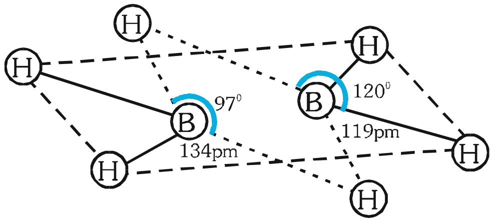
(c) $B_2H_6 + 2KOH \longrightarrow 2KOBH_2 + 2H_2$

(d) $B_2H_6 + \underset{\text{dry}}{HCl} \xrightarrow[AlCl_3]{\text{anh.}} B_2H_5Cl + H_2$

Structure of diborane







Structure of diborane (B_2H_6)

The structure of diborane is shown in fig. The four terminal hydrogen atoms and the two boron atoms lie in one plane. Above and below this plane, there are two bridging hydrogen atoms. The four terminal B-H bonds are regular two centre-two electron bonds while the two bridge (B-H-B) bonds are different and can be described in terms of three centre - two e^- bonds.

Bonding in diborane :– Each B atom uses sp^3 hybrids for bonding. Out of the four sp^3 hybrids on each B atom, one is without an electron shown in broken lines. The terminal B-H bonds are normal 2c-2e bonds but the two bridge bonds are 3c-2e bonds. The 3c-2e bridge bonds are also referred to as **banana bonds or tau bonds.**

3. BORIC ACID

PREPARATION

It is prepared by borax reacting with sulphuric acid.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$$

PHYSICAL PROPERTIES

(a) Its crystals are soft, white, needle like having a soapy touch.

(b) It is steam volatile.

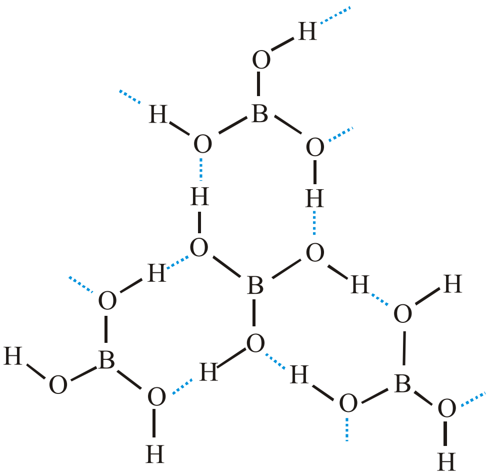
CHEMICAL PROPERTIES

(a) Ortho boric acid does not donate proton, like most of the acids but rather it accepts OH^-, therefore it is a lewis acid and is represented by $B(OH)_3$.

$$B(OH)_3 + 2H_2O \rightleftharpoons H_3O^+ + [B(OH)_4]^- \quad (P_{k_a} = 9.25)$$

(b) $B(OH)_3$ partially reacts with water to form H_3O^+ and $[B(OH)_4^-]$ and behaves as a weak acid. Thus $B(OH)_3$ can not be titrated satisfactorily with NaOH because a sharp end point is not obtained. If polyhydroxy compound like glycerol, mannitol or sugar are added to titration mixture than it can be titrated with NaOH.

$$B(OH)_3 + NaOH \longrightarrow Na[B(OH)_4]$$



Structure of boric acid, the dotted lines represent hydrogen bonds

(c) Effect of temperature at 100°C H_3BO_3 losses water and convert into metaboric acid.

$$H_3BO_3 \xrightarrow{100°C} HBO_2 + H_2O$$

metaboric acid form tetraboric acid on heating at 160° C.

$$4HBO_2 \xrightarrow{160°C} H_2B_4O_7 + H_2O$$

On strong heating B_2O_3 is produced

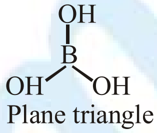
$$H_2B_4O_7 \longrightarrow 2B_2O_3 + H_2O$$

(d) Boric acid react with ethyl alcohol to form ethyl borate which burns with green edged flame.

$$H_3BO_3 + 3C_2H_5OH \longrightarrow B(OC_2H_5)_3 + 3H_2O$$

Structure of orthoboric acid

At lower concentration, its structure is a plane triangle.

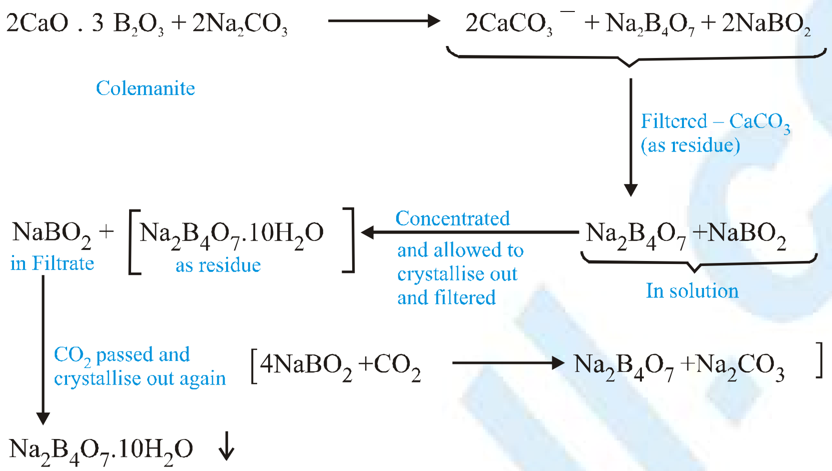


4. BORAX

PREPARATION

(a) In making glass, enamel and glaze of pottery.

(b) As antiseptic in medicinal soaps preparation.



(c) Orthoboric acid on neutralization with Na_2CO_3 gives borax.

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

(d) Colemanite is converted into borax by boiling it with concentrated solution of Na_2CO_3.

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

CHEMICAL PROPERTIES

The solution of borax is alkaline in nature due to hydrolysis.

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

5. BORON TRIHALIDES

Boron combines with halogens and forms the halides of type BX_3, (X = F, Cl, Br, I)

PREPARATION

Except BF_3, other trihalides can be prepared by the treatment of halogens on a mixture of B_2O_3 and carbon at high temperature.

$$B_2O_3 + 3C + 3X_2 \longrightarrow 2BX_3 + 3CO \ (X = Cl_2, Br_2, I_2)$$

PROPERTIES

(a) Due to small size and high charge density of B^{3+} ion, halides are covalent in nature.

(b) These are non-electrolytes, as in liquid state they do not conduct electricity.

(c) The boiling point are very low. The boiling point increases as the atomic number of halogen increases.

(d) BF_3 is gas, BCl_3 (B.P. 13° C), BBr_3 (B.P. 90° C) are fuming liquids while BI_3 (M.P. 310° C) is a fusible solid.

(e) The trihalides are electron deficient compounds. Boron atom acquires six electrons on account of three B – X bonds, i.e., 2 electrons, short to complete an octet. Thus the boron atom in BX_3 molecule can accept two more electron. i.e, an electron pair from the donor atoms like N, P, O, S, F, etc., in NH_3, PH_3, H_2O, H_2S, HF, F^- etc., respectively to form addition compounds (donor-acceptor compounds).

$$H_3N: \quad + \quad BF_3 \longrightarrow [H_3N \longrightarrow BF_3]$$

Donor Acceptor

(Lewis base) (Lewis acid)

(f) The relative lewis acid character of boron trihalides is found to follow the following order.

$BI_3 > BBr_3 > BCl_3 > BF_3$

but the expected order on the basis of electronegativity of the halogens (electronegativity of halogens decreases from F to I) should be –

$BF_3 > BCl_3 > BBr_3 > BI_3$

This anamoly is explained on the basis of the relative tendency of the halogen atom to back donate its unutilised electrons to vacant p–orbital of boron atom forming $p\pi - p\pi$ bond.

Extent of back bonding decrease from BF_3 to BI_3 with increase in size p-orbital of halogen.

$p\pi - p\pi$ back bonding is maximum in BF_3 due same energy and same size of 2p orbital of boran and filled 2p-orbital of F.

(g) All boron trihalides, except boron trifluoride, are hydrolysed to boric acid.

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$

The degree of hydrolysis increases from BCl_3 to BI_3 because covalent character increases. Due to resistance of BF_3 to hydrolysis and its tendency to act as lewis acid BF_3 is used as a catalyst in organic reactions.

BF_3 form addition product with water as B – F bond is very strong

$$BF_3 + H_2O \longrightarrow H^+[BF_3HO]^-$$

6. ALUMINIUM

PROPERTIES

(a) Burning in air

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

(b) Reaction with water

$$Al + 3H_2O \longrightarrow Al(OH)_3 + \frac{3}{2}H_2$$

(c) $2Al + 6H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3SO_2 + 6H_2O$

$Al + HNO_3 \longrightarrow Al_2O_3$ (passive layer) and does not react further.

(d) $2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$

(e) $2Al + N_2 \longrightarrow 2AlN$

$4Al + 3C \longrightarrow Al_4C_3$

7. ALUMINIUM CHLORIDE ($AlCl_3$)

(a) Hydrated $AlCl_3 \rightarrow AlCl_3.6H_2O$

(i) $AlCl_3$ is prepared by dissolving aluminium oxide or its hydroxide in dilute HCl.

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$
$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

(b) Anhydrous $AlCl_3$

(i) Anhydrous aluminium chloride can be obtained by passing dry chlorine gas and dry HCl gas over heated aluminium in vaccum.

$$2Al + 3Cl_2(dry) \longrightarrow 2AlCl_3$$

(ii) **Macaffe's process** - The anhydrous salt is prepared by heating alumina with coke and chlorine.

$$Al_2O_3 + 3C + \underset{(dry)}{3Cl_2} \longrightarrow 2AlCl_3 + 3CO\uparrow$$

PROPERTIES

(a) Aluminium chloride is a white crystalline substance which fumes in moist air. It fumes in moist air due to its hydrolysis.

$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl\uparrow$$

(b) On heating it sublimates at 180^0C.

(c) At sublimation point its vapour density corresponds to formula Al_2Cl_6 i.e, it exists as a dimer. At higher temperatures i.e, above 750^0C it exists as a monomer $AlCl_3$.

(d) It is largely covalent hence it does not conduct current in fused state.

USES of $AlCl_3$

Anhydrous $AlCl_3$ is employed as a catalyst in organic reactions i.e, Friedal crafts reaction.

8. ALUM

(a) Alums are double sulphates with their general formula $R_2SO_4.M_2(SO_4)_3.24H_2O$ where R = monovalent radical like Na^+, K^+, NH_4^+ and M = Trivalent radical like Al^{+3}, Cr^{+3}. Fe^{+3}.

(b) The different alums are -

(i) Potash alum	–	$K_2SO_4.Al_2(SO_4)_3.24H_2O$
(ii) Chrome alum	–	$K_2SO_4\ Cr_2(SO_4)_3.\ 24\ H_2O$
(iii) Iron alum	–	$(NH_4)_2SO_4.\ Fe_2(SO_4)_3.\ 24H_2O$
(iv) Ammonium alum	–	$(NH_4)_2SO_4.\ Al_2(SO_4)_3.\ 24H_2O$

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

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

PROPERTIES

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

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

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

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

USES

(a) Alum is used to stop bleeding.

(b) It is used for purification of water.

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

(d) Alum is used for tanning of leather.

CARBON FAMILY

1. ALLOTROPIC FORM OF CARBON

(A) CRYSTALLINE

(a) Diamond

(i) Three dimensional polymeric structure.

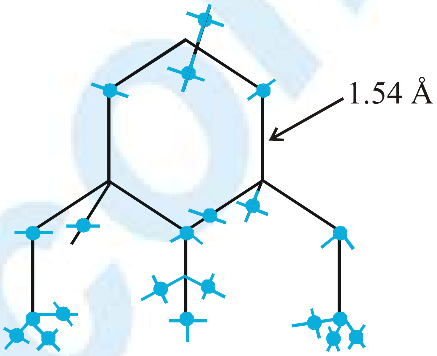
(ii) In diamond each carbon is in sp^3 hybridized state and is linked to four other neighbouring carbon atoms held at the corners of a regular tetrahedron by covalent bonds.

(iii) In this structure C-C distance is 1.54 Å with a bond angle of 109.5°.

(iv) Due to these strong covalent bonds, diamond is the hardest substance having abnormally high melting point (3600° C) and is extremely inert, chemically.

(v) It has very high refractive index (2.5), i.e. light rays are slowed down by the tightly bound electron.

(vi) Due to unavailability of mobile electrons it is non-conductor of electricity.



Crystal structure of diamond

(b) Graphite

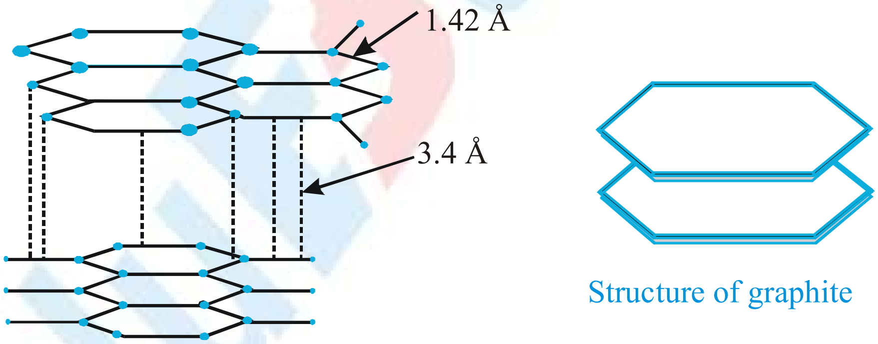
(i) Unlike diamond, it has a two dimensional **laminar** structure.

(ii) The adjacent layers of sheet are held together by weak vander Waal forces.

(iii) Here each carbon atom is in sp^2 hybridised state and is thus attached to three other carbon atoms by three σ bonds forming a hexagonal planar structure.

(iv) The fourth electron present in an unhybridised p-orbital of each carbon atom of a hexagonal unit then overlap with each other to form a pi bond.

(v) The C—C bond length in graphite is shorter (1.42 Å) than that of diamond (1.54Å).



Structure of graphite

(vi) Since π-electrons ($\pi - e^-$) are free to move throughout the entire layers, graphite is a good conductor of electricity. Its conductivity increases with temperature.

(vii) It is a soft **greasy,** dark greyish coloured crystalline solid having density 2.5 g mL^{-1}

(viii) Since it leaves a black mark on paper it is called black lead or plumbago

(ix) It is thermodynamically more stable than diamond and its free energy of formation is 1.9 kJ less than diamond.

$$\text{Graphite} \xrightarrow[\text{50,000 - 60,000 atm}]{1600°\text{C}} \text{diamond}$$

Amorphous

(c) Fullerenes

(i) Discovered by smily & robert curl (Noble prize - 1996)

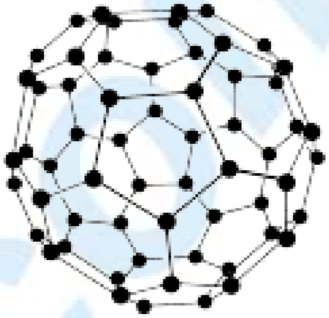
(ii) Fullerene normally contain C_{60} with smaller quantity of C_{70}

Structure of C60

(i) C_{60} is also called buckminster fullerene in honour of robert buckminster fuller.

(ii) Shape of C_{60} is Soccer ball & C_{70} is Rugby ball.

(iii) C_{70} & C_{60} having hexagonal & pentagonal unit.



(B) AMORPHOUS

Coal

(a) Naturally form & artificially.

(b) It is found in different form.

Ex. Peat, Lignite, Bituminous, Anthracite

(c) Max percent of C = Anthracite   Min percent of C = Peat

(d) Calorific value Max in = Anthracite

2. CARBIDES

Carbides are of three types according to the type of bonding

(a) Salt like carbides (ionic bonding)

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

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

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

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

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

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

Acetylides : These are the carbides which yield acetylene on hydrolysis. They contain the ion C_2^{2-}

Ex. CaC_2, BaC_2 and MgC_2

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

Note: Most of these carbides have ionic NaCl - type of structure.

Allylides : These carbides give methylacetylene or allylene ($CH_3-C\equiv CH$). On hydrolysis they contain C_3^{4-} ions.

The only example of this class is Mg_2C_3

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

(b) Covalent carbides (giant molecular structure)

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

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

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

(c) Alloy type or interstitial type carbide

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

3. CARBON MONOXIDE (CO)

PREPARATION

(a) It is invaribely present in automobile exhaust gas.

$$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$$

(b) Pure CO

$$HCOOH \xrightarrow{H_2SO_4} CO + H_2O$$

(c) Industrially it is obtained in the form of water gas and producer gas when air (moist) is passed over a bed of white hot coke.

$$2\,C + O_2 + 4N_2 \longrightarrow 2CO + 4N_2$$

$$C + H_2O \longrightarrow CO + H_2 \text{ (water gas)}$$

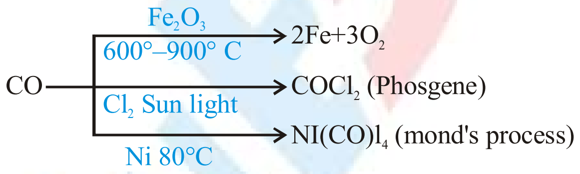
PROPERTIES

(a) It is highly poisonous as it combines with haemoglobin to form carboxy haemoglobin which is not capable to absorb oxygen.

(b) It burns with blue flame to form CO_2. This is an exothermic process

$$2\,CO + O_2 \longrightarrow 2CO_2 + \text{Heat}$$

(c) Chemical reactions



How to detect

Burns with blue flame CO is passed through $PdCl_2$ solution giving rise to black ppt.

$$CO + PdCl_2 + H_2O \longrightarrow CO_2\uparrow + \underset{\text{Black metallic deposition}}{Pd\downarrow} + 2HCl$$

How to estimate

$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

What are its absorbers

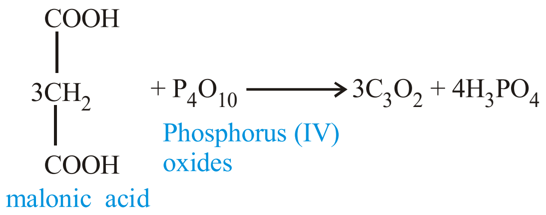
$$Cu_2Cl_2 : CuCl + CO + 2H_2O \longrightarrow [CuCl(CO)(H_2O)_2]$$

4. CARBON SUB OXIDE

$O=C=C=C=O$

PREPARATION

By heating malonic acid with phosphorus penta oxide



$$3\,\begin{matrix}\text{COOH}\\ |\\ CH_2\\ |\\ \text{COOH}\end{matrix} + P_4O_{10} \longrightarrow 3C_3O_2 + 4H_3PO_4$$

malonic acid

Phosphorus (IV) oxides

PROPERTIES

(a) Colourless gas, Boiling point 6°C

(b) Very readily polymerises to give coloured salts.

(c) It decomposes at 200°C

$$C_3O_2 \xrightarrow{200°C} CO_2 + 2C$$

5. SILICON (Si)

Silicon is the second most abundant (27.2%) element after oxygen (45.5%) in the earth's crust. It does not occur free in nature but in the combined state, it occurs widely in form of silica and silicates. All mineral rocks, clays and soils are built of silicates of magnesium, aluminium, potassium or iron. Aluminium silicate is however the most common constituent of rocks and clays.

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

(a) Feldspar – $K_2O.Al_2O_3.6SiO_2$

(b) Kaolinite – $Al_2O_3.\,2\,SiO_2.\,2H_2O$

(c) Asbestos – $CaO.\,3MgO.4SiO_2$

PREPARATION

(a) **From silica (sand) :** Elemental silicon is obtained by the reduction of silica (SiO_2) with high purity coke in an electric furnace.

$$SiO_2\,(s) + 2C\,(s) \longrightarrow Si\,(s) + 2CO\,(g)$$

(b) **From silicon tetrachloride ($SiCl_4$) or silicon chloroform ($SiHCl_3$) :** Is obtained by reduction of highly purified silicon tetrachloride or silicon chloroform with dihydrogen.

$$SiCl_4\,(\bullet) + 2H_2\,(g) \longrightarrow Si\,(s) + 4HCl\,(g)$$

$$SiHCl_3\,(s) + H_2\,(g) \longrightarrow Si\,(s) + 3HCl\,(g)$$

PHYSICAL PROPERTIES

(a) Elemental silicon is very hard having diamond like Structure.

(b) It has shining luster with a melting point of 1793 K and boiling point of about 3550 K.

(c) Silicon exists in three isotopes, i.e. ${}^{28}_{14}Si$, ${}^{29}_{14}Si$ and ${}^{30}_{14}Si$ but ${}^{28}_{14}Si$ is the most common isotope.

CHEMICAL PROPERTIES

Silicon is particularly unreactive at room temperature towards most of the elements except fluorine. Some important chemical reactions of silicon are discussed below

(a) **Action of air :** Silicon reacts with oxygen of air at 1173 K to form silicon dioxide and with nitrogen of air at 1673 K to form silicon nitride.

$$Si(s) + O_2(g) \xrightarrow{1173\ K} \underset{\text{(Silicon dioxide)}}{SiO_2}$$

$$3Si(s) + 2N_2(g) \xrightarrow{1673\ K} \underset{\text{Silicon nitride}}{Si_3N_4(s)}$$

(b) **Action of steam :** It is slowly attacked by steam when heated to redness liberating dihydrogen gas.

$$Si(s) + 2H_2O(g) \xrightarrow{\text{redness}} Si_3O_2 + 2H_2(g)$$

(c) **Reaction with halogens** : It burns spontaneously in fluorine gas at room temperature to form silicon tetrafluoride (SiF_4).

$$Si(s) + 2F_2(g) \xrightarrow{\text{Room Temperature}} SiF_4(\bullet)$$

However, with other halogens, it combines at high temperatures forming tetrahalides.

(d) **Reaction with carbon :** Silicon combines with carbon at 2500 K forming silicon carbide (SiC) known as carborundum.

$$Si(s) + C(s) \xrightarrow{2500\ K} SiC(s)$$

carborundum is an extremely hard substance next only to diamond. It is mainly used as an abrasive and as a refractory material.

USES

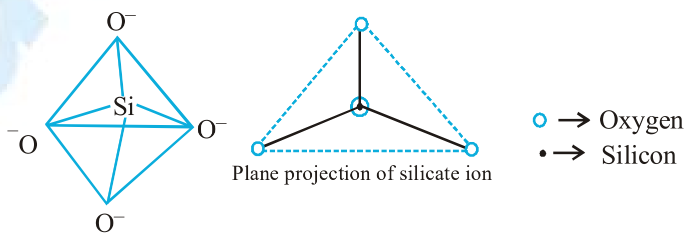
(a) Silicon is added to steel as such or more usually in form of ferrosilicon (an alloy of Fe and Si) to make it acid-resistant.

(b) High purity silicon is used as semiconductors in electronic devices such as transistors.

(c) It is used in the preparation of alloys such as silicon-bronze, magnesium silicon bronze and ferrosilicon.

6. SILICATES

Silicates have basic unit of SiO_4^{4-}, each silicon atom is bonded with four oxide ions tetrahedrally.



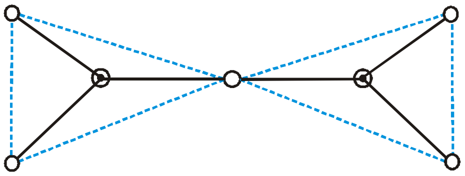
Plane projection of silicate ion

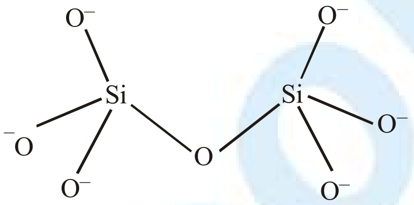
There are following types of silicates

(a) Orthosilicates : These silicates contain single **discrete** unit of SiO_4^{4-} tetrahedral.

Ex. Willemite $[Zn_2SiO_4]$

(b) Pyrosilicates



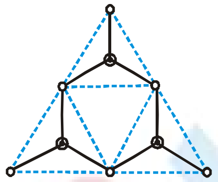


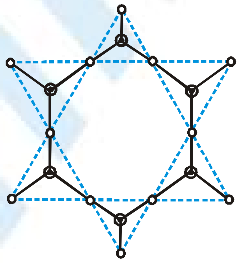
These silicates contain two units of SiO_4^{4-} joined along a corner containing oxygen atom. These are also called as island silicate.

Ex. Hemimorphite $Zn_3(Si_2O_7)Zn(OH)_2 \cdot H_2O$, Pyrosilicates ion $Si_2O_7^{6-}$

(c) Cyclic structure : Cyclic or ring silicate having general formula $(SiO_3^{2-})_n$ or $(SiO_3)_n^{2n-}$

Structure and example of cyclic silicates containing $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$ ions are given below

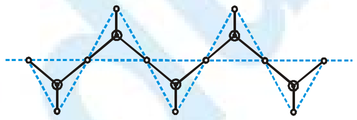




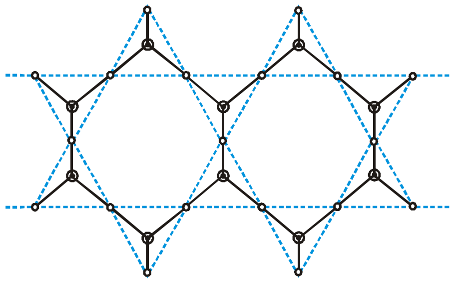
Ex. Beryl $Be_3Al_2Si_6O_{18}$

(d) Chain silicates : Chain silicates are formed by sharing two oxygen atoms by each tetrahedral. Anions of chain silicate have two general formula.

(i) $(SiO_3)_n^{2n-}$



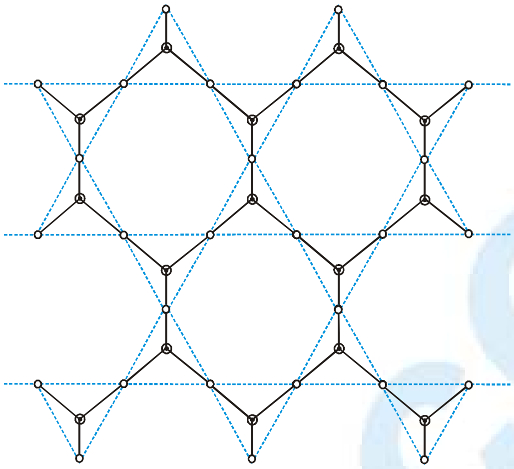
(ii) $(Si_4O_{11})_n^{6n-}$



Ex. Spodumene $Li_2Al(SiO_3)_2$, Tremolite $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$

(e) Two dimensional sheet silicates : In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent SiO_4^{4-} tetrahedral, such sharing forms two dimensional sheet structure with general formula $(Si_2O_5)_n^{2n-}$

Ex. Talc $Mg(Si_2O_5)_2Mg(OH)_2$



(f) **Three dimensional sheet silicates :** These silicates involve all four oxygen atoms in sharing with adjacent SiO_4^{4-} tetrahedral.

Ex. Quartz, Zeolites and Ultramarines

7. SILANE

(a) Only these two are found. SiH_4 & Si_2H_6 (Formula – Si_nH_{2n+2}).

(b) Higher molecules are not formed. So, Si can't show catenation property.

$$\text{Hot Mg} + \text{Si–vap} \longrightarrow Mg_2Si \xrightarrow{\text{dil. } H_2SO_4} MgSO_4 + SiH_4 + Si_2H_6 + \ldots$$

(c) SiH_4 is more reactive than CH_4. due to following reason

(i) $Si^{\delta+} - H^{\delta-}$ and $C^{\delta-} - H^{\delta+}$

C-electronegative than H

Si less electronegative than H

So bond polarity is reversed when Nu^- attacks, so it faces repulsion in C but not in Si

(ii) Silicon is having vacant d orbital which is not in case of carbon

(iii) Silicon is larger in size compared to C. By which the incoming Nu^- doesn't face any steric hindrance to attack at Si whereas CH_4 is tightly held from all sides.

8. SILICONES

These are organosilicon polymers containing R_2SiO repeating units and empirical formula analogous to ketone (R_2CO)

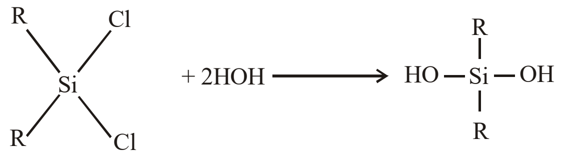
$$-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-\text{linkage}$$

Alkyl substituted : These are formed by hydrolysis of alkyl chlorosilanes and their polymerisation. The alkyl or aryl substituted chlorosilanes are prepared by the reaction of Grignard reagent and silicon tetrachlorides.

Organic polymers containing silicon in them are called as **silicones**.

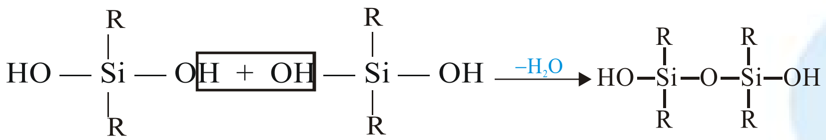
(a) **Straight chain silicone**

$$2RCl \xrightarrow[\text{Cu}]{\text{Si}} R_2SiCl_2$$



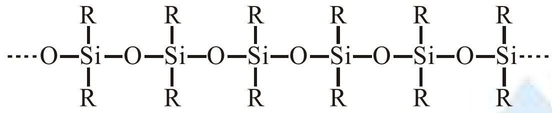
Dialkyldichloro Silane

(b)



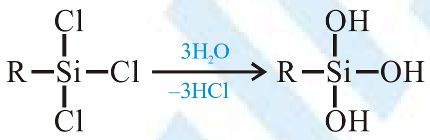
$$HO-\overset{R}{\underset{R}{Si}}-O\boxed{H + OH}-\overset{R}{\underset{R}{Si}}-OH \xrightarrow{-H_2O} HO-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-OH$$

The terminal 'OH' groups which are active, allow the polymerisation reaction to continue and the length of the chain continues to increase

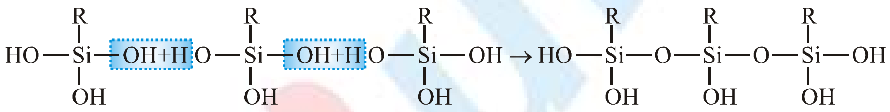


$$\cdots O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}\cdots$$

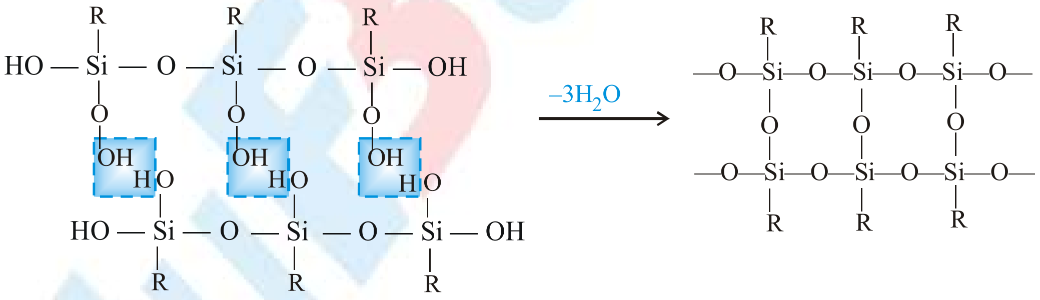
(c) A complex **cross-linked** polymer is obtained on the hydrolysis of alkyl trichloro silane.



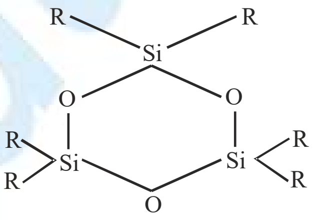
$$R-\overset{Cl}{\underset{Cl}{Si}}-Cl \xrightarrow[-3HCl]{3H_2O} R-\overset{OH}{\underset{OH}{Si}}-OH$$



$$HO-\overset{R}{\underset{OH}{Si}}-\boxed{OH + H}O-\overset{R}{\underset{OH}{Si}}-\boxed{OH + H}O-\overset{R}{\underset{OH}{Si}}-OH \rightarrow HO-\overset{R}{\underset{OH}{Si}}-O-\overset{R}{\underset{OH}{Si}}-O-\overset{R}{\underset{OH}{Si}}-OH$$



(d) Cyclic (ring) silicones are formed when water is eliminated from the terminal –OH groups of linear silicones.



R_3SiCl on hydrolysis forms only a dimer

$$R_3SiO\boxed{H + OH}SiR_3 \longrightarrow R_3Si-O-SiR_3$$

USES

(a) They are used as greases, varnishes and resins.

(b) As they are water repellants, they are used for water-proofing.

(c) They are good electric insulators.

9. SILICA (SiO_2)

Silica or silicon dioxide occurs in nature in the free state as sand, quartz and flint and in the combined state as silicates like Feldspar $K_2O.Al_2O_3.6SiO_2$, Kaolinite $Al_2O_3.2SiO_2.2H_2O$ etc.

PROPERTIES

(a) Pure silica is colourless, but sand is usually coloured yellow or brown due to the presence of ferric oxide as an impurity.

(b) Silicon dioxide is insoluble in water and all acids except hydrofluoric acid.

$$SiO_2(s) + 4HF(\bullet) \longrightarrow SiF_4(\bullet) + 2H_2O(\bullet)$$

(c) It also combines with metallic oxides at high temperature giving silicates.

$$SiO_2(s) + CaO(s) \xrightarrow{\Delta} CaSiO_3(s)$$

(d) When silica is heated strongly with metallic salts, silicates are formed and the volatile oxides are driven off as vapours.

$$SiO_2(s) + Na_2CO_3(s) \longrightarrow Na_2SiO_3(s) + CO_2(g)$$

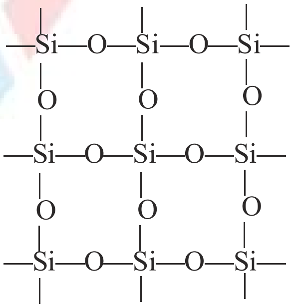
$$SiO_2(s) + Na_2SO_4(s) \longrightarrow Na_2SiO_3(s) + SO_3(g)$$

$$3SiO_2(s) + Ca_3(PO_4)_2(s) \longrightarrow 3\,CaSiO_3(s) + P_2O_5(g)$$

The first two examples quoted here are important in glass making.

Structures of Silica

Silica has a three-dimensional network structure. In silica, silicon is sp^3-hybridized and is thus linked to four oxygen atoms and each oxygen atom is linked to two silicon atoms forming a three-dimensional giant molecule as shown in figure. This three-dimensional network structure Imparts stability to SiO_2 crystal and hence a large amount of energy is required to break the crystal resulting in high melting point.



USES

(a) Sand is used in large quantities to make the cement.

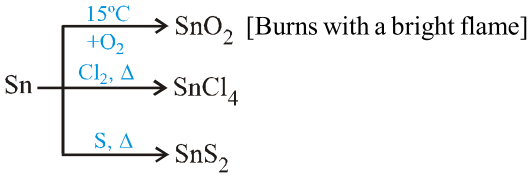
(b) Being transparent to ultraviolet light, large crystal of quartz are used for making lenses for optical instruments and for controlling the frequency of radio-transmitters.

(c) Powdered quartz is used for making silica bricks.

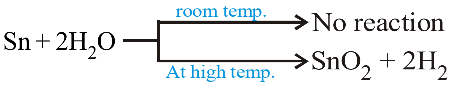
(d) Silica gel ($SiO_2.xH_2O$) is used as a desiccate (for absorbing moisture) and as an adsorbent in chromatography.

10. COMPOUNDS OF Sn (Tin)/ Lead

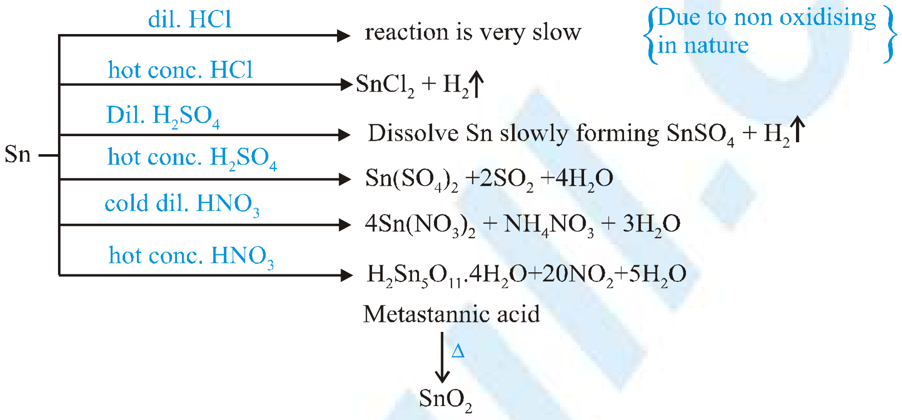
(a)



(b)



(c) Reaction with acid

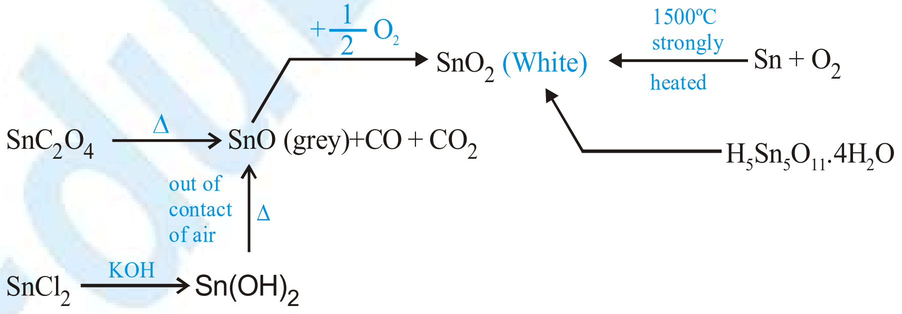


(d) $Sn + 2NaOH + H_2O \longrightarrow \underset{\text{Sodium stannate}}{Na_2SnO_3} + 2H_2\uparrow$

Note: KOH [In absence of air] Na_2SnO_2 forms and in contact with air it readily converts into Na_2SnO_3

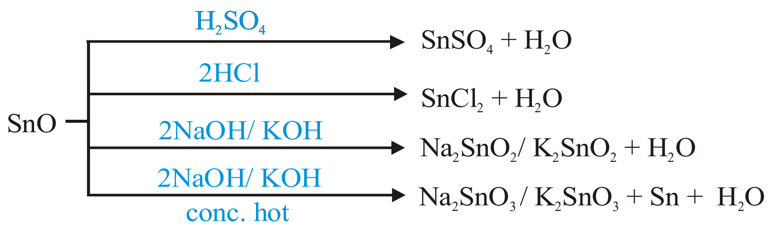
11. SnO (GREY) and SnO_2 (WHITE)

PREPARATION



PROPERTIES

Both are amphoteric in nature



$$Bi(OH)_3 + [Sn(OH)_4]^{2-} \longrightarrow \underset{\text{black}}{Bi\downarrow} + [Sn(OH)_6]^{2-}$$

$$SnO_2 + 2H_2SO_4 \longrightarrow Sn(SO_4)_2 + 2H_2O$$

(Soluble only in hot conc. H_2SO_4)

$$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$$

$$SnO_2 + 4S + 2Na_2CO_3 \longrightarrow Na_2SnS_3 + Na_2SO_4 + 2CO_2$$

Note : insoluble in all acids even if in aqua ragia.

12. STANNOUS CHLORIDE ($SnCl_2$)

PREPARATION

(a) $Sn + 2HCl \xrightarrow{\text{hot conc.}} SnCl_2 + H_2\uparrow$

(b) Anhydrous salt cannot be obtained by heating the hydrated salt as it undergoes hydrolysis and a white solid of tin hydroxy chloride is formed.

$$SnCl_2 . 2H_2O \longrightarrow Sn(OH)Cl + HCl\uparrow + H_2O\uparrow \Rightarrow \text{Hence anh. } SnCl_2 \text{ cannot be obtained.}$$

$$\downarrow$$

$$SnO + HCl\uparrow$$

$$SnCl_4 + 4H_2O \longrightarrow Sn(OH)_4 + 4HCl\uparrow \text{ fumes comes out}$$

(c) A piece of Sn is always added to preserve a solution fo $SnCl_2$.

$$6\,SnCl_2 + 2H_2O + O_2 \longrightarrow 2\,SnCl_4 + 4Sn\,(OH)\,Cl\downarrow \text{ (white ppt)}$$

$$SnCl_4 + Sn \longrightarrow 2SnCl_2$$

PROPERTIES

(a) $SnCl_2 + HCl \longrightarrow \underbrace{HSnCl_3 \xrightarrow{HCl} H_2SnCl_4}_{\text{Chlorostannous acid}}$

(b) Reducing Properties

$$Sn^{+2} + 2Fe^{+3} \longrightarrow 2Fe^{+2} + Sn^{+4}$$

$$2Cu^{+2} + Sn^{+2} \longrightarrow 2Cu^{+} + Sn^{+4}$$

$$Hg^{+2} + Sn^{+2} \longrightarrow Hg\downarrow + Sn^{+4}$$

$$C_6H_5NO_2 + 3SnCl_2 + 6HCl \longrightarrow C_6H_5NH_2 + 3SnCl_4 + 2H_2O$$

$$K_2Cr_2O_7 + SnCl_2 + HCl \longrightarrow Cr^{+3} + Sn^{+4} + KCl + H_2O$$

(c) Readily combines with $I_2 \Rightarrow SnCl_2I_2 \Rightarrow$ This reaction is used to estimate tin.

13. STANNIC CHLORIDE ($SnCl_4$)

PREPARATION

(a) $Sn + 2Cl_2 \xrightarrow{\text{excess}} SnCl_4$

(Molten) (dry)

(b) $2HgCl_2 + SnCl_2 \longrightarrow 2Hg\downarrow + SnCl_4$

(c) $Sn + \text{Aqua ragia} \longrightarrow SnCl_4 + NO + H_2O$

PROPERTIES

(a) $SnCl_4 + 2HCl \longrightarrow H_2SnCl_6$ (Hexachloro stannic(IV) acid)

(b) $SnCl_4 + 2NH_4Cl \longrightarrow (NH_4)_2SnCl_6$

Note: $SnCl_4.5H_2O$ is known as butter of tin ⇒ used as mordant.

$(NH_4)_2SnCl_6$ is known as 'Pink salt' ⇒ used as calico printing.

Mosaic gold : SnS_2 yellow crystalline substance

$Sn + 4NH_4Cl \longrightarrow (NH_4)_2SnCl_4 + 2NH_3 + H_2$

$2(NH_4)_2SnCl_4 + 2S \longrightarrow SnS_2 + 2NH_4Cl + (NH_4)_2SnCl_6$

Distinction of Sn^{+2}/Sn^{+4}

(a) H_2S (b) Hg^{+2} (c) $Fe^{+3} + [K_3Fe(CN)_6] \xrightarrow{Sn^{+2}}$ Blue ppt.

14. OXIDES OF LEAD

(a) Lead monoxide (pbo)

PREPARATION : It exists in two forms.

$PbO \longrightarrow$ Yellow (Massicot) $\xrightarrow[\text{and powdered}]{\text{Fused, cooled}}$ Litharge

$PbO \longrightarrow$ Reddish yellow (litharge)

Laboratory preparetion

$2\,Pb(NO_3)_2 \longrightarrow 2PbO + 4\,NO_2 + O_2$

$PbO_2 \xrightarrow{\text{above } 600^\circ C}$

$Pb_3O_4 \longrightarrow$

$Pb_2O_3 \longrightarrow$

PbO, hot oxide easily reduced to Pb by H_2 or C

$\xrightarrow{H_2} Pb + H_2O$

$\xrightarrow{C} Pb + CO$

PROPERTIES : It is an amphoteric oxide insoluble in water.

$PbO + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O$

$PbO + 2NaOH \longrightarrow Na_2PbO_2 + H_2O$

(b) Sesquioxide (Pb_2O_3)

PREPARATION

$2Pb + NaOCl \longrightarrow Pb_2O_3 + NaCl$

hot sol^n. of NaOH Limited amount

PROPERTIES

$Pb_2O_3 + 2HNO_3 \longrightarrow PbO_2 + Pb(NO_3)_2 + H_2O$

Note: This reaction suggests that Pb_2O_3 contains PbO_2.

(c) Red lead (Minium or sindhur) (Pb_3O_4)

PREPARATION

$$6\,PbO + O_2 \underset{>470°C}{\overset{340°C}{\rightleftharpoons}} Pb_3O_4$$

PROPERTIES

$$2Pb_3O_4 + 6H_2SO_4 \longrightarrow 6PbSO_4 + 6H_2O + O_2$$

$$Pb_3O_4 + 8\,HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2$$

$$Pb_3O_4 + 4CO \longrightarrow 3Pb + 4CO_2$$

(d) Lead Dioxide (PbO_2)

Preparetion

(i) $Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$

(ii) $(CH_3COO)_2Pb + Ca(OH)_2 \longrightarrow Pb(OH)_2 + (CH_3COO)_2Ca$

(iii) $2Pb(OH)_2 + \underset{\text{Calcium hypochlorite}}{2Ca(OCl)_2} \longrightarrow 2PbO_2 + CaCl_2 + 2H_2O + O_2$

(iv) $Pb(OH)_2 + \underset{\text{Bleaching powder}}{CaOCl_2} \longrightarrow PbO_2 + CaCl_2 + H_2O$

PROPERTIES : Insoluble in water and HNO_3, But reacts with (hot conc.) HCl/H_2SO_4 and in hot NaOH/KOH.

$$PbO_2 + 4HCl \xrightarrow{\text{Cold conc.}} PbCl_2 + Cl_2 + 2H_2O$$

$$2PbO_2 + 2H_2SO_4 \xrightarrow{\text{conc.}} 2PbSO_4 + 2H_2O + O_2$$

$$PbO_2 + 2NaOH \xrightarrow[\text{conc. sol.}]{\text{heat}} \underset{\text{Sodium plumbate}}{Na_2PbO_3} + 4H_2O$$

$$PbO_2 + SO_2 \longrightarrow PbSO_4\text{[spontaneously]} \quad \left\{\begin{array}{l} PbS + 4O_3 \longrightarrow PbSO_4 + 4O_2 \\ PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O \end{array}\right\}$$

$$PbO_2 + 2HNO_3 + (COOH)_2 \longrightarrow Pb(NO_3)_2 + 2CO_2 + 2H_2O$$

$$2MnSO_4 + 5PbO_2 + 6\,HNO_3 \longrightarrow 3Pb(NO_3)_2 + 2PbSO_4\downarrow + 2HMnO_4 + 2\,H_2O$$

Note: PbO_2 is a powerful oxidising agent.

15. LEAD CHLORIDE/PLUMBUS CHLORIDE ($PbCl_2$)

$PbCl_2$ Exists as $H_2[PbCl_6]$

$$PbO_2 + 4HCl \longrightarrow PbCl_4 + 2H_2O$$

{ice cold conc. saturated with Cl_2}

$$PbCl_4 + 2HCl \longrightarrow H_2[PbCl_6]$$

16. LEAD TETRAACETATE

PREPARATION

$Pb_3O_4 + 8AcOH$ (hot glacial) $\longrightarrow Pb(OAc)_4 + 2Pb(OAc)_2 + 4H_2O$

$Pb(OAc)_2$ is also converted into $Pb(OAc)_4$ by passing into Cl_2

$2Pb(OAc)_2 + Cl_2 \longrightarrow Pb(OAc)_4 + PbCl_2\downarrow$

PROPERTIES : It is used as oxidising agent in organic chemistry to oxidise 1, 2-diol to aldehydes and Ketones.

$$\begin{array}{l} RCH(OH) \\ | \\ RCH(OH) \end{array} \xrightarrow{[O]} 2RCHO + H_2O$$

17. TETRAETHYL LEAD

$4\,Na - Pb(\text{alloy } 10\% - Na) + 4C_2H_5Cl\,(\text{vap.}) \longrightarrow 3Pb + Pb(Et)_4 + 4NaCl$

- It is antiknocking agent.
- Pb is used as a lead storage cell.

$$Pb + PbO_2 + 2H_2SO_4 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2PbSO_4 + 2H_2O$$

NITROGEN FAMILY

1. NITROGEN (N_2)

PREPARATION

(a) $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

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

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

$2NaN_3 \xrightarrow{\Delta} 2Na + 3N_2$ } by this method

(d) $2\,NH_3 + 3NaOCl \xrightarrow{\Delta} N_2 + 3NaCl + 3H_2O$

(e) $2NO + \underset{\text{red over heated}}{2Cu} \longrightarrow \underset{\text{Black}}{2CuO} + N_2$

(f) Cl_2 passed into liquor NH_3

$3Cl_2 + 2NH_3 \longrightarrow N_2 + 6HCl$

$6NH_3 + 6HCl \longrightarrow 6NH_4Cl$

$3Cl_2 + 8NH_3 \longrightarrow N_2 + 6NH_4Cl$

In this method NH_3 conc. should not be lowered down beyond an particular limit.

$3Cl_2 + NH_3 \longrightarrow NCl_3 + 3HCl$

(Trimendously explosive)

PROPERTIES

(a) It is inert due to high bond energy.

(b) It is absorbed by hot metal like Ca, Mg, Al etc.

$$3Ca + N_2 \longrightarrow Ca_3N_2$$

$$2Al + N_2 \longrightarrow 2AlN$$

$$Al_2O_3 + 3C + N_2 \xrightarrow{\Delta} 2AlN + 3CO$$

Inorganic graphite (BN)x : White slippery solid having 2D-sheet structure.

$$(BN)_x \xrightarrow{3000°C} (BN)_x$$

3–D network structure similar to diamond (Borazon) which is harder than diamond and used for dimond cutting.

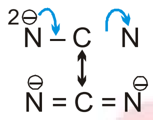
$$Na_2B_4O_7 + 2NH_4Cl \xrightarrow{\Delta} 2NaCl + 2NH_3 + 2B_2O_3 + H_2O$$

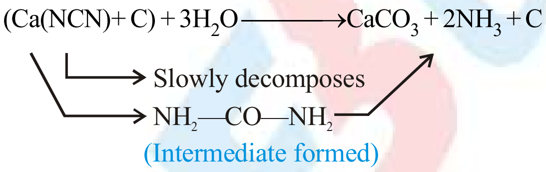
$$B_2O_3 + 2NH_3 \xrightarrow{\Delta} 2BN + 3H_2O$$

(c) N_2 can be absorbed by calcium carbide at the temp around 1000°C

$$CaC_2 + N_2 \xrightarrow{1000°C} \underset{\text{nitrolim}}{CaNCN} \text{ (It is very good fertiliser)}$$

Cyanamide ion





$$(Ca(NCN) + C) + 3H_2O \longrightarrow CaCO_3 + 2NH_3 + C$$

2. AMMONIA (NH_3)

PREPARATION

(a) Nitrate or nitrite reduction : $NO_3^-/NO_2^- + Zn/Al + NaOH \longrightarrow NH_3 + [Zn(OH)_4]^{2-}/[Al(OH)_4]^-$

(b) Metal nitride hydrolysis : $N^{3-} + 3H_2O \longrightarrow NH_3\uparrow + 3OH^-$

(c) Haber's process : $N_2 + 3H_2 \xrightarrow[200\text{ - }1000\text{ atm}]{450°C} 2NH_3$

catalyst Fe/Mo

Note: NH_3 can't be dried by H_2SO_4, P_2O_5 and anhydrous $CaCl_2$ because –

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

$$H_2O + NH_3 + P_2O_5 \longrightarrow (NH_4)_3PO_4$$

$CaCl_2 + 8NH_3 \longrightarrow CaCl_2.8\,NH_3$ (forms adduct)

Quick lime is used for this purpose

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

$$\left.\begin{matrix} \\ NH_3\ (base) \end{matrix}\right\}\text{Hence nointeraction}$$

PROPERTIES

(a) It dissolves several electropositive metals like Li, Na, K, Rb, Cs, Sr, Ba etc.

Ex. K in liq $NH_3 \Rightarrow$ (i) Blue in colour

(ii) Conducts electricity

(iii) Having reducing property

$$\begin{tikzcd} K \arrow[r] & K^+ \arrow[d] & + & e^- \arrow[d] \\ & K^+(NH_3)_n & & \underset{\text{solvated } e^-}{e\,(NH_3)_x} \end{tikzcd}$$

It is the cause for above property

$K_2[Ni(CN)_4] \xrightarrow[NH_3]{\text{K in liq}} K_4[Ni(CN)_4]$

Squareplanar Tetrahedral

(b) $Ag(NO_3)\,(aq) + BaCl_2\,(aq) \longrightarrow AgCl\downarrow + Ba(NO_3)_2$

$$\begin{tikzcd} & AgCl\downarrow + Ba(NO_3)_2 \arrow[dl] \arrow[dr] & \\ \underset{Ba(NO_3)_2}{\text{Filtrate}} & & \underset{AgCl}{\text{Residue}} \arrow[d, "\text{liq } NH_3"] \\ & & Cl^- + [Ag(NH_3)_2]^+ \arrow[r, "Ba(NO_3)_2", "\text{crystal}"'] & BaCl_2{}^- + [Ag(NH_3)_2]^+ + NO_3^- \end{tikzcd}$$

(c) CH_3COOH is strong acid in liquid NH_3 while in water is weak acid.

$AcOH \rightleftharpoons AcO^- + H^+$

$NH_3 + H^+ \rightleftharpoons NH_4^+$ and $H_2O + H^+ \longrightarrow H_3O^+$

Basisity order $NH_3 > H_2O$

(d) Hydrolysis and Ammonolysis occurs is a same way.

$SiCl_4 + 4H_2O \longrightarrow 4HCl + Si(OH)_4 \xrightarrow{\Delta} Si_3O_2 + 2H_2O$

$SiCl_4 + 8NH_3 \longrightarrow 4NH_4Cl + Si(NH_2)_4 \xrightarrow{\Delta} Si_3N_2 + NH_3\uparrow$

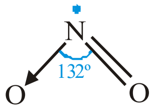
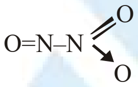
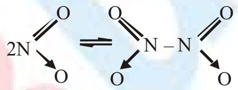
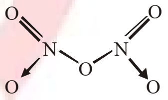
Rate of hydrolysis and Ammonolysis will be affected by the presence of HCl vapour & NH_4Cl vapour respectively.

(e) **NH_4^+– Salts PREPARATION**

$$\begin{tikzcd} \text{Gypsum suspension saturated with } NH_3 \text{ and } CO_2 \text{ passed} \arrow[r] & CaCO_3 + (NH_4)_2SO_4 \arrow[r, "NaNO_3"] \arrow[d, "NaCl"] & NH_4NO_3 \\ NH_4(NO_2) & NH_4Cl \arrow[l, "NaNO_2"'] \arrow[r, "CaCO_3"] & (NH_4)_2CO_3 \end{tikzcd}$$

3. OXIDES OF NITROGEN

PREPARATION and PROPERTIES of Oxides of Nitrogen

Formula	Name	Preparation & Structure	Properties
N_2O	Dinitrogen (Nitrous oxide) Laughing gas	$NH_4NO_3 \rightarrow N_2O + 2H_2O$ $N \equiv N \rightarrow O$ (sp, Linear polar molecule)	Colourless gas, rather unreactive, diamegnatic neutral to litmus
NO	Nitrogen monoxide (Nitric oxide)	(a) $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO$ (b) $4NH_3 + 5O_2 \xrightarrow[900^\circ C]{Pt} 4NO + 6H_2O$	Colourless gas, paramagnetic, Neutral to litmus
NO_2	Nitrogen dioxide Mixed anhydride	$Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$ 	Brown gas, reactive, paramagnetic, angular and polar $2NO_2 \xrightarrow{H_2O} HNO_2 + HNO_3$
N_2O_3	Dinitrogen trioxide	$NO + NO_2\ \ N_2O_3 \underset{Room\ T}{\overset{Low\ T}{\rightleftharpoons}} N_2O_3$ $O = N - O - N = O$ or 	Dark blue in liquid (–30ºC) or solid state, unstable in the gas phase $N_2O_3 \xrightarrow{H_2O} 2HNO_2$
N_2O_4	Dinitrogen tetroxide	$2NO_2 \overset{Low\ T}{\rightleftharpoons} N_2O_4$ 	Colourless, exists in equilibrium with NO_2 both in the gaseous and liquid state, in solid state, N_2O_4 is unstable.
N_2O_5	Dinitrogen pentoxide	$2HNO_3 + P_2O_5 \rightarrow H_2O + N_2O_5$ $H_2O + P_2O_5 \rightarrow 2HPO_3$ 	No existance in gas phase, in the solid state exists as nitronium nitrate $[NO_2]^+ [NO_3]^-$

4. NITROUS ACID (HNO_2)

PREPARATION

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

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

PROPERTIES

(a) **Oxidising property** : Because of its easy oxidation to liberate nascent oxygen, it acts as a strong oxidant

$$2HNO_2 \longrightarrow H_2O + 2NO + (O)$$

$$2KI + 2HNO_2 + 2HCl \longrightarrow 2KCl + 2H_2O + 2NO + I_2$$

$$SnCl_2 + 2HNO_2 + 2HCl \longrightarrow SnCl_4 + 2NO + 2H_2O$$

$$SO_2 + 2HNO_2 \longrightarrow H_2SO_4 + 2NO$$

$$H_2S + 2HNO_2 \longrightarrow 2H_2O + S \downarrow + 2NO$$

$$2FeSO_4 + 2HNO_2 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NO + 2H_2O$$

$$Na_3AsO_3 + 2HNO_2 \longrightarrow Na_3AsO_4 + 2NO + H_2O$$

(b) Reducing property : Nitrous acid also acts as a reducing agent as it can be oxidised into nitric acid.

$$HNO_2 + (O) \longrightarrow HNO_3$$

$$2KMnO_4 + 5HNO_2 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O$$

$$K_2Cr_2O_7 + 3HNO_2 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3HNO_3 + 4H_2O$$

$$H_2O_2 + HNO_2 \longrightarrow H_2O + HNO_3$$

$$2HNO_2 + \underset{\text{Urea}}{NH_2CONH_2} \longrightarrow 2N_2 + CO_2 + 3H_2O$$

$$HNO_2 + NH_3 \longrightarrow NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

$$HNO_2 + C_2H_5NH_2 \longrightarrow C_2H_5OH + N_2 + H_2O$$

$$HNO_2 + C_6H_5\text{-}NH_2 \cdot HCl \xrightarrow{< 5^\circ C} \underset{\text{Benzene diazonium chloride}}{C_6H_5N = NCl} + 2H_2O$$

5. NITRIC ACID (HNO_3)

It was named aqua fortis (means strong water) by alchemists.

PREPARATION

(a) Laboratory Method

$$KNO_3 + \text{conc.}\ H_2SO_4 \longrightarrow KHSO_4 + HNO_3\ (\text{vap})$$

vapours of nitric acid evolved are condensed in a glass receiver.

(b) Industrial PREPARATION

(i) Birkeland Eyde Process or arc process

Step 1 $N_2 + O_2 \xrightarrow[\text{Electric Arc}]{3000^\circ C} 2NO - \text{heat}$

Step 2 $NO + O_2 \longrightarrow NO_2$

Step 3 $NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$

Step 4 $HNO_2 \longrightarrow HNO_3 + NO + H_2O$

(ii) Ostwald's Process

Step 1 $NH_3 + O_2 \xrightarrow[700\text{ - }800^\circ C]{\text{Pt. gauze}} 2NO - \text{heat}$

Step 2 $NO + O_2 \longrightarrow NO_2$

Step 3 $NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$

Step 4 $HNO_2 \longrightarrow HNO_3 + NO + H_2O$

PHYSICAL PROPERTIES

Nitric acid usually acquires yellow colour due to its decomposition by sunlight into NO_2.

$$4HNO_3 \xrightarrow{\text{sunlight}} 4NO_2 + 2H_2O + O_2$$

The yellow colour of the acid can be removed by warming it to 60-80°C and bubbling dry air through it. it has extremely corrosive action on the skin and causes painful sores.

CHEMICAL PROPERTIES

It is very strong acid and it exhibits usual properties of acids. It reacts with basic oxides, carbonates, bicarbonates and hydroxides forming corresponding salts.

$$CaO + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O$$

$$Na_2CO_3 + 2HNO_3 \longrightarrow 2NaNO_3 + H_2O + CO_2$$

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

Oxidising nature : Nitric acid acts as a strong oxidising agent as it decomposes to give nascent oxygen easily.

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + O$$

or $$2HNO_3 \longrightarrow H_2O + 2NO + 3O$$

(a) Oxidation of non-metals : The nascent oxygen oxidises various non-metals to their corresponding highest oxyacids.

(i) Sulphur is oxides to sulphuric acid

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

(ii) Carbon is oxidised to carbonic acid

$$C + 4HNO_3 \longrightarrow H_2CO_3 + 4NO_2 + 2H_2O$$

(iii) Phosphorus is oxidised to orthophosphoric acid.

$$2P + 10HNO_3 \xrightarrow{\text{conc. and hot}} 2H_3PO_4 + 10NO_2 + 2H_2O$$

(iv) Iodine is oxidised to iodic acid

$$I_2 + 10HNO_3 \xrightarrow{\text{conc. and hot}} 2HIO_3 + 10NO_2 + 4H_2O$$

(b) Oxidation of metalloids : Metalloids like non-metals also form highest oxyacids

(i) Arsenic is oxidised to arsenic acid

$$As + 5HNO_3 \xrightarrow{\text{conc. and hot}} 2H_3AsO_4 + 5NO_2 + H_2O$$

(ii) Antimony is oxidised to antimonic acid

$$Sb + 5HNO_3 \xrightarrow{\text{conc. and hot}} 2H_3SbO_4 + 5NO_2 + H_2O$$

(iii) Tin is oxidised to meta-stannic acid.

$$Sn + 2HNO_3 \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$$

(c) Oxidiation of compounds

(i) Sulphur dioxide is oxidised to sulphuric acid

$$SO_2 + 2HNO_3 \longrightarrow H_2SO_4 + 2NO_2$$

(ii) Hydrogen sulphide is oxidised to sulphur

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

(iii) Ferrous sulphate is oxidised to ferric sulphate in presence of H_2SO_4

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

(iv) Iodine is liberated from KI.

$$6KI + 8\,HNO_3 \longrightarrow 6KNO_3 + 2NO + 3I_2 + 4H_2O$$

(v) HBr, HI are oxidised to Br_2 and I_2, respectively.

$$2HBr + 2HNO_3 \longrightarrow Br_2 + 2NO_2 + 2H_2O \quad \text{Similarly}$$

$$2HI + 2HNO_3 \longrightarrow I_2 + 2NO_2 + 2H_2O$$

(vi) Ferrous sulphide is oxidised to ferric sulphate

$$FeS + 8HNO_3 \longrightarrow Fe_2(SO_4)_3 + 8NO_2 + 4H_2O$$

(vii) Stannous chloride is oxidised to stannic chloride in presence of HCl

$$2HNO_3 + 14H \longrightarrow \underset{\text{Hydroxylamine}}{NH_2OH} + NH_3 + 5H_2O$$

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

$$7SnCl_2 + 14\,HCl + 3HNO_3 \longrightarrow 7SnCl_4 + NH_2OH + NH_4NO_3 + 5H_2O$$

(viii) Cane sugar is oxidised to oxalic acid

$$C_{12}H_{22}O_{11} + 36\,HNO_3 \longrightarrow 6(COOH)_2 + 36NO_2 + 23H_2O$$

Action on Metals : Nitric acid reacts with most of the metals except noble metals like gold and platinum. Towards its reaction with metals, HNO_3 acts as an acid as well as an oxidising agent. Like Other acids, HNO_3 liberate nascent H from metals which further reduces the nitric acid into number of products like NO, NO_2, N_2O, N_2, NH_2OH or NH_3 according to the following reactions :

$$\text{Metal} + HNO_3 \longrightarrow \text{Nitrate} + H$$

$$2HNO_3 + 2H \longrightarrow 2NO + 2H_2O$$

$$2HNO_3 + 6H \longrightarrow 2NO + 4H_2O$$

$$2HNO_3 + 10H \longrightarrow N_2 + 6H_2O$$

$$2HNO_3 + 16H \longrightarrow 2NH_3 + 6H_2O$$

The progress of the reaction is controlled by a number of factors :

(a) The nature of the metal

(b) The concentration of the acid,

(c) The temperature of the reaction

(d) The presence of other impurities

Concentration of nitric acid	Metal	Main products
Very dilute HNO_3(6%)	Mg, Mn (2%)	H_2 + Metal nitrate
	Fe, Zn, Sn	NH_4NO_3 + metal nitrate + H_2O
Dilute HNO_3 (20%)	Pb, Cu, Ag, Hg	NO + metal nitrate + H_2O
	Fe, Zn	N_2O + metal nitrate + H_2O
	Sn	NH_4NO_3 + $Sn(NO_3)_2$
Conc. HNO_3(70%)	Zn, Fe, Pb, Cu, Ag, Hg	NO_2 + metal nitrate + H_2O
	Sn	NO_2 + H_2SnO_3

Action on Proteins

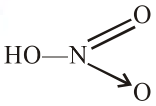
(a) Nitric acid attacks proteins forming a yellow nitro compound called xanthoprotein. It, therefore, stains skin and renders wool yellow. This property is utilized for the test of proteins.

(b) **Oxidation :** Number of organic compound are oxidised.

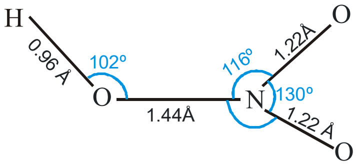
Sawdust catches fire when nitric acid is poured on it. Turpentine oil bursts into flames when treated with fuming nitric acid. Toluene is oxidised to benzoic acid with dil. HNO_3.

Structure

Nitric acid is a monobasic acid, i.e. the molecule consist of one hydroxyl group as it is formed by the hydrolysis of nitryl chloride, NO_2Cl. It may be structurally represented as below :



Gaseous nitric acid is a planar molecule. The bond lengths and bond angles as present in the molecule are represented in the figure :



6. Allotropic modifications of phosphorus

Phosphorus exists in a number of allotropic forms. These forms are :

(a) Yellow or white phosphorus **(b)** Red phosphorus **(c)** Black phosphorus

(a) White or yelllow phosphorus

PREPARATION

(i) $$\underbrace{\text{Bone ash or Apatite rock}}_{\text{both have same formula}} \left\{ \begin{array}{l} Ca_3(PO_4)_2 + 3SiO_2 \xrightarrow{1200^\circ C} 3CaSiO_3 + P_2O_5 \\ 2P_2O_5 + \underset{\text{(Coke)}}{10C} \xrightarrow{1500^\circ C} \underset{\text{white 'P'}}{P_4} + 10CO\uparrow \end{array} \right.$$

(ii) $$Ca_3(PO_4)_2 + 3H_2SO_4 \xrightarrow{\text{conc.}} 3CaSO_4 + 2H_3PO_4$$

$$H_3PO_4 \xrightarrow[-H_2O]{320^\circ C} HPO_3$$

meta phosphoric acid

$$\underset{\text{Coke}}{12C} + 4HPO_3 \xrightarrow{1000^\circ C} 2H_2\uparrow + 12CO\uparrow + \underset{\text{white 'P'}}{P_4}$$

PROPERTIES

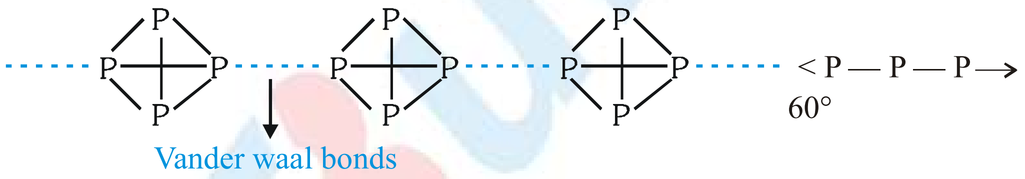
(i) It has characteristic garlic smell and is poisonous in nature. Persons working with phosphorus develop a disease in which the jaw bones decay. This disease is knwon as **phossy jaw.**

(ii) In contact with air, it undergoes slow combustion and glows in dark. This property is called **phosphorescence.**

(iii) Its ignition temperature is low (about 30° C). It readily catches fire giving dense fumes of phosphorus pentoxide. It is, therfore, kept in water.

$$P_4 + 5O_2 \longrightarrow P_4O_{10} \text{ or } 2P_2O_5$$

Structure



(b) Red phosphorus

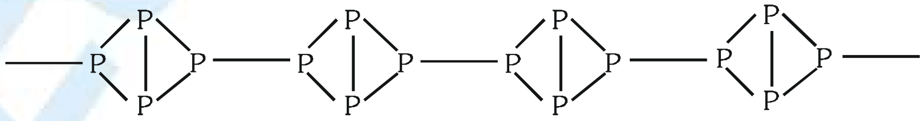
PREPARATION

Red phosphorus is formed by heating yellow phosphorus, between 240–250° C, in presence of an inert gas.

$$\text{White 'P'} \xrightarrow[\substack{\text{in an inert atm. like} \\ N_2 \text{ or } CO_2 \\ I_2 \text{ : catalyst}}]{240\text{-}250^\circ C} \text{Red 'P'}$$

$$\text{Red 'P'} \xrightarrow[\substack{\text{in an inert atm and then} \\ \text{rapid cooling to room temp.}}]{\text{heated to } 550^\circ C} \text{White 'P'}$$

Structure of red phosphorus :- It is regarded as a polymer consisting of chains of P_4 tetrahedral linked together by covalent bond.



Proposed Molecular Structure of Red Phosphorus

(c) Black P

PREPARATION : This is most stable form of Phosphorus

$$\text{White(P)} \xrightarrow[\text{at high P}]{470\text{K}} \text{Black P}$$

Black P contain zig-zag & double layered structure.

Order of density & mp

Black > Red > White

Comparison between White and Red Phosphorus

Property	White phosphorus	Red phosphorus
Physical state	Soft waxy solid.	Brittle powder.
Colour	White when pure. Attains yellow colour on standing.	Red.
Odour	Garlic	Odourless.
Solubility in water	Insoluble.	insoluble
Solubility in CS_2	Soluble.	Insoluble.
Physiological action	Poisonous.	Non-poisonous.
Chemical activity	Very active.	Less active.
Stability	Unstable.	Stable.
Phosphorescence	Glows in dark	Does not glow in dark.
Reaction with NaOH	Evolves phosphine.	No action.
Molecular formula	P_4	Complex polymer.

7. PHOSPHINE GAS (PH_3)

PREPARATION

(a) $4H_3PO_3 \xrightarrow{\Delta} PH_3 + 3H_3PO_4$

(b) $PH_4I + KOH \longrightarrow KI + PH_3 + H_2O$

$(PH_3 + HI)$

(c) $2AlP + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + PH_3\uparrow$

$\Big\}$ purest PH_3

PHYSICAL PROPERITIES

(a) It is having 'rotten fish' smell.

(b) It is soluble in CS_2 and insoluble in water.

$$\overset{\cdot\cdot}{P}H_3 + H_2O \longrightarrow PH_4^+ + OH^-$$

in s-orbital, so donating capacity is less

Note : PH_4^+ is formed with acids.

(c) Like NH_3, PH_3 also can form addition product.

$CaCl_2 \cdot 8NH_3, Cu_2Cl_2 \cdot 2PH_3, AlCl_3 \cdot 2PH_3, SnCl_4 \cdot 2PH_3$

PH_3 can be absorbed by Ca(OCl)Cl.

$$PH_3 + 3Ca(OCl)Cl + 3H_2O \longrightarrow PCl_3 + 3HCl + 3Ca(OH)_2$$

$$2NH_3 + 3Ca(OCl)Cl \longrightarrow N_2 + 3CaCl_2 + 3H_2O$$

CHEMICAL PROPERTIES

(a) $PH_3 + O_3 \xrightarrow{150°C} P_2O_5 + H_2O$

(b) $PH_3 + 3Cl_2 \longrightarrow PCl_3 + 3HCl$

(c) $PH_3 + 4N_2O \xrightarrow[\text{sparking}]{\text{electrical}} H_3PO_4 + 4N_2$

(d) $\underset{\text{Detection of } PH_3}{2PH_3} + 3CuSO_4 \longrightarrow \underset{\text{Black ppt.}}{Cu_3P_2\downarrow} + 3H_2SO_4$

(e) $PH_3 + 6AgNO_3 \longrightarrow \underset{\text{Yellow ppt.}}{[Ag_3P - 3AgNO_3\downarrow]} + 3HNO_3$

$$Ag_3P \cdot 3AgNO_3 + 3H_2O \longrightarrow \underset{\text{Black ppt.}}{6Ag\downarrow} + 3HNO_3 + H_3PO_3$$

(f) $PH_3 + 4HCHO + HCl \longrightarrow \underset{\text{(White / colourless solid)}}{[P(CH_2OH)_4]^+Cl^-}$ (which is used for making fire-proof cotton fabrics)

8. OXIDES OF PHOSPHORUS

It forms three important oxides which exist in dimeric forms.

Phosphorus trioxide (P_4O_6)

PREPARATION

Phosphorus trioxides is formed when phosphorus is burnt in a limited supply of air.

$$P_4 + 3O_2 \text{ (limited)} \longrightarrow P_4O_6$$

PROPERTIES

(a) **Heating in air :** On heating in air, it forms phosphorus pentoxide.

$$P_4O_6 + 2O_2 \longrightarrow \underset{\text{Phosphorus (V) oxide}}{P_4O_{10}}$$

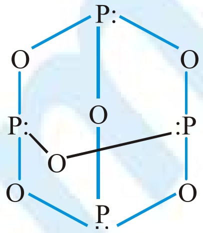
(b) **Action of water :** It dissolves in cold water to give phosphorus acid.

$$P_4O_6 + 6H_2O \text{ (cold)} \longrightarrow \underset{\text{Phosphorus acid}}{4H_3PO_3}$$

It is, therefore, considered as anhydride of phosphorus acid.

Note: With hot water, it gives phosphoric acid and inflammable phosphine.

Structure


Structure of P_4O_6

(a) Each atom of phosphorus in P_4O_6 is present at the corner of a tetrahedron

(b) Each phosphorus atom is covalently bonded to three oxygen atoms and each oxygen atom is bonded to two phosphorus atoms.

(c) It is clear from the structure that the six oxygen atoms lie along the edges of the tetrahedron of P atoms.

Phosphorus (V) oxide (P_4O_{10})

PREPARATION : It is prepared by heating white phosphorus in excess of air.

$$P_4 + 5O_2\,(\text{excess}) \xrightarrow{\Delta} P_4O_{10}$$

PROPERTIES

(a) It is snowy white solid.

(b) **Action with water :** It readily dissolves in cold water forming metaphosphoric acid.

$$P_4O_{10} + 2H_2O\,(\text{Cold}) \longrightarrow \underset{\text{Metaphosphoric acid}}{4HPO_3}$$

With hot water it gives phosphoric acid.

$$P_4O_{10} + 6H_2O\,(\text{Hot}) \longrightarrow \underset{\text{Phosphoric acid}}{4H_3PO_4}$$

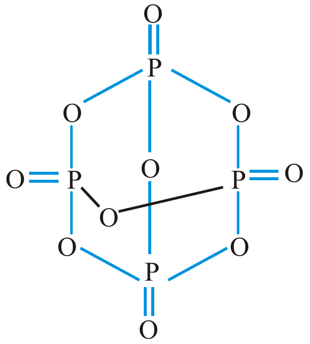
(c) **Dehydrating nature :** Phosphorus pentoxide has strong affinity for water and, therefore, acts as a powerful dehydrating agent. It extracts water from many inorganic and organic compounds.

(d) P_4O_{10} is a very strong dehydrating agent and extracts water from many compounds including sulphuric acid and nitric acid.

$$2HClO_4 \xrightarrow[-H_2O]{P_4O_{10}} \underset{\text{Chlorine (VII) oxide}}{Cl_2O_7}$$

$$\underset{\text{Acetamide}}{2CH_3CONH_2} \xrightarrow[-H_2O]{P_4O_{10}} \underset{\text{Methyl cyanide}}{CH_3CN}$$

Structure


Structure of P_4O_{10}

(a) Its structure is similar to that of P_4O_6.

(b) In addition, each phosphorus atom forms a double bond with oxygen atom as shown in figure.

OXYGEN FAMILY

1. OXYGEN (O_2)

PREPARATION

(a) From oxides

(i) By thermal decomposition of the oxides

$$3MnO_2 \xrightarrow{\Delta} Mn_3O_4 + O_2$$

$$3Pb_3O_4 \xrightarrow{\Delta} 6PbO + O_2$$

$$2BaO_2 \xrightarrow{\Delta} 2BaO + O_2$$

$$2HgO \xrightarrow{450°C} 2Hg + O_2$$

$$2Ag_2O \xrightarrow{350°C} 4Ag + O_2$$

(ii) By the action of water on sodium peroxide (Oxone)

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

(iii) By the action of conc. H_2SO_4 on MnO_2

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

(b) From salts

(i) Alkali metal nitrates on heating give out oxygen

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

$$2KNO_3 \longrightarrow 2KNO_2 + O_2$$

(ii) $KClO_3$, $K_2Cr_2O_7$ and $KMnO_4$ decompose at high temperatures evolving oxygen.

$$2KClO_3 \xrightarrow{400°C} 2KCl + 3O_2$$

$$4K_2Cr_2O_7 \xrightarrow{400°C} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

$$2KMnO_4 \xrightarrow{250°C} K_2MnO_4 + MnO_2 + O_2$$

(iii) By heating $KMnO_4$ or $K_2Cr_2O_7$ with concentrated H_2SO_4.

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

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

(iv) By adding H_2O_2 to acidified $KMnO_4$ solution.

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

(c) Laboratory method

In laboratory, oxygen is prepared by heating of a mixture of potassium chlorate and manganese dioxide in 4 :1 ratio. (MnO_2 used as a catalyst)

$$\underset{\text{Potassiumchlorate}}{2KClO_3} \xrightarrow[\Delta]{MNO_2} 2KCl + 3O_2$$

(d) Electrolysis of water : Electrolysis of either acidified water using platinum electrodes or alkaline water using nickel electrodes is made in an electrolytic cell for obtaining oxygen and hydrogen.

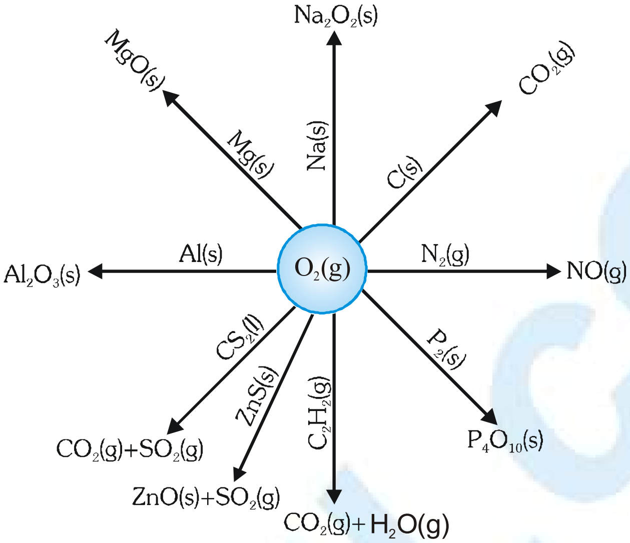
$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

At cathode : $2H^+ + 2e \longrightarrow H_2$ At anode : $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$

PROPERTIES

It is non inflammable but a supporter of combustion.

Some typical reactions of dioxygen –



2. OZONE (O_3)

PREPARATION

(a) Unstable deep blue, diamagnetic gas, with fishy smell. Toxic enough (more toxic than KCN). It's intense blue colour is due to the absorption of red light.

(b) Ozonised oxygen is separated by passing into spiral tube cooled by liquid air. Ozone condense at – 112.4ºC. [B.P. of O_2 – 183ºC ; B.P. of liquid air is – 190ºC]

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$

$$F_2 + 3H_2O \longrightarrow 6HF + O_3$$

PROPERTIES

(a) Oxidising property

It is one of best oxidising agent, in acid solution, its standard, reduction potential value is 2.07V.

$$O_3 + 2H^+ + 2e \longrightarrow O_2 + H_2O \qquad E^o = +2.07\ V$$

(i) Metal Sulphides to Sulphates.

$$MS + 4O_3 \longrightarrow MSO_4 + 4O_2 \qquad [M = Pb, Cu, Zn, Cd]$$

(ii) $2HX + O_3 \longrightarrow X_2 + H_2O + O_2 \qquad [X = Cl, Br, I]$

(iii) $NaNO_2 + O_3 \longrightarrow NaNO_3 + O_2$

$Na_2SO_3 + O_3 \longrightarrow Na_2SO_4 + O_2$

$Na_3AsO_3 + O_3 \longrightarrow Na_3AsO_4 + O_2$

(iv) $S + H_2O + 3O_3 \longrightarrow H_2SO_4 + 3O_2$

$2P + 3H_2O + 5O_3 \longrightarrow 2H_3PO_4 + 5O_2$

$2As + 3H_2O + 5O_3 \longrightarrow 2H_3AsO_4 + 5O_2$

(v) Moist $I_2 \longrightarrow HIO_3 + 5O_2$

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

Dry $I_2 \longrightarrow I_4O_9$ (yellow)

$2I_2 + 9O_3 \longrightarrow I_4O_9 + 9O_2$

(vi) $2K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$

$2K_4[Fe(CN)_6] + O_3 + H_2O \longrightarrow 2K_3[Fe(CN)_6] + 2KOH + O_2$

$2FeSO_4 + O_3 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + O_2 + H_2O$

(vii) $2KI$ (acidified) $+ O_3 + 2HCl \longrightarrow I_2 + 2KCI + H_2O + O_2$

$$\left.\begin{array}{l} 2KI(\text{neutral}) + O_3 + 2HCl \longrightarrow \underbrace{I_2 + 2KOH}_{KI+KOI} + O_2 \\ KI + KOI + 2HCl \longrightarrow 2KCl + I_2 + H_2O \\ I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I \end{array}\right\} O_3 \text{ estimated by this reaction.}$$

$$\text{alkaline} \left\{\begin{array}{l} KI + 3O_3 \longrightarrow KIO_3 + 3O_2 \\ KI + 4O_3 \longrightarrow KIO_4 + 4O_2 \end{array}\right.$$

(viii) Hg loses its fluidity (tailing of Hg)

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

$2Ag + O_3 \longrightarrow \underset{\text{Brown}}{Ag_2O} + O_2$

(ix) $BaO_2 + O_3 \longrightarrow BaO + 2O_2$

$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$

$Na_2O_2 + O_3 + H_2O \longrightarrow 2NaOH + 2O_2$

(x) $2KOH + 5O_3 \longrightarrow 2KO_3 + 5O_2 + H_2O$

Note: In all above reaction O_3 gives up O_2 but some reactions are there which consumes all O-atom.

- $3SO_2 + O_3 \longrightarrow 3SO_3$
- $3SnCl_2 + 6HCl + O_3 \longrightarrow 3SnCl_4 + 3H_2O$

Absorbent

(a) Turpentine oil

(b) Oil of cinnamon

USES

(a) Sterilizing water

(b) Detection of position of the double bond in the unsaturated compound.

3. HYDROGEN PEROXIDE (H_2O_2)

PREPARATION

(a) $Na_2O_2 + H_2O \xrightarrow{\text{ice cold water}} 2NaOH + H_2O_2$

(b) $BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$

Instead of H_2SO_4, H_3PO_4 is added now-a-days because H_2SO_4 catalyses the decomposition of H_2O_2 whereas H_3PO_4 favours to restore it.

$3BaO_2 + 2H_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 3H_2O_2$

$Ba_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3BaSO_4 + 2H_3PO_4$ (reused again)

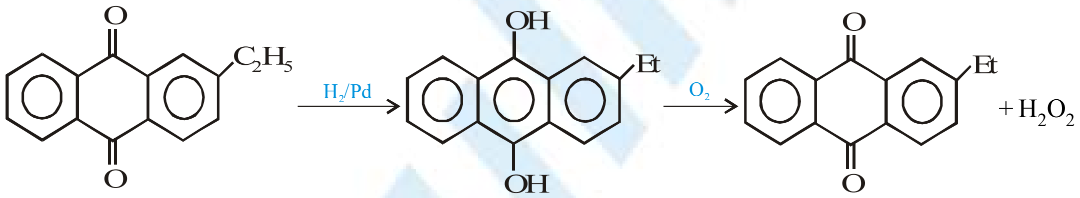
(c) Electrolysis of 50% H_2SO_4 using high current density.

$2H_2SO_4 \rightleftharpoons 2H^+ + 2HSO_4^-$

At anode; $2HSO_4^- \longrightarrow H_2S_2O_8 + 2e$ At cathode; $2H^+ + 2e \rightarrow H_2$

$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$

(d)



PROPERTIES

(a) Colourless, odourless liquid (B.P.152°C)

(b) **Acidic nature**

$H_2O_2 + 2NaOH \longrightarrow Na_2O_2 + H_2O$

$H_2O_2 + Ba(OH)_2 \longrightarrow BaO_2 + 2H_2O$

$H_2O_2 + Na_2CO_3 \longrightarrow Na_2O_2 + H_2O + CO_2$

(c) **Oxidising and reducing nature**

$H_2O_2 + 2H^+ + 2e \longrightarrow 2H_2O$ [acidic medium]

$H_2O_2 + 2e \longrightarrow 2OH^-$ [alkali medium]

Oxidising nature

$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$ (Used in washing of oil painting)

$NaNO_2 + H_2O_2 \longrightarrow NaNO_3 + H_2O$

$Na_2SO_3 + H_2O_2 \longrightarrow Na_2SO_4 + H_2O$

$Na_3AsO_3 + H_2O_2 \longrightarrow Na_3AsO_4 + H_2O$

$2KI + H_2O_2 \longrightarrow 2KOH + I_2$

$H_2S + H_2O_2 \longrightarrow S\downarrow + 2H_2O$

$$\left[\begin{array}{lll} X_2 + H_2O_2 \longrightarrow 2HX + O_2 & X = Cl, Br. & \\ \text{Standered Reduction Potential} & \text{order of} & Cl_2 > Br_2 > H_2O_2 > I_2 \end{array}\right]$$

$H_2SO_4 + 2FeSO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$

$2K_4[Fe(CN)_6] + H_2O_2 + H_2SO_4 \longrightarrow 2K_3[Fe(CN)_6] + K_2SO_4 + 2H_2O$

$2[Cr(OH)_4]^- + 3H_2O_2 + 2OH^- \longrightarrow 2CrO_4^{2-} + 8\,H_2O$

$CrO_4^{2-} + 2H^+ + 2H_2O_2 \longrightarrow CrO_5\,(Blue)\downarrow + 3H_2O$

$4CrO_5 + 12H^+ \longrightarrow 4Cr^{+3} + 7O_2 + 6H_2O$

$Mn^{+2} + OH^- + H_2O_2 \longrightarrow MnO_2 + 2H_2O$ **(This reaction can be utilised to detect NH3)**

Reducing nature

$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$

$O_3 + H_2O_2 \longrightarrow H_2O + 2O_2$

$MnO_2 + H_2O_2 + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + O_2$

$PbO_2 + H_2O_2 \longrightarrow PbO + H_2O + O_2$

$Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$

$PbO_2 + H_2O_2 \longrightarrow PbO + H_2O + O_2$

$PbO + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O$

$Pb_3O_4 + H_2O_2 + 6HNO_3 \longrightarrow 3Pb(NO_3)_2 + 4H_2O + O_2$

$X_2 + H_2O_2 \longrightarrow 2HX + O_2\ [X = Cl, Br]$

$2KMnO_4 + 3H_2O_2 \longrightarrow 2KOH + 2MnO_2 + 2H_2O + 3O_2$

$2MnO_4^- + 2OH^- \longrightarrow 2MnO_4^{2-} + H_2O + O$

$2MnO_4^{2-} + 2H_2O \longrightarrow 2MnO_2 + 4OH^- + 2O$

$2MnO_4^- + H_2O \longrightarrow 2MnO_2 + 2OH^- + 3O$

$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 5O_2 + 8H_2O$

$2[Fe(CN)_6]^{3-} + 2OH- + H_2O_2 \longrightarrow 2[Fe(CN)_6]^{4-} + 2H_2O + O_2$

$NaOCl + H_2O_2 \longrightarrow NaCl + H_2O + O_2$

$NaIO_4 + H_2O_2 \longrightarrow NaIO_3 + H_2O + O_2$

USES

(a) As a rocket propellant

$NH_2 . NH_2 + 2H_2O_2 \longrightarrow N_2 + 4H_2O$ [highly exothermic and large increase in volume]

(b) In detection of Cr^{+3}, Ti^{+4} etc.

$Ti(SO_4)_2 + H_2O_2 + 2H_2O \longrightarrow \underset{\text{Yellow or orange}}{\underset{\text{Pertitanic acid}}{H_2TiO_4}} + 2H_2SO_4$

4. HYDROGEN SULPHIDE (H_2S) SULPHURATED HYDROGEN

PREPARATION

By the action of dil. HCl or H_2SO_4 on iron pyrites.

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

Note : The gas is then dried over fused $CaCl_2$ or P_2O_5. Conc. H_2SO_4 cannot be used for drying purpose because H_2S oxidize to sulphur.

PROPERTIES

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

(a) It burn in air with blue flame

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

If the air supply is in excess

$2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_3$

(b) It is a mild acid.

$H_2S \longrightarrow H^+ + SH^-$

$SH^- \longrightarrow H^+ + S^{-2}$

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

$H_2S + X_2 \longrightarrow 2HX + S$

Tests of H_2S

(a) Unpleasant odour resembling that of rotten eggs.

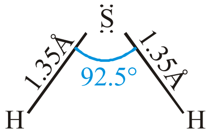
(b) It turns lead acetate into paper black

$(CH_3COO)_2Pb + H_2S \longrightarrow \underset{\text{Black}}{PbS\downarrow} + 2\,CH_3COOH$

(c) It gives a violet colouration with a solution of sodium nitroprusside.

Structure of H_2S

(a) Similar to structure of water molecule i.e. V– shaped structure with bond length (H–S) 1.35A° and bond angle (H–S–H) is 92.5°



USES

(a) It is mainly employed in salt analysis for the detection of cation.

(b) Reducing agent for H_2SO_4, $KMnO_4$, $K_2Cr_2O_7$, O_3, H_2O_2, $FeCl_3$

5. SULPHUR DIOXIDE (SO_2)

PREPARATION

Prepared by any of the following methods.

(a) $Cu + 2H_2SO_4 \xrightarrow{\Delta,\ conc} CuSO_4 + SO_2 + 2H_2O$

(b) $C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$

(c) $4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

PROPERTIES

(a) It has a pungent and suffocating odour.

(b) It acts as lewis base due to presence of a lone pair of electrons.

(c) Acidic nature

It dissolves in H_2O to give sulphurous acid, hence known as sulphurous anhydride.

$SO_2 + H_2O \longrightarrow H_2SO_3$

Due to acidic nature, it can react with bases to give salts.

$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$

(d) Reducing nature

In the presence of moisture it can liberate nascent hydrogen or in presence of an oxidising agent it can easily take an oxygen atom.

$$\begin{tikzcd}
 & H_2SO_4 + NO_2 \\
 & H_2SO_4 + HCl + FeCl_2 \\
SO_2 \arrow[ur, "HNO_3"] \arrow[uur, "FeCl_3 + H_2O"] \arrow[r, "KMnO_4 + H_2SO_4"] \arrow[dr, "K_2Cr_2O_7 + H_2SO_4"] & K_2SO_4 + MnSO_4 + H_2SO_4 \\
 & K_2SO_4 + Cr_2(SO_4)_3 + H_2O
\end{tikzcd}$$

(e) Oxidising nature

$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S\downarrow$

$SO_2 + 2CO \longrightarrow 2CO_2 + S\downarrow$

(f) Bleaching nature

(i) Sulphur dioxide acts as bleaching agent in the presence of water, it is oxidised with the liberation of nascent hydrogen which reduces the colouring matter to colourless.

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

Colouring matter + 2[H] $\longrightarrow$ Colourless compound.

(ii) Since the colourless (reduced) compound is reoxidised by air to coloured compound, bleaching by SO_2 is temporary.

Note : Chlorine has permanent bleaching action, so reaction is not reversible.

6. SULPHURIC ACID H_2SO_4 (OIL OF VITRIOL)

King of chemical (due to very great commericial importance)

PREPARATION

H_2SO_4 is prepared by two methods

(a) Lead chamber process

The mixture containing SO_2, air & nitric oxide when treated with steam, sulphuric acid is formed.

Stage I : $2NO\ (\text{Catalyst}) + O_2 \longrightarrow 2NO_2$

Stage II : $2SO_2 + 2NO_2 \longrightarrow 2SO_3 + 2NO$

Stage III : $SO_3 + H_2O \longrightarrow H_2SO_4$

(b) Contact process

In this process SO_2 is oxidised by air in the presence of catalyst (platinised asbestos).

Stage I : $S + O_2 \xrightarrow{\Delta} SO_2$

Stage II : $2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$

Stage III : $SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$ (oleum)

Stage IV : Sulphuric acid of any desired concentration can be obtained from oleum by dilution with water

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

CHEMICAL PROPERTIES

(a) As an oxidising agent

(i) H_2SO_4 gives oxygen on strong heating, hot conc.H_2SO_4 acts as an oxidising agent.

$$H_2SO_4 \xrightarrow{\Delta} H_2O + SO_2 + [O]$$

(ii) Non metals oxidised to their oxides.

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

(iii) Dilute acid releases hydrogen with all metals except mercury, copper and noble metals.

$$H_2SO_4 + Zn \longrightarrow ZnSO_4 + H_2\uparrow$$

Hot conc. H_2SO_4 releases SO_2 on reaction with metals.

$$Zn + 2H_2SO_4 \longrightarrow ZnSO_4 + 2H_2O + SO_2$$

(iv) Oxidation of compounds

$$2HX + H_2SO_4 \xrightarrow{\Delta} X_2 + SO_2 + 2H_2O\ (\text{where } X = \text{Br or I})$$

(b) As a dehydrating agent

(i) Conc. H_2SO_4 is a powerful dehydrating agent. Its corrosive action on skin is due to dehydration of skin which then burns and produces itching sensation.

(ii) It's dehydrating property is due to strong affinity for water.

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

This is called as charring of sugar.

$$CH_3CH_2OH \xrightarrow[160°C]{conc.\ H_2SO_4} CH_2{=}CH_2 + H_2O$$

$$HCOOH \xrightarrow{H_2SO_4} CO + H_2O$$

$$\begin{array}{l} COOH \\ | \\ COOH \end{array} \xrightarrow{conc.\ H_2SO_4} CO + CO_2 + H_2O$$

$$\text{Chloro benzene} + \text{Chloral} \xrightarrow[-H_2O]{conc.\ H_2SO_4} D.D.T.$$

2 : 1

USES

(a) In the manufacture of fertilisers like ammonium sulphate, calcium superphosphate etc.

(b) As a drying agent.

7. SODIUM THIOSULPHATE ($Na_2S_2O_3 \cdot 5H_2O$)

PREPARATION

(a) $Na_2SO_3 + S\ \text{(powder)} \xrightarrow{boiling} Na_2S_2O_3 \xrightarrow{evaporation} Na_2S_2O_3.5H_2O$, monoclinic crystal

$$Na_2CO_3 + 2SO_2 + H_2O \longrightarrow 2NaHSO_3 + CO_2$$

$$2NaHSO_3 + \underset{\text{Excess}}{Na_2CO_3} \longrightarrow 2Na_2SO_3 + H_2O + CO_2$$

(b) $\underset{\text{Salt cake}}{Na_2SO_4} + \underset{\text{Coke}}{4C} \xrightarrow{roasting} 4CO + Na_2S \xrightarrow{SO_2} Na_2S_2O_3 + S$

(c) $2Na_2S + Na_2CO_3 + 4SO_2 \longrightarrow 3Na_2S_2O_3 + CO_2$

(d) $6NaOH + 4S \longrightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$

$$3Ca(OH)_2 + 12\ S \longrightarrow CaS_2O_3 + 2CaS_5 + 3H_2O$$

(e) $Na_2SO_3 + Na_2S + I_2 \longrightarrow Na_2S_2O_3 + 2NaI$

(f) $2Na_2S + 2O_2 + H_2O \longrightarrow Na_2S_2O_3 + 2NaOH$

PROPERTIES

$$Na_2S_2O_3 \xrightarrow{\Delta} Na_2S_5 + 3Na_2SO_4$$

$$Na_2S_2O_3 \xrightarrow{2H} H_2S_2O_3 \xrightarrow{\Delta} H_2O + SO_2 + S\downarrow \text{ (Whiteturbidity)}$$

$$Na_2S_2O_3 \xrightarrow{I_2} S_4O_6^{2-} + 2I^-$$

$$Na_2S_2O_3 \xrightarrow{Cl_2 + \text{water}} SO_4^{2-} + S + 2HCl$$

$$Na_2S_2O_3 \xrightarrow{Br_2 + \text{water}} SO_4^{2-} + S + 2HBr$$

$$Na_2S_2O_3 \xrightarrow{4OI^- + 5OH^-} 2SO_4^{2-} + 4I^- + H_2O$$

$$Na_2S_2O_3 \xrightarrow{4Cl_2 + 5H_2O} Na_2SO_4 + 8HCl + H_2SO_4$$

Action of $AgNO_3$: A white precipitate of silver thiosulphate is obtained by the action of $AgNO_3$ which changes to yellow, brown and finally black due to the formation of silver sulphide.

$$2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 + 2NONO_3$$

$$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$$

Action of silver halides : Halides form complexes with sodium thiosulphate. Silver bromide forms argento thiosulphate complex.

$$AgBr + 2Na_2S_2O_3 \longrightarrow \underset{\substack{\text{Sodium argento thiosulphate} \\ \text{(Colourless)}}}{Na_3[Ag(S_2O_3)_2]} + NaBr$$

This property is used in photography for fixing.

Action on copper sulphate : Cuprous thiosulphate is formed which dissolves in excess of sodium thiosulphate to form a complex.

$$CuSO_4 + Na_2S_2O_3 \longrightarrow \underset{\text{Cupric thiosulphate}}{CuS_2O_3} + Na_2SO_4$$

$$2CuS_2O_3 + Na_2S_2O_3 \longrightarrow \underset{\text{Cuprous thiosulphate}}{Cu_2S_2O_3} + Na_2S_4O_6$$

$$3Cu_2S_2O_3 + 2Na_2S_2O_3 \longrightarrow \underset{\text{Sodium cupro thiosulphate}}{Na_4[Cu_6(S_2O_3)_5]}$$

USES

(a) As an antichlor to remove excess of chlorine from bleached fabrics.

(b) In photography as a fixing agent in the name of hypo.

(c) In the extraction of silver and gold.

(d) As a reagent in iodometric and iodometric titrations for the estimation of iodine $CusO_4$, $K_2Cr_2O_7$, $KMnO_4$, Na_3AsO_3 etc.

(e) Sodium hyposulphite ($Na_2S_2O_4$) is used for reducing indigo or other vat dyes.

GROUP - VII
HALOGENS FAMILY

Method of Prepration

F_2 : By electrolysis of KHF_2 (which is obtained from CaF_2)

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

$$HF + KF \longrightarrow KHF_2$$

$\left\{ \text{KF decrease the m.p. of the mix. depending upon the composition.} \right\}$

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

Cl_2 :

(i) By electrolysis of aq. NaCl

$$2NaCl + 2H_2O \longrightarrow \underbrace{2NaOH + H_2}_{\text{at cathode}} + \underset{\text{(anode)}}{Cl_2}$$

(ii) $$\underset{\text{(Molten)}}{2NaCl} \xrightarrow{\text{Electrolysis}} \underset{\text{(cathode)}}{2Na} + \underset{\text{(anode)}}{Cl_2}$$

(iii) In laboratory : Oxidising HCl by $KMnO_4$ or MnO_2

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

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

Br_2 : From Bromine water (contains 65 ppm of Br^-)

$Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2$ (Br_2 is volatite in nature

Hence it is collected by

(i) removal of Br_2 vapour by stream of air.

(ii) absorbing it into Na_2CO_3 solution.

$$Br_2 + 6OH^- \longrightarrow Br^- + BrO_3^- + 3H_2O$$

Then acidified to get pure Br_2

$$5\,Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

I_2 : Chille salt petre contains traces of$NaIO_3$ which is reduced to I^- by $NaHSO_3$, then oxidation of I^- to I_2 by IO_3^-.

$$2IO_3^- + 6HSO_3^- \longrightarrow 2I^- + 6SO_4^{2-} + 6H^+$$

$$5I^- + IO_3^- \xrightarrow{6H^+} 3I_2 + 3H_2O$$

Ex. Liquid I_2 conducts electricity. Explain

Sol. Due to its self ionisation $3I_2 \longrightarrow I_3^+ + I_3^-$

Ex. $X_2 + OH^- \longrightarrow X^- + OX^- + H_2O$ but on acidification the disproportionated product gives

$\longrightarrow X^- + XO_3^- + H_2O$ back the same element.

$X_2 = Cl_2, Br_2, I_2$ But For F_2 i.e. $X^- + OX^- + 2H^+ \longrightarrow X_2 + H_2O$

$5X^- + XO^-_3 + 6H^+ \longrightarrow 3X_2 + 2H_2O$

$2F_2 + 2NaOH \longrightarrow 2NaF + F_2O + H_2O$ $X = Cl, Br, I$

$F_2O + 2NaOH \longrightarrow 2NaF + O_2 + H_2O$

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

HALOGEN ACID

Acidity order : HI > HBr > HCl >> HF. (due to hydrogen bonding & less effective overlap with H atom)

Ex. CaF_2 used in HF prep^n must be free from SiO_2. Explain

Sol. $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + HF$

If SiO_2 present as impurity

$$\left.\begin{array}{l} 4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O \\ SiF_4 + 2HF \longrightarrow H_2[SiF_6] \end{array}\right\}$$ Hence presence of one molecule SiO_2 consumer 6 molecule of HF

Ex. HF can not be stored in glass vessel. Explain.(same reason.)

Ex. In the salt-cake method of prep^n. of HCl, NH_4Cl is being used instead of NaCl. Explain.

Sol. $NaCl + H_2SO_4 \xrightarrow{150°C} \underset{\text{Insoluble}}{NaHSO_4} + HCl$

$NaCl + NaHSO_4 \xrightarrow{550°C} \underset{\text{(Salt Cake)}}{Na_2SO_4} + HCl$

$2NH_4Cl + H_2SO_4 \longrightarrow 2HCl + (NH_4)_2SO_4$

[NH_4HSO_4 intermediate is water soluble and easy to handle]

** Another alternative process to avoid the formation of $NaHSO_4$

$$NaCl + \underbrace{SO_2 + H_2O + \frac{1}{2}O_2}_{\text{gaseous mixture}} \longrightarrow Na_2SO_4 + 2HCl$$

Ex. In the similar type of preparation of HBr and HI from bromide and iodide, H_2SO_4 can not be used and H_3PO_4 is used. Explain.

Sol. Since H_2SO_4 is an oxidising agent it oxidises HBr & HI to Br_2 and I_2 respectively.

$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$

Hence, $NaBr + H_3PO_4 \longrightarrow NaH_2PO_4 + 3HBr$

Another process ; $PBr_3 + 3H_2O \longrightarrow H_3PO_4 + 3HBr$

Ex. Boiling point order HX : HF > HI > HBr > HCl

↓

Due to H-bonding

Ex. HCl, H_2SO_4, HNO_3 are bases in liquid HF where as $HClO_4$ is acid. Comment.

Sol. $HCl + HF \longrightarrow H_2Cl^+ + F^-$; $H_2SO_4 + HF \longrightarrow H_3SO_4^+ + F^-$; $HNO_3 + HF \longrightarrow H_2NO_3^+ + P^-$

But $HClO_4 + HF \longrightarrow H_2F^+ + ClO_4^-$

* HF is weak acid but addition of BF_3, AsF_5, PF_5, SbF_5 makes it strongly acidic. Explain

OXOACIDS

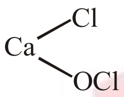
HOF : $H_2O + F_2 \xrightleftharpoons{-40°C} HOF + HF$

HOX : very unstable becuase it reacts with both H_2O and F_2 as follows :

$\left.\begin{matrix} HOCl \\ HOBr \\ HOI \end{matrix}\right\} X_2 + H_2O \longrightarrow HOX + HX$ $\left\{\begin{matrix} HOF + F_2 \longrightarrow F_2O + HF \\ HOF + H_2O_2 \longrightarrow H_2O + HF \end{matrix}\right.$

OX^- disproportionates in hot solution eg. $3OCl^- \longrightarrow 2Cl^- + ClO_3^-$

X = Cl, Br, I

Bleaching Powder : 

$Ca\begin{matrix} \diagup Cl \\ \diagdown OCl \end{matrix}$

Prepn. : $Cl_2(g) + \underset{\text{Slaked lime}}{Ca(OH)_2} \xrightarrow{40°C} Ca(OCl)Cl + H_2O$

(a) On long standing it undergoes

(i) auto oxiation $6Ca(OCl)Cl \longrightarrow Ca(ClO_3)_2 + 5CaCl_2$

(ii) $2Ca(OCl)Cl \xrightarrow[\text{Cat.}]{CoCl_2} 2CaCl_2 + O_2$

(iii) $Ca(OCl)Cl + H_2O \longrightarrow Ca(OH)_2 + Cl_2$

Oxidising Prop

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

$CaOCl_2 + 2FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + CaCl_2 + H_2O$

$CaOCl_2 + KNO_2 \longrightarrow CaCl_2 + KNO_3$

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

$CaOCl_2 + 2KI + 2HCl \longrightarrow CaCl_2 + 2KCl + H_2O + I_2$

$CaOCl_2 + 2KI + 2AcOH \longrightarrow CaCl_2 + 2KOAc + H_2O + I_2$

$CaOCl_2 + Na_3AsO_3 \longrightarrow Na_3AsO_4 + CaCl_2$

Reaction with acid

$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$; $Ca(OCl)Cl + H_2SO_4 \longrightarrow CaSO_4 + H_2O + C$

$Ca(OCl)Cl + CO_2 \longrightarrow CaCO_3 + Cl_2$

HXO_2

$$BaO_2 + 2ClO_2 \longrightarrow Ba(ClO_2)_2 + O_2,\ Ba(ClO_2)_2 + \underset{\text{(dil)}}{H_2SO_4} \longrightarrow BaSO_4 \downarrow + HClO_2$$

Only Known $HClO_2$. It is stable in alkaline solution but disproportionates in acid solution.

$$5HClO_2 \xrightarrow{H^+} 4ClO_2 + HCl + 2H_2O$$

HXO_3 : $HClO_3 > HBrO_3 > HIO_3$ are known and acidic order is as shown

PREPARATION

$HClO_3$: $Cl_2 + 6NaOH \xrightarrow{\text{hot}} 5NaCl + NaClO_3 + 3H_2O$

Similarly electrolysis of hot halide solution with severe stirring gives the same product.

$$2Cl^- + 2H_2O \longrightarrow Cl_2 + 2OH^- + H_2$$

$$Cl_2 + 6NaOH \underset{\text{(recycled)}}{\longrightarrow} 5NaCl + NaClO_3 + 3H_2O \left\{ \begin{array}{l} NaClO_3 + KCl \longrightarrow \underset{\text{on cooling}}{KClO_3\downarrow} + NaCl[KClO_3 \text{ prep.}^n] \\ NaClO_3 + BaCl_2 \longrightarrow Ba(ClO_3)_2\downarrow + \underset{\text{first}}{NaCl\downarrow} \\ Ba(ClO_3)_2 + H_2SO_4 \longrightarrow BaSO_4 + \downarrow HClO_3 \end{array} \right.$$

PROPERTIES

* $3HClO_3 \xrightarrow{\text{evaporation}} 2ClO_2 + H_2O + HClO_4$

$$\left. \begin{array}{l} * \quad IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O \\ ClO_3^- + 3SO_3^{2-} \longrightarrow Cl^- + 3SO_4^{2-} \end{array} \right\} \text{Oxidising property}$$

Disproportionation : $4KClO_3 \xrightarrow[\text{absence of catalyst}]{\text{low temp.}} KCl + 3KClO_4$

$$2KClO_3 \xrightarrow[MnO_2\text{ (Cat.)}]{400° - 500°} 2KCl + 3O_2$$

HXO_4 : $NaClO_3 + H_2O \xrightarrow{\text{electrolysis}} NaClO_4 + H_2$

$$KClO_4 + H_2SO_4\text{ (conc.)} \longrightarrow HClO_4 + KHSO_4$$

Electrode reaction

$$\left\{ \begin{array}{l} A : ClO_3^- + H_2O \longrightarrow ClO_4^- + 2H^+ + 2e \\ C : 2H^+ + 2e \longrightarrow H_2 \end{array} \right.$$

$$ClO_4^- \xrightarrow[KCl]{} KClO_4 \xrightarrow{H_2SO_4} HClO_4$$

Props : $K^+ + HClO_4 \longrightarrow KClO_4(\downarrow) + H^+$

$Zn + 2HClO_4 \longrightarrow Zn(ClO_4)_2 + H_2$

$Fe + 2HClO_4 \longrightarrow Fe(ClO_4)_2 + H_2$

Acidity order : $HOX < HXO_2 < HXO_3 < HXO_4$

Oxidising power : $HOX > HXO_2 > HXO_3 > HXO_4$

Thermal stability : $HOX < HXO_2 < HXO_3 < HXO_4$

OXIDES OF CHILORINE

+1	+4	+6	+7
Cl_2O	ClO_2	Cl_2O_6	Cl_2O_7
(Brownish yellow)	(Pale yelloow)	(liq. – dark red solid – yellow)	colourless solid

PREPARATION

Cl_2 does not combine directly to produce its oxides but indirect methods are there.

$Cl_2O: \underset{\text{dry}}{2Cl_2} + \underset{\text{in cooled tube}}{2HgO(s)} \longrightarrow \underset{\text{Basic Hg(II) chloride}}{HgO.\,HgCl_2} + Cl_2O\uparrow$ (Brownish yellow gas)

↓

Condensed to oragne liq.

PROPERTIES

It dissolves in water : $Cl_2O + H_2O \longrightarrow 2HClO$

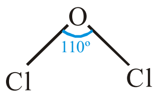
Explodes violently with NH_3.

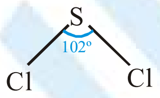
$3Cl_2O + 10\,NH_3 \rightarrow 2N_2 + 6NH_4Cl + 3H_2O$

It is oxidising agent

$Cl_2O + 2HCl \longrightarrow 2Cl_2 + H_2O$

Structures :





{ Back bonding

ClO_2 : PREPARATION

$\underset{\text{(powder)}}{3KClO_3} + \underset{\text{conc.}}{3H_2SO_4} \longrightarrow 3KHSO_4 + HClO_4 + \underset{\text{Pale yellow gas}}{2ClO_2\uparrow} + H_2O$

$2HClO_3 + H_2C_2O_4 \xrightarrow{60^oC} 2H_2O + 2ClO_2 + 2CO_2$

$2AgClO_3 + Cl_2 \xrightarrow{90^oC} 2AgCl + 2ClO_2 + O_2$ [By this reaction pure ClO_2 obtained]

ClO_2 dissolves in water producing dark green solution which decomposes in presence of light.

$ClO_2 \longrightarrow ClO + O$

$2ClO + H_2O \longrightarrow HCl + HClO_3$

but in alkali gives mixture of chlorite and chlorate.

$2ClO_2 + 2NaOH \longrightarrow NaClO_2 + H_2O$

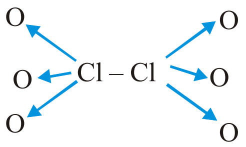
where $2ClO_2 + 2NaOH + H_2O_2 \longrightarrow \underset{\text{used in bleaching textiles and paper.}}{2NaClO_2} + O_2 + 2H_2O$

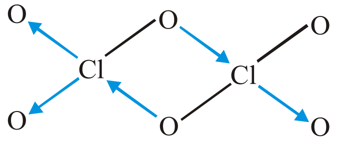
ClO_2 does not dimerise because odd e^-s undergoes delocalisation (in its own vaccant 3d-orbital)

Cl_2O_4 $(Cl.ClO_4)$ is not the dimer of ClO_2. Actually it is Cl-perchlorate.

$CsClO_4 + ClOSO_2F \longrightarrow Cs(SO_3)F + ClOClO_3$

Cl_2O_6 : Possible structures are :





ClO_2^+ ClO_4^-

liq $\longrightarrow$ dark red
Solid $\longrightarrow$ Yellow

Ex. Prove that Cl_2O_6 is consisting ClO_2^+ and ClO_4^-

Prep^n : $2ClO_2 + 2O_3 \xrightarrow{0^\circ C} Cl_2O_6 + 2O_2$

$Cl_2O_6 \rightleftharpoons 2ClO_3$ (monomer is paramagnetic)

Reactions : $Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO$

$Cl_2O_6\ NaOH \longrightarrow NaClO_3 + NaClO_4 + H_2O$

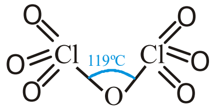
$Cl_2O_6 + HF \longrightarrow ClO_2F + HClO_4$

$Cl_2O_6 + NO_2 \longrightarrow ClO_2 + [NO_2]^+[ClO_4]^-$

Cl_2O_7 (colourless solid) : It is the anhydride of $HClO_4$ and prepared from it by the action P_2O_5.

$2HClO_4 + P_2O_5 \rightarrow 2HPO_3 + Cl_2O_7$

Structure :



INTER HALOGEN

Types :

AX	AX$_3$	AX$_5$	AX$_7$
ClF	ClF_3	ClF_5	IF_7
BrF	BrF_3	BrF_5	
BrCl	$(ICl_3)_2$	IF_5	
ICl	IF_3(unstable)		
IBr			
IF (unstable)			

- * $5IF \longrightarrow IF_5 + 2I_2$ [The overall system gains B.E. by 250 kJ /mol]
- * There are never more than two halogens in a moelcule.
- * bonds are essentially covalent and b.p. increases as the E.N. difference increases.
- * AX_5 & AX_7 type formed by large atoms like Br & I to accommodate mroe atoms around it.
- * The interhalogens are genrally more reactive than the halogens (except F_2) due to weaker A–X bonds compared to X – X bond.

Reactions : $ICl + H_2O \longrightarrow HCl + HOI$

$BrF_5 + 3H_2O \longrightarrow HBrO_3 + 5HF$

} Oxohalide is always formed with larger halogen present during hydrolysis of interhalogen compounds

$IF_5 + 3H_2O \longrightarrow HBrO_3 + 5HF$

$IF_7 + H_2O \longrightarrow IOF_5 + 2HF$ (less) } Parallel reaction

$4H_2O \longrightarrow HIO_4 + 7HF$

(i) ClF is hightly reactive and as a fluorinating agent.

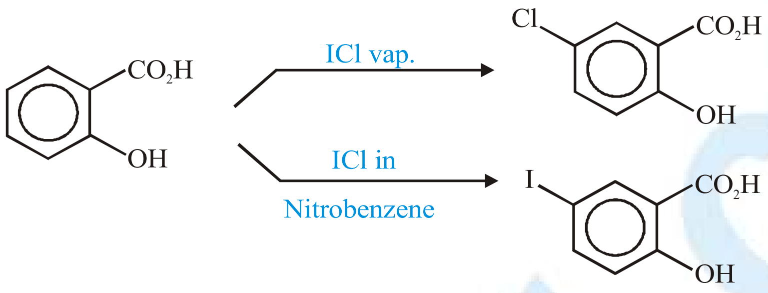
$6ClF + 2Al \longrightarrow 2AlF_3 + 3Cl_2$

$6ClF + U \longrightarrow UF_6 + 3Cl_2$

$6ClF + S \longrightarrow SF_6 + 3Cl_2$

$ClF + SF_4 \longrightarrow SF_5Cl$

One pecularity with Cl :



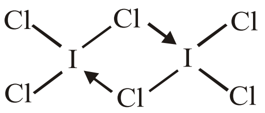
is chlorination (I)

is chlorination (II)

In IInd case, the attacking species is I^+ which has been supported by the formation of I^+ in fuse state as follows :

$3ICl \longrightarrow [I_2Cl]^+ + [ICl_2]^-$

* ICl_3 does not exist
but its dimer exist. $\rightleftharpoons 2ICl_3 \rightleftharpoons I_2Cl_6$
Structure is palnar.



(Bright yellow solid)

I_2Cl_6 : liq. has appreciable electrical conductivity like other interhalogens.

$I_2Cl_6 \rightleftharpoons [ICl_2]^+ + [ICl_4]^-$

$BrF_3 \rightleftharpoons [BrF_2]^+ + [BrF_4]^-$

$IF_5 \rightleftharpoons [IF_4]^+ + [IF_6]^-$

$3ICl \rightleftharpoons [I_2Cl]^+ + [ICl_2]^-$

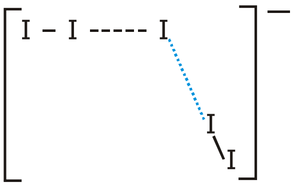
Polyhalides

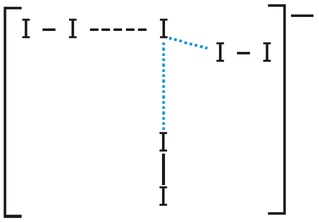
(i) $Ki + I_2 \longrightarrow KI_3$
(ii) $ICl + KCl \longrightarrow K^+[ICl_2]^-$
(iii) $ICl_3 + KCl \longrightarrow K^+[ICl_4]^-$
(iv) $IF_5 + CsF \longrightarrow Cs^+[IF_6]^-$
(v) $ICl + KBr \longrightarrow K^+[BrICl]^-$

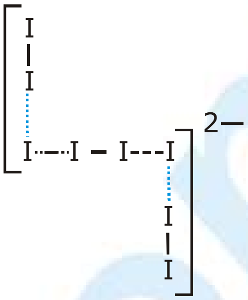
$Rb[ICl_2] \xrightarrow{\Delta} RbCl + ICl$ [not $RbI + Cl_2$]

Here the products on heating depends on the lattice energy of the product halide. The lattice energy of alkali halide with smaller halogen is highest since the interatomic distance is least.

Structure of I_5^-, I_7^-, I_8^{-2}







in $[N(CH_3)_4]^+ I_7^-$ in Cs_2I_8

- Only F_3^- not known [due to absence of d-orbital] [i.e. $Cs_2I_3 - I_2 - I_3$]

  I_3^-, Br_3^-, Cl_3^- are known Cl_3^- compounds are very less.

  Stability order : $I_3^- > Br_3^- > Cl_3^-$: depends upon the donating ability of X^-.

PSEUDO HALOGEN

There are univalent ion consisting of two or more atoms of which at least one is N, that have property similar to those of the halide ions. **E.g.**

(i) Na-salts are soluble in water but Ag-salts are insoluble in water.

(ii) H-compounds are acids like HX.

(iii) some anions can be oxidised to give molecules X_2.

Anions :	**Acids**	**Dimer**
CN^-	HCN	$(CN)_2$
SCN^-	HSCN(thiocyanic acid)	$(SCN)_2$
$SeCN^-$		$(SeCN)_2$
OCN^-	HOCN (cyanic acid)	
NCN^{2-}(Bivalent)	H_2NCN(cyanamide)	
ONC^-	HONC (Fulminic acid)	
N_3^-	HN_3 (Hydrazoic acid)	

$CN^{\ominus}$ shows maximum similarties with Cl^-, Br^-, I^-

(i) froms HCN

(ii) forms $(CN)_2$

(iii) AgCN, $Pb(CN)_2$, are insoluble

(iv) Inter pseudo halogen compounds ClCN, BrCN, ICN can be formed

(v) AgCN is insoluble in H_2O but soluble in NH_3

(vi) forms large no. of complex e.g. $[Cu(CN)_4]^{3-}$ & $[CuCl_4]^{-3}$
$[Co(CN)_6]^{-3}$ & $[CoCl_6]^{-3}$

NOBLE GASES

- I.E. order : $He > Ne > Ar > Kr > Xe > Rn$
- M.P. order : $He < Ne < Ar < Kr < Xe < Rn$

↓

- B.P. order : (–269ºC) same
- Atomic radius order : Same
- Density order : Same
- * Relative abundance : Ar is highest (Ne, Kr, He, Rn)

"He" (helium) has the lowest b.p (–269ºC) of any liquid (lowest of any substance)

(i) It is used in cryoscopy to obtain the very low temperature required for superconductor and laser.

(ii) It is used in airships though H_2 is cheaper and has lower density compared to He because H is highly inflammable.

(iii) He is used in preference to N_2 to dil. O_2 in the gas cylinders used by divers. This is because N_2 is quite soluble in blood, so a sudden change in pressure causes degassing and gives bubbles of N_2 in the blood. This causes the painful condition called bends.

He is slightly soluble so the risk of bends is reduced.

- Noble gases are all able to diffuse through glass, rubber, plastics and some metals
- He liquid can exist in two forms . I-form when changes to II-form at λ-point temperature many physical properties change abruptly.

Ex.

(i) Sp. heat changes by a factor of 1013

(ii) Thermal conductivity increases by 10^6 and it becomes 800 times faster than Cu

(iii) It shows zero resistance

(iv) It can flow up the sides of the vessel

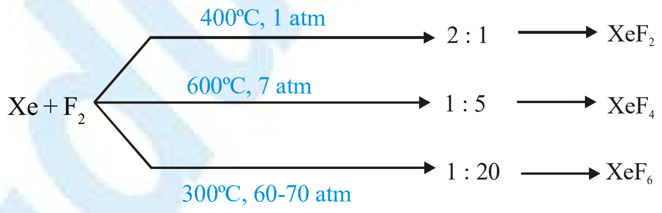
- Ar, Kr, Xe can form clathrate compounds but He, Ne cannot due to their smaller size.

What is noble gas hydrate ?

Ex. $Xe\,.\,6H_2O$, $Ar\,.\,6H_2O$, $Kr.\ 6H_2O$ $\left.\right\}$ formed only when water freezes at high pressure together with noble gas

Xenon Fluorides :–

(1)



(2) H_2 reduces Xe – fluorides to Xe

$XeF_2 + H_2 \longrightarrow Xe + 2HF$ and so on

(3) Xe - fluorides oxidise Cl^- to Cl_2 and I^- to I_2

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

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

(4) Hydrolysis

XeF_2 reacts slowly with water

$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$

XeF_4 and XeF_6 react violently with water giving XeO_3

$3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_2 + 12HF + \frac{3}{2}O_2$

$XeF_6 + 2H_2O \longrightarrow XeO_3 + 6HF$

$\downarrow$

(explosive, white hygroscopic solid)

(5) SiO_2 also converts XeF_6 into $XeOF_4$

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

violet

Similary, $XeO_3 + XeOF_4 \longrightarrow 2XeO_2F_2$, $XeO_3 + 2XeF_6 \longrightarrow 3XeOF_4$

(6) Xe - fluorides are also hydrolysed in alkaline medium.

$2XeF_2 + 4OH^- \longrightarrow 2Xe + 4F^- + 2H_2O + O_2$

$XeF_6 + 7OH^- \longrightarrow HXeO_4^- + 3H_2O + 6F^-$

Xenate ion

$2HXeO_4^- + 2OH^- \longrightarrow XeO_6^{4-}\downarrow + Xe + 2H_2O + O_2$

(7) They are used as fluorinating agent

$2SF_4 + XeF_4 \longrightarrow 2SF_6 + Xe$

$Pt + XeF_4 \longrightarrow PtF_4 + Xe$

(8) Act as a fluoride donor

$XeF_2 + MF_5 \longrightarrow [XeF]^+[MF_6]^-$ (M = As, Sb, P)

$XeF_6 + BF_3 \longrightarrow [XeF_5]^+[BF_4^-]$

$XeF_6 + HF \longrightarrow [XeF_5]^+[HF_2]^-$

(9) Act as Flouride acceptor also :

$XeF_6 + RbF/CsF \longrightarrow Rb^+/Cs^+[XeF_7]^-$

$2Cs^+[XeF_7]^- \xrightarrow[50^\circ C]{\Delta} XeF_6 + Cs_2[XeF_8]$

$XeF_4 + MF \longrightarrow M^+ + XeF_5^-$

(alkali metals fluoride)

BORON FAMILY

(1) Amorphous boron of low purity (called moissan boron) is obtained by reducing B_2O_3 with Mg or Na at a high temperature. It is 95–98% pure (being contaminated with metal borides), and is black in colour.

$$Na_2[B_4O_5(OH)_4].8H_2O \xrightarrow{\text{acid}} H_3BO_3 \xrightarrow{\text{heat}} B_2O_3 \xrightarrow{\text{Mg or Na}} 2B + 3\,MgO$$

(2) **BORANES**

Boranes are boron hydrogen compounds with general molecular formula B_nH_{n+4} or $B_n\ H_{n+6}$. They are electron deficient compounds.

(3) **ALUM**

Alums are double sulphates with their general formula $R_2SO_4.M_2(SO_4)_3.24H_2O$ where R = monovalent radical like Na^+, K^+, NH_4^+ and M = Trivalent radical like Al^{+3}, Cr^{+3}. Fe^{+3}.

CARBON FAMILY

(1) Carbon is found in nature in various allotropic forms which are:

(i) Crystalline Form : Diamond, Graphite, Fullerenes

(ii) Amorphous Form : Coal

(2) **SILICON (Si)**

Silicon is the second most abundant (27.2%) element after oxygen (45.5%) in the earth's crust. It does not occur free in nature but in the combined state, it occurs widely in form of silica and silicates. All mineral rocks, clays and soils are built of silicates of magnesium, aluminium, potassium or iron. Aluminium silicate is however the most common constituent of rocks and clays.

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

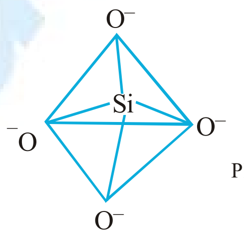
(a) Feldspar – $K_2O.Al_2O_3.6SiO_2$

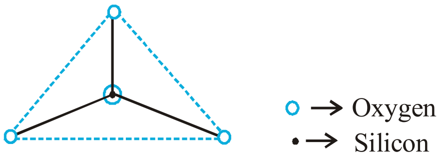
(b) Kaolinite – $Al_2O_3.\ 2\ SiO_2.\ 2H_2O$

(c) Asbestos – $CaO.\ 3MgO.4SiO_2$

Silicates are also important :

Silicates have basic unit of SiO_4^{4-}, each silicon atom is bonded with four oxide ions tetrahedrally.





Plane projection of silicate ion

NITROGEN FAMILY

NITROGEN (N_2)

PREPARATION

(a) $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

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

(c) $$\left.\begin{array}{l} Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2 \\ 2NaN_3 \xrightarrow{\Delta} 2Na + 3N_2 \end{array}\right\} \text{Purest } N_2 \text{ obtained by this method}$$

(d) $2\,NH_3 + 3NaOCl \xrightarrow{\Delta} N_2 + 3NaCl + 3H_2O$

(e) $2NO + \underset{\text{red over heated}}{2Cu} \longrightarrow \underset{\text{Black}}{2CuO} + N_2$

(f) Cl_2 passed into liquor NH_3

$$\begin{array}{l} 3Cl_2 + 2NH_3 \longrightarrow N_2 + 6HCl \\ 6NH_3 + 6HCl \longrightarrow 6NH_4Cl \\ \hdashline 3Cl_2 + 8NH_3 \longrightarrow N_2 + 6NH_4Cl \end{array}$$

In this method NH_3 conc. should not be lowered down beyond an particular limit.

$3Cl_2 + NH_3 \longrightarrow NCl_3 + 3HCl$

(Tremendously explosive)

OXYGEN FAMILY

OXYGEN (O_2)

PREPARATION

(a) From oxides

(i) By thermal decomposition of the oxides

$3MnO_2 \xrightarrow{\Delta} Mn_3O_4 + O_2$

$3Pb_3O_4 \xrightarrow{\Delta} 6PbO + O_2$

$2BaO_2 \xrightarrow{\Delta} 2BaO + O_2$

$2HgO \xrightarrow{450°C} 2Hg + O_2$

$2Ag_2O \xrightarrow{350°C} 4Ag + O_2$

(ii) By the action of water on sodium peroxide (Oxone)

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

(iii) By the action of conc. H_2SO_4 on MnO_2

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

(b) From salts

(i) Alkali metal nitrates on heating give out oxygen

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

$$2KNO_3 \longrightarrow 2KNO_2 + O_2$$

(ii) $KClO_3$, $K_2Cr_2O_7$ and $KMnO_4$ decompose at high temperatures evolving oxygen.

$$2KClO_3 \xrightarrow{400°C} 2KCl + 3O_2$$

$$4K_2Cr_2O_7 \xrightarrow{400°C} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

$$2KMnO_4 \xrightarrow{250°C} K_2MnO_4 + MnO_2 + O_2$$

(iii) By heating $KMnO_4$ or $K_2Cr_2O_7$ with concentrated H_2SO_4.

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

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

(iv) By adding H_2O_2 to acidified $KMnO_4$ solution.

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

(c) Laboratory method

In laboratory, oxygen is prepared by heating of a mixture of potassium chlorate and manganese dioxide in 4 :1 ratio. (MnO_2 used as a catalyst)

$$\underset{\text{Potassiumchlorate}}{2KClO_3} \xrightarrow[\Delta]{MNO_2} 2KCl + 3O_2$$

(d) Electrolysis of water : Electrolysis of either acidified water using platinum electrodes or alkaline water using nickel electrodes is made in an electrolytic cell for obtaining oxygen and hydrogen.

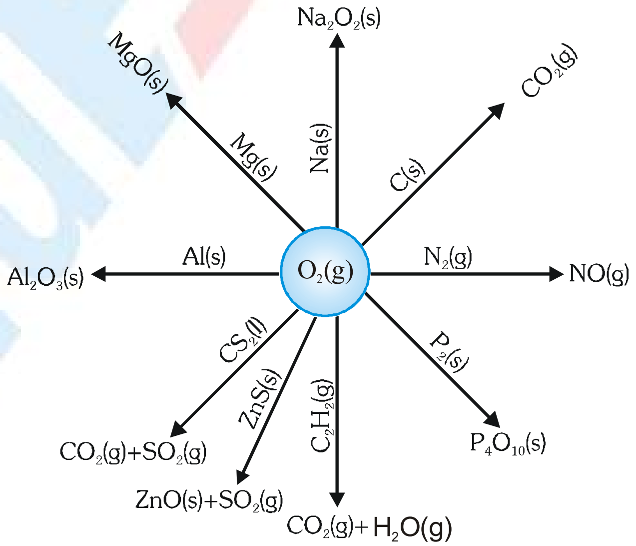
$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

At cathode : $2H^+ + 2e \longrightarrow H_2$ At anode : $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$

PROPERTIES of O_2

It is non inflammable but a supporter of combustion.

Some typical reactions of dioxygen –



HALOGEN FAMILY

METHOD OF PREPRATION

F_2 : By electrolysis of KHF_2 (which is obtained from CaF_2)

$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

$HF + KF \longrightarrow KHF_2$ $\left\{\text{KF decrease the m.p. of the mix. depending upon the composition.}\right\}$

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

Cl_2 :

(i) By electrolysis of aq. NaCl

$2NaCl + 2H_2O \longrightarrow \underbrace{2NaOH + H_2}_{\text{at cathode}} + \underset{\text{(anode)}}{Cl_2}$

(ii) $\underset{\text{(Molten)}}{2NaCl} \xrightarrow{\text{Electrolysis}} \underset{\text{(cathode)}}{2Na} + \underset{\text{(anode)}}{Cl_2}$

(iii) In laboratory : Oxidising HCl by $KMnO_4$ or MnO_2

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

$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

Br_2 : From Bromine water (contains 65 ppm of Br^-)

$Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2$ (Br_2 is volatite in nature

Hence it is collected by

(i) removal of Br_2 vapour by stream of air.

(ii) absorbing it into Na_2CO_3 solution.

$Br_2 + 6OH^- \longrightarrow Br^- + BrO_3^- + 3H_2O$

Then acidified to get pure Br_2

$5\,Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$

I_2 : Chille salt petre contains traces of$NaIO_3$ which is reduced to I^- by $NaHSO_3$, then oxidation of I^- to I_2 by IO_3^-.

$2IO_3^- + 6HSO_3^- \longrightarrow 2I^- + 6SO_4^{2-} + 6H^+$

$5I^- + IO_3^- \xrightarrow{6H^+} 3I_2 + 3H_2O$