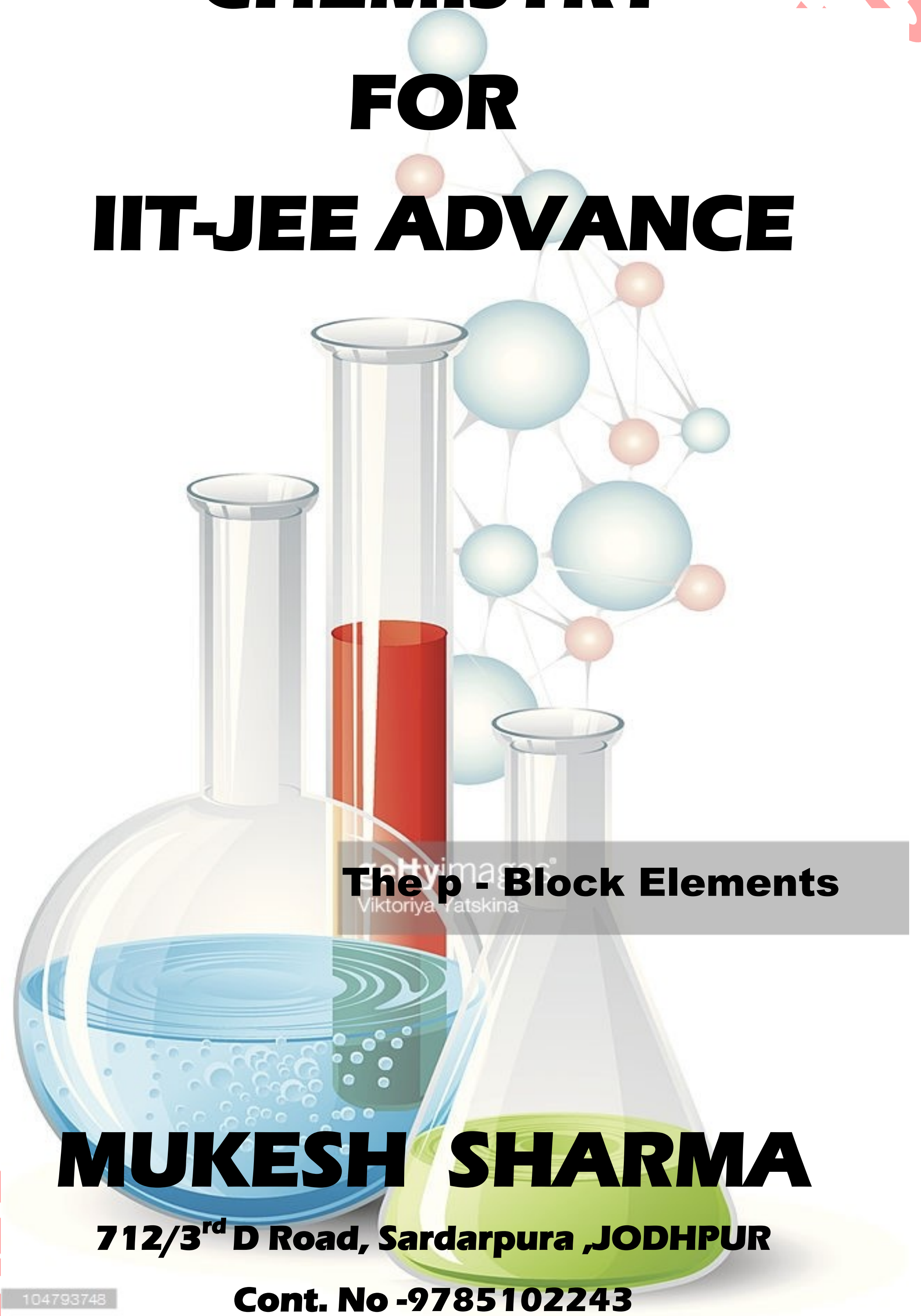
CHEMISTRY FOR IIT-JEE ADVANCE



The p - Block Elements

MUKESH SHARMA

712/3rd D Road, Sardarpura ,JODHPUR

Cont. No -9785102243

More on..Chemistry by mukesh sir blogspot.in

The p - Block Elements

The elements in which the last electron enters the other most p orbital are called p- block elements. As the maximum number of electrons that can be accommodated in a set of p-orbitals is six, therefore there are six groups of p - blocks in the periodic table.

Group 13 Elements : Boron Family

The Elements are B (Non metal), Al, Ga, In, T (Metals)
General electronic configuration [Noble gas] $ns^2\ np^1$

Atomic and Physical properties.

(1) ***Atomic and Ionic radii***

Atomic radii : B > Ga < Al < In < T

(2) ***Ionization Enthalpies.***

B > T > Ga > Al > In (Sum of three IE values)

(3) ***Melting and Boiling points***

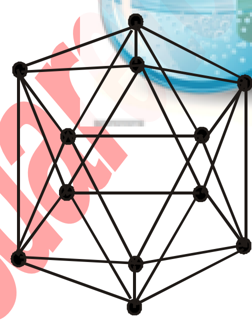
M.P. B > Al > Tl > In > Ga
B.P. B > Al > Ga > In > Tl

(4) ***Electropositive Character***

Due to high IE they are less electropositive on moving down the group metallic character increases due to decrease in IE [∴ B is nonmetals and other elements are metals.]

B <	Al < Ga < In < Tl
Non metal	Metals

Note : Boron exists in many allotropic forms. All the allotropes have basic building B_{12} icosahedral units made up of polyhedron having 20 faces and 12 corners.For example one is the simplest form : α - rhombohedral boron.



But Al , In & T all have close packed metal structure.

Chemical Properties :

B already discussed.

(1) ***Reaction with Air at Water***

Al should react air to form a very thin oxide film (10^{-4} to 10^{-6} mm thick) on the surface and protects the metal from further attack

$$2\,Al(s) + \frac{3}{2}\,O_2(g) \rightarrow Al_2O_3(s) \qquad \Delta H° = -1670 \text{ kJ/mole (Thermal reaction)}$$

Ga and In are attacked neither by cold water nor hot water unless oxygen is present. T form an oxide on surface

(2) ***Reaction with Oxides and Bases***

Al dissolve in dilute mineral acids liberating H_2

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$$

Al also dissolves in aqueous NaOH ($\therefore$ amphoteric) liberating H_2 and forming aluminates

$$2Al + 2NaOH + 6H_2O \rightarrow 2\,Na[Al(OH)_4] + H_2$$

or

$$2NaAlO_2 + 2H_2O$$

Ga, In, T dissolve in dilute acids liberating H_2 Ga is amphoteric like Al and it dissolves in aq. NaOH liberating H_2 and forming gallates.

Isolation of "B":

(i) Preparation of B_2O_3 from Borax or Colemanite

$$Na_2B_4O_7 + HCl/H_2SO_4 \longrightarrow NaX + H_2B_4O_7$$

$$H_2B_4O_7 + 5H_2O \longrightarrow 4H_3BO_3 \xrightarrow{\Delta} B_2O_3 + H_2O$$

(ii) Reduction of B_2O_3

$$B_2O_3 + Na/K/Mg/Al \longrightarrow B + Na_2O/K_2O/MgO/Al_2O_3$$

Chemical Props.:

(i) Burning in air: $4B + 3O_2 \longrightarrow 2B_2O_3$

$4Al + 3O_2 \longrightarrow 2Al_2O_3$

(ii) Reaction with water

$$B + H_2O\ (\text{Cold \& hot}) \longrightarrow \text{no reaction}$$

$$2B + 3H_2O \longrightarrow B_2O_3 + H_2$$

(red hot)

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

(iii) $B + HCl \longrightarrow$ no reaction

$B + H_2SO_4\ (dil) \longrightarrow$ no reaction

$2B + 3H_2SO_4\ (conc.) \longrightarrow 2H_3BO_3 + 3SO_2$

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

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

$Al + HNO_3(80\%) \longrightarrow Al_2O_3$ (passive layer) and does not react further.

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

$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$

(v) $2B + N_2 \longrightarrow 2BN$ $\quad$ $2Al + N_2 \longrightarrow 2AlN$

$4B + C \longrightarrow B_4C$ $\quad$ $4Al + 3C \longrightarrow Al_4C_3$

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

Preparation of B_2H_6:

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

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

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

(iv) $3LiAlH_4 + 4BF_3 \longrightarrow 3LiF + 3AlF_3 + 2B_2H_6$

or $LiBH_4$ $\quad$ or $3(BF_3)$

Reaction of B_2H_6 :

(i) $B_2H_6 + O_2 \xrightarrow[\text{air spontaneously}]{\text{burns in}} B_2O_3 + H_2O$

(ii) $B_2H_6 + H_2O$ (Cold is enough) $\longrightarrow H_3BO_3 + 6H_2$

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

Orthoboric Acid

H_3BO_3 is soluble in water and behaves as weak monobasic acid. It does not donate protons like most the acids, but rather it accepts OH^-. It is therefore is Lewis acid ($B(OH)_3$)

$B(OH)_3 + 2H_2O \rightleftharpoons H_3O^+ + [B(OH)_4]^-$

or

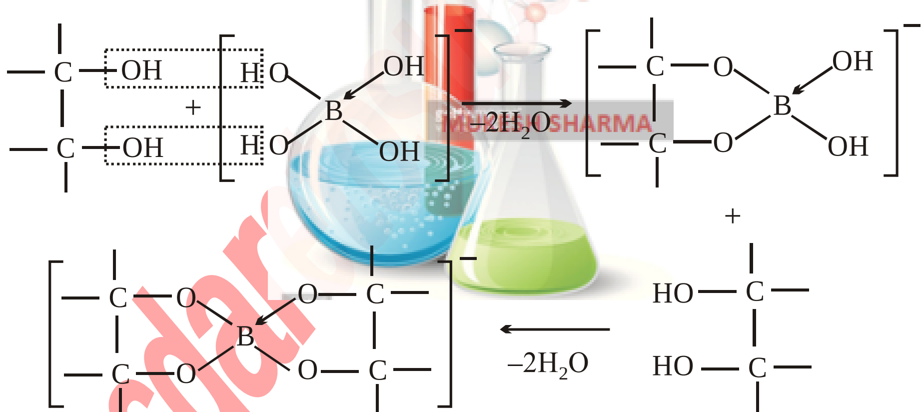
H_3BO_3

Since $B(OH)_3$ only partially reacts with water to form H_3O^+ and $[B(OH)_4]^-$ it behaves as a weak acid. Thus it cannot be titrated satisfactorily with NaOH as a sharp end point is not obtained. If certain polyhydroxy compounds such as glycerol, mannitol or sugar are added to the titration mixture then $B(OH)_3$ behaves as a strong monobasic acid. and hence can now be titrated with NaOH and end point is diluted using phenolphthalein as indicator.

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

$$NaBO_2 + 2H_2O$$

The added compound must be a as diol to enhance the acidic proprieties in this way the cis-diol forms very stable complexes with $[B(OH)_4]^-$ formed in forward direction above, thus effectively removing it from solution. Hence reaction proceeds in forward direction (Le-Chatelier principle.)



* ***Heating of boric acid :***

$H_3BO_3 \xrightarrow{100°C} HBO_2 \xrightarrow{140°C} H_2B_4O_7 \xrightarrow[\text{red hot}]{\Delta} B_2O_3$

Metaboric acid — tetraboric acid — Glassy mass

* $H_3BO_3 + H_2O_2 \longrightarrow (H_2O) + (HO)_2B{-}O{-}O{-}H \xrightarrow{NaOH} Na_2\left[(HO)_2\,B\begin{smallmatrix}O{-}O\\O{-}O\end{smallmatrix}B\,(OH)_2\right]\cdot 6H_2O$

Sodium peroxy borate used in washing powder as brightener

Preparation of Borax :

$$\underset{\text{Colemanite}}{2CaO \cdot 3B_2O_3} + 2Na_2CO_3 \longrightarrow 2CaCO_3 \downarrow + Na_2B_4O_7 + 2NaBO_2$$

Filtered $- CaCO_3$ (as residue) ↓

$$\underset{\text{in Filtrate}}{NaBO_2} + \left[\underset{\text{as residue}}{Na_2B_4O_7 \cdot 10H_2O}\right] \xleftarrow[\text{and allowed to crystallise out and filtered}]{\text{Concentrated}} \underset{\text{in solution}}{Na_2B_4O_7 + NaBO_2}$$

↓ CO_2 passed and crystallise out again

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

$Na_2B_4O_7 \cdot 10H_2O \downarrow$
as 2nd Crop. of the reaction.

Uses of borax: (i) In making glass, enamel and glaze of pottery.
(ii) As antiseptic in medicinal soaps preparation.

Al_2O_3 preparation :

(i) $2Al(OH)_3 \xrightarrow{300°C} Al_2O_3 + 3H_2O$

(ii) $Al_2(SO_4)_3 \xrightarrow{\Delta} Al_2O_3 + 3SO_3$

(iii) $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \xrightarrow{\Delta} Al_2O_3 + 2NH_3 + 4SO_3 + 25H_2O$

Uses: (i) In making refractory brick
(ii) as abrasive
(iii) To make high alumina cement

$AlCl_3$ preparation:

(i) $\underset{\text{(over heated)}}{2Al} + \underset{\text{dry}}{6HCl\ (vap.)} \longrightarrow 2AlCl_3 + 3H_2$

(ii) $Al_2O_3 + 3C + 3Cl_2 \xrightarrow[1000°C]{\Delta} 2AlCl_3\ (vap.) + 3CO$

↓ Cooled

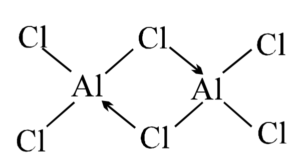
Solid anh. $AlCl_3$

Props:

(i) Its anhydrous formed is deliquescent and fumes in air.

(ii) It sublimes at 180°C.

(iii) It is covalent and exists in the form of dimer even if in non polar solvents e.g. alc., ether, benzene, where it is soluble in fair extent.



Uses: (i) Friedel-Craft reaction
(ii) Dyeing, drug. & perfumes etc.

Alumns: M_2SO_4, $M'_2(SO_4)_3 \cdot 24\ H_2O$ ***Props:*** Swelling characteristics

where $M = Na^+, K^+, Rb^+, Cs^+, As^+, Tl^+, NH_4^+$

$M' = Al^{+3}, Cr^{+3}, Fe^{+3}, Mn^{+3}, Co^{+3}$

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Potash alum
$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Ammonium alum
$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$	Chrome alum
$(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$	Ferric alum

Preparation: $Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$

$Al_2(SO_4)_3 + K_2SO_4 + aq.\ sol^n \longrightarrow$ crystallise

Uses:
(i) Act as coagnlant
(ii) Purification of water
(iii) Tanning of leather
(iv) Mordant in dying
(v) Antiseptic

Group 14 Elements (Carbon Family)

The Elements are C [Non metals] ,
Si, Ge [Metalloids],
Sn, Pb, [Metals]

General electronic configuration [noble gas] $ns^2\ np^2$

(I) Atomic and Physical properties

(1) ***Atomic Radii***

Covalent radii : C < Si < Ge < Sn < Pb

(2) ***Ionizations Enthalpies***

C > Si > Ge > Pb > Sn (IE_1 values)

(3) ***Melting and Boiling Points***

M.P. C > Si > Ge > Pb > Sn

B.P. Si > Ge > Sn > Pb

(4) ***Metallic Character***

C < Si < Ge < Sn < Pb (Metallic character)

C, Si [Non metal]

Ge [Metal]

Sn, Pb [Metal]

(II) **Chemical Properties (Discussed in sheet)**

* Unique Character of C

* ***Catenation***

The property of forming bonds with atoms of the same element or tendency to self linking called catenation. Carbon shows maximum catenation. On moving down the group catenation tendency decreases. This because the strength of C – C bond is very high and in case of other elements, strength of M – M (where M = Si, Ge, Sn, Pb) bond is decreases down the group.

Bond	Bond Energy ($kJmol^{-1}$)
C – C	348
Si – Si	297
Ge – Ge	260
Sn – Sn	240

Types of Carbide

(i) Ionic and salt like:

Classification on basis of no. of carbon atoms present in hydrocarbon found on their hydrolysis
- (a) C_1 unit
- (b) C_2 unit
- (c) C_3 unit

C_1 unit: Al_4C_3, Be_2C

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

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

C_2 unit: CaC_2, BaC_2

$CaC_2 + 12H_2O \longrightarrow Ca(OH)_2 + CH{\equiv}CH$

C_3 unit: Mg_2C_3

$Mg_2C_3 + H_2O \longrightarrow 2Mg(OH)_2 + CH_3–C{\equiv}CH$: Propyne

(ii) Covalent carbide : SiC & B_4C

(iii) Interstitial carbide : MC (Transition element or inner transitional elements forms this kind of carbide)

Interstitial carbide formation doesn't affect the metalic lusture and electrical conductivity.(no chemical bond is present, no change in property)

SiC

Preparation

$SiO_2 + 2C(coke) \xrightarrow[2500°C]{2000\ to} Si + 2CO\uparrow$

$Si + C \xrightarrow[2500°C]{2000\ to} SiC$ diamond like structure colourless to yellow solid in room temp.

↓

when impurity is present

Properties

(i) It is very hard and is used in cutting tools and abrassive powder(polishing material)

(ii) It is very much inert

(iii) It is not being affected by any acid except H_3PO_4

CO

— How to detect

— How to estimate

— What are its absorbers

(i) How to detect

(a) burns with blue flame

(b) CO is passed through $PdCl_2$ solution giving rise to black ppt.

$CO + PdCl_2 + H_2O \longrightarrow CO_2\uparrow + Pd\downarrow + 2HCl$

Black metallic deposition

(ii) How to estimate

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

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

(iii) What are its absorbers

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

Uses:

In the Mond's process of Ni - extraction

CO is the purifying agent for Ni

$$\text{Impure Ni} + CO \xrightarrow{50°C} Ni(CO)_4 \xrightarrow{150°C} Ni + 4CO$$

recycled

Producer gas: $CO + N_2 + H_2$

Water gas: $CO + H_2$

Water gas is having higher calorific value than producer gas. in water gas, both CO & H_2 burns while in producer gas N_2 doesn't burn.

Teflon $-\!\!(CF_2 - CF_2)\!\!-_n$

$$CHCl_3 + HF \xrightarrow[\text{SbFCl}_4 \text{ catalyst}]{\text{heated with}} CF_2HCl \xrightarrow[\text{again } -HCl]{\text{heated}} CF_2{=}CF_2 \xrightarrow[\text{high temp. and press}]{\text{Polymerisation at}} -\!\!(CF_2 - CF_2)\!\!-_n$$

Purpose

Temp. withstanding capacity upto 500–550°C (1st organic compound withstand this kind of high temp.)

SILICON (Si)

Occurrence

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

(i) Feldspar – $K_2O.\ Al_2O_3.\ 6SiO_2$

(ii) Kaolinite – $Al_2O_3.\ 2SiO_2.\ 2H_2O$

(iii) Asbestos – $CaO.\ 3MgO.\ 4SiO_2$

Preparation

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

$$SiO_2(s) + 2C(s) \xrightarrow{\text{high temperature}} Si(s) + 2CO(g)$$

(ii) From silicon tetrachloride ($SiCl_4$) or silicon chloroform ($SiHCl_3$) : Silicon of very high purity required for making semiconductors is obtained by reduction of highly purified silicon tetrachloride or silicon chloroform with dihydrogen followed by purification by zone refining.

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

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

PHYSICAL PROPERTIES :

(i) Elemental silicon is very hard having diamond like structure.

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

(iii) Silicon exists in three isotopes, i.e. ^{28}Si, ^{29}Si and ^{30}Si but ^{28}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.

(i) ***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,.

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

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

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

$$Si(s) + 2H_2O(g) \xrightarrow{\text{redness}} SiO_2(s) + 2H_2(g)$$

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

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

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

(iv) ***Reaction with carbon :*** Silicon combines with carbon at 2500 °C forming silicon carbide (SiC) known as carborundum.

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

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

USES:

(i) 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.
(ii) High purity silicon is used as semiconductors in electronic devices such as transistors.
(iii) It is used in the preparation of alloys such as silicon-bronze, magnesium silicon bronze and ferrosilicon.

COMPOUNDS OF SILICON:

What is silane. Si_nH_{2n+2} SiH_4 & Si_2H_6
Only these two are found
Higher molecules are not formed. Si can't show catanetion property

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

Ques. SiH_4 is more reactive than CH_4. Explain

<u>Reasons</u>

(i) $Si^{\delta+} - H^{\delta-}$ in $C^{\delta-} - H^{\delta+}$
C - electro-ve than H
Si less electro-ve than H

So bond polarity is reversed when Nu^- attacks, 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.

Silicones

It is organo silicon polymer

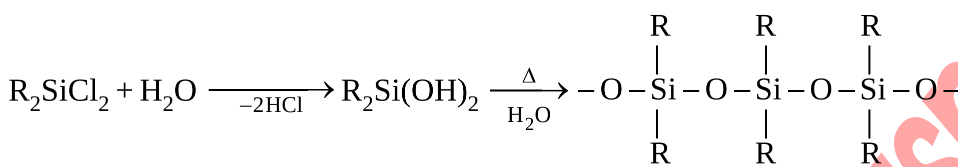
$CCl_4 + H_2O \longrightarrow$ no hydrolysis

but $CCl_4 + H_2O \longrightarrow COCl_2 + 2HCl$

super heated steam

$SiCl_4 + H_2O \longrightarrow Si(OH)_4 + 4HCl$

$\xrightarrow[-2H_2O]{\Delta} SiO_2$(3-D silicate)

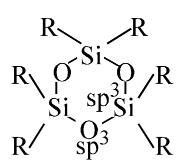


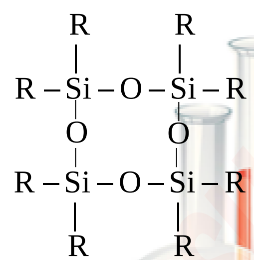
Linear silicone

$R_2CCl_2 + H_2O \xrightarrow[-2HCl]{} R_2C(OH)_2 \xrightarrow{-H_2O} R-\overset{O}{\overset{\|}{C}}-R$

(looses H_2O readily)

Silicones may have the cyclic structure also having 3, 4, 5 and 6 nos. of silicon atoms within the ring. Alcohol analogue of silicon is known as silanol

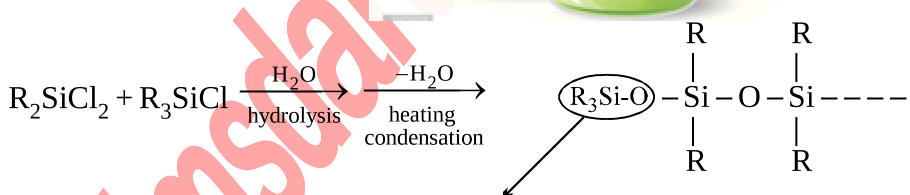




cyclic silicone
not planar

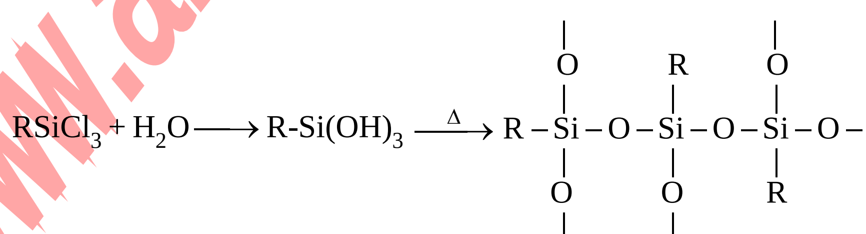
$R_3SiCl \xrightarrow{H_2O} R_3SiOH \xrightarrow[\Delta]{-H_2O} R_3Si\text{-}O\text{-}SiR_3$

Silanol



This end of the chain can't be extended hence R_3SiCl is called as chain stopping unit

* Using R_3SiCl in a certain proportion we can control the chain length of the polymer



cross linked silicone
3 dimensional network

It provides the crosslinking among the chain making the polymer more hard and hence controling the proportion of $RSiCl_3$ we can control the hardness of polymer.

Uses

(1) It can be used as electrical insulator (due to inertness of Si–O–Si bonds)

(2) It is used as water repellant (surface is covered) eg. car polish, shoe polish, massonary works in buildings

(3) It is used as antifoaming agent in sewage disposal, beer making and in cooking oil used to prepare potato chips.

(4) As a lubricant in the gear boxes.

SILICA (SiO_2)

Occurrence:

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:

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

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

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

(iii) It also combines with metallic oxides at high temperature giving silicates e.g.

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

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

$$SiO_2(s) + Na_2CO_3(s) \xrightarrow{\text{high temp.}} Na_2SiO_3(s) + CO_2(g)$$

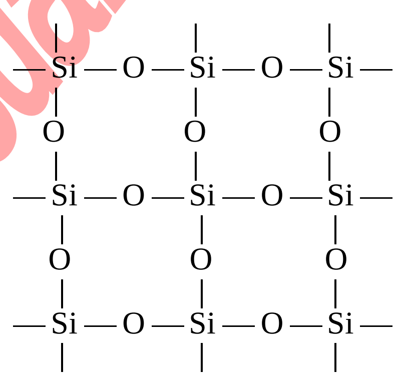
$$SiO_2(s) + Na_2SO_4(s) \xrightarrow{\text{high temp.}} Na_2SiO_3(s) + SO_3(g)$$

$$3SiO_2(s) + Ca_3(PO_4)_2(s) \xrightarrow{\text{high temp.}} 3CaSiO_3(s) + P_2O_5(g)$$

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:

(i) Sand is used in large quantities to make mortar and cement.

(ii) 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.

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

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

TIN & ITS COMPOUND

(i) $Sn \xrightarrow[+O_2]{1500°C} SnO_2$ [Burns with a bright flame]

$Sn \xrightarrow{Cl_2, \Delta} SnCl_4$

$Sn \xrightarrow{S, \Delta} SnS_2$

(ii) $Sn + 2H_2O \xrightarrow{\text{room temp.}}$ No reaction

$Sn + 2H_2O \xrightarrow{\text{At high temp.}} SnO_2 + 2H_2$

(iii) Reaction with acid.

Sn:
- $\xrightarrow{\text{dil.HCl}}$ reaction is very slow {Due to nonoxidising in nature}
- $\xrightarrow{\text{hot.conc.HCl}}$ $Sn + 2HCl \longrightarrow SnCl_2 + H_2\uparrow$
- $\xrightarrow{\text{dil. } H_2SO_4}$ dissolve Sn Slowly forming $SnSO_4 + H_2\uparrow$
- $\xrightarrow{\text{hot conc. } H_2SO_4}$ $Sn + 4H_2SO_4 \longrightarrow Sn(SO_4)_2 + 2SO_2 + 4H_2O$
- $\xrightarrow{\text{cold dil. } HNO_3}$ $4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$
- $\xrightarrow{\text{hot conc. } HNO_3}$ $5Sn + 20HNO_3 \longrightarrow H_2Sn_5O_{11}.4H_2O + 20NO_2 + 5H_2O$

Metastannic acid $\xrightarrow{\Delta} SnO_2$

(iv) $Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2\uparrow$.

or

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

Oxides:
SnO (grey)
& SnO_2 (white)

$SnC_2O_4 \xrightarrow[\text{out of contact of air}]{\Delta} SnO \text{ (grey)} + CO + CO_2$

$SnO \xrightarrow{+\frac{1}{2}O_2} SnO_2 \text{ (White)}$

$Sn + O_2 \xrightarrow[\text{heated}]{1500°C \text{ strongly}} SnO_2 \text{ (White)}$

$H_2Sn_5O_{11}.4H_2O \longrightarrow SnO_2$

$SnCl_2 \xrightarrow{KOH} Sn(OH)_2 \xrightarrow{\Delta \text{(in absence of air)}} SnO$

Both are amphoteric in nature :

$SnO + H_2SO_4 \longrightarrow SnSO_4 + H_2O$

$SnO + 2HCl \longrightarrow SnCl_2 + H_2O$

$SnO + 2NaOH \text{ or } KOH \xrightarrow{\text{cold}} Na_2SnO_2 \text{ or } K_2SnO_2 + H_2O$

But conc. hot alkali behaves differently.

$2SnO + 2KOH \text{ or } NaOH \longrightarrow K_2SnO_3 \text{ or } Na_2SnO_3 + Sn + H_2O$

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

$SnO_2 + 2H_2SO_4 \xrightarrow{\Delta} Sn(SO_4)_2 + 2H_2O$

(**Soluble only** in hot conc. H_2SO_4)

$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$

$SnCl_2$ & $SnCl_4$:

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

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

$Sn(OH)Cl \longrightarrow SnO + HCl\uparrow$

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

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

$$6SnCl_2 + 2H_2O + O_2 \longrightarrow 2SnCl_4 + 4Sn(OH)Cl\downarrow \text{ (white ppt)}$$
$$SnCl_4 + Sn \longrightarrow 2SnCl_2$$
$$SnCl_4 + 4H_2O \longrightarrow Sn(OH)_4\downarrow \text{ (white ppt.)} + 4HCl$$

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

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

$SnCl_4 + 2NH_4Cl \longrightarrow (NH_4)_2\,SnCl_6$ (colourless crystalline compound known as " pink salt ")

(4) Red Prop. of $SnCl_2$:

$$Sn^{+2} + 2Fe^{+3} \longrightarrow 2Fe^{+2} + Sn^{+4}$$
$$2Cu^{+2} + Sn^{+2} \longrightarrow 2Cu^{+} + Sn^{+4}$$
$$Hg^{+2} + Sn^{+2} \longrightarrow Hg\downarrow + Sn^{+4}$$
$$PhNO_2 + SnCl_2 / HCl \longrightarrow PhNH_2 + Sn^{+4}$$
$$K_2Cr_2O_7 + SnCl_2 + HCl \longrightarrow Cr^{+3} + Sn^{+4} + KCl + H_2O$$

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

Formation of $SnCl_4$:

(i) $\underset{\text{(molten)}}{Sn} + \underset{\text{(dry)}}{Cl_2\text{(Excess)}} \longrightarrow SnCl_4$ (ii) $2HgCl_2 + SnCl_2 \longrightarrow 2Hg\downarrow + SnCl_4$

(iii) $Sn + \text{Aq. rigia} \longrightarrow SnCl_4 + NO + H_2O$

* $SnCl_4.\,5H_2O$ is known as butter of tin $\Rightarrow$ used as mordant.

$(NH_4)_2\,SnCl_6$ is known as 'pink salt' $\Rightarrow$ used as calico printing.

Mosaic gold : SnS_2 yellow crystalline substance :

$$Sn + 4NH_4Cl \longrightarrow (NH_4)_2\,SnCl_4 + 2NH_3 + H_2$$
$$2(NH_4)_2\,SnCl_4 + 2S \longrightarrow SnS_2 + 2NH_4Cl + (NH_4)_2SnCl_6$$

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

(i) H_2S (ii) Hg^{+2} (iii) $Fe^{+3} + K_3[Fe(CN)_6] \xrightarrow{Sn^{+2}}$ Blue ppt.

COMPOUNDS OF LEAD

Oxides of lead :

(i) PbO (ii) Pb_3O_4 (Red) (iii) Pb_2O_3(reddish yellow) (Sesquioxide)

(iv) PbO_2 (dark brown)

(1) PbO → Yellow (Massicot) $\xrightarrow[\text{and powdered}]{\text{fused,cooled}}$ Litharge

PbO → Reddish yellow (litharge)

Laboratory Prep^n. :

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

$PbO_2 \xrightarrow{\text{above }600°C}$, $Pb_3O_4 \longrightarrow$, $Pb_2O_3 \longrightarrow$ } PbO , hot oxide easily reduced to Pb by H_2 or C.

$\xrightarrow{H_2} Pb + H_2O$

$\xrightarrow{C} Pb + CO$

Preparation of Pb_2O_3 :

$$\underset{\text{hot sol}^n\text{. of it in NaOH}}{2PbO} + \underset{\text{Limited amount}}{NaOCl} \longrightarrow Pb_2O_3 + NaCl$$

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

This reaction suggests that Pb_2O_3 contains PbO_2.

(2) **Pb_3O_4** : $6PbO + O_2 \underset{>470°C}{\overset{340°C}{\rightleftharpoons}} 2Pb_3O_4$ {In the same way, prove that its formula is 2PbO. PbO_2}

$Pb_3O_4 + 4HNO_3$ (cold.conc) or (hot dil.) $\longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$

But $2Pb_3O_4 + 6H_2SO_4 \xrightarrow{\Delta} 6PbSO_4 + 6H_2O + O_2$

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

(3) **PbO_2** : Insoluble in water. HNO_3, But reacts with HCl + H_2SO_4(hot conc.) and in hot NaOH / KOH.

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

(ii) $Pb(OAc)_2 + Ca(OCl)Cl + H_2O \longrightarrow PbO_2$[Brown(dark)] + $CaCl_2 + 2CH_3CO_2H$

↓

Excess bleaching powder is being removed by stirring with HNO_3

Reaction : $PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O$

$2PbO_2 + 2H_2SO_4 \xrightarrow{\Delta} 2PbSO_4 + 2H_2O + O_2$

$PbO_2 + 2NaOH \longrightarrow Na_2PbO_3 + H_2O$

PbO_2 : Powerful oxidising agent :

(i) $PbO_2 + SO_2 \longrightarrow PbSO_4$ [spontaneously]

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

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

$PbCl_4$: Exists as $H_2[PbCl_6]$

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

{ice cold conc. saturated with Cl_2}

$PbCl_4 + 2HCl \longrightarrow H_2PbCl_6$

TetraEthyl lead :

4Na–Pb(alloy 10%–Na.) + $4C_2H_5Cl$(vap.) $\longrightarrow$ 3Pb + $Pb(Et)_4$ + 4NaCl

It is antiknocking agent.

Group 15 Elements (Nitrogen Family)

The elements are N,P [Non metal]
As [Matalloid]
Sb, Bi [Metal]

The General electronic configuration is [noble gas] $ns^2\ np^3$

(I) **Atomic and Physical properties**

(1) ***Atomic and Ionic radii***

Covalent radius : N < P < As < Sb < Bi

(2) ***Ionization enthalpies***

N > P > As > Sb > Bi (IE_1 values)

(3) ***Electronegativity*** N > P > As > Sb = Bi

(4) ***Metallic Character***

N < P	As <	Sb < Bi
Non metal	Metalloid	Metals

(5) ***Catenation***

* The group 15 elements also show catenation property but to much smaller extent than carbon. For example hydrazine (H_2NNH_2) has two N atoms bonded together HN_3 has three N atoms.

HN_3 $\quad H-\ddot{N}=\overset{+}{N}=\ddot{N}{:}^{\ominus}$

* Among group 15 elements P has the maximum tendency for catenation forming cyclic as well as open chain compounds consisting of many phosphorous atoms.

P_2H_4 has tow P atoms bonded together the lesser tendency of elements of group 15 to show catenation in compression to carbon is their low dissociation enthalpies.

C – C	353.3 kJ /mole
N – N	16.8 kJ / mole
P – P	201.6 kJ / mole
As – As	147.4 kJ / mole

(6) ***Allotropy***

Except N and Bi all other elements of this group show allotropy.

Phosphorous	:	White, Black and Red
Arsenic	:	Yellow or Grey
Antimony	:	Yellow or Silvery grey.

Preparation of N_2 :

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

(ii) $(NH_4)_2\,Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$

(iii) $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$
$2NaN_3 \xrightarrow{\Delta} 2Na + 3N_2$ } Purest N_2 obtained by this method

(iv) $2NH_3 + 3NaOCl \longrightarrow N_2 + 3NaCl + 3H_2O$

(v) $2NO + 2Cu \longrightarrow 2CuO + N_2$
(red,overheated) (Black)

(vi) 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 a particular limit.

$3Cl_2 + NH_3 \longrightarrow NCl_3 + 3HCl$
(Trimendously explosive)

Properties of N_2 :

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

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

$3Ca + N_2 \longrightarrow Ca_3N_2$

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

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

$(BN)_x$: Inorganic graphile
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.

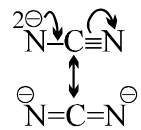
$Na_2B_4O_7 + 2NH_4Cl \xrightarrow{\Delta} 2NaCl + 2NH_3 + 2B_2O_3 + H_2O$
$B_2O_3 + 2NH_3 \longrightarrow 2BN + 3H_2O$

(iii) N_2 can be absorbed by calcium carbide at the temp around 1000°C CaC_2

$$\underset{\text{cyanamide ion}}{CaC_2 + N_2} \xrightarrow{1000°C} \underset{\text{nitro lim}}{CaNCN + C}$$

It is a very good fertiliser.

Cyanamide ion



(iv)

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

→ Slowly decomposes

→ $NH_2–CO–NH_2$ (Intermidiate formed)

TYPES OF NITRIDE :

(i) Salt like or ionic : Li_3N, Na_3N, K_3N (?), Ca_3N_2, Mg_3N_2, Be_3N_2

(ii) Covalent : AlN, BN, Si_3N_4, Ge_3N_4, Sn_3N_4

(iii) Interstitial : MN $(M = Sc, Ti, Zr, Hf, La)$

HCP or FCC

No of metal atom per unit cell is equal to no of octahedral voids per unit cell.
All the octahedral voids are occupied by nitrogen atoms. Hence the fornmula is MN.

HCP : Hexagonal closed pack
FCC : Face centred cubic

NH_3 preparation :

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

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

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

catalyst Fe / Mo

Q.1 NH_3 can't be dried by H_2SO_4, P_2O_5 and anh.$CaCl_2$ because:

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2\,SO_4$$
$$H_2O + NH_3 + P_2O_5 \longrightarrow (NH_4)_3\,PO_4$$
$$CaCl_2 + 8NH_3 \longrightarrow CaCl_2 \,.\, 8NH_3$$

forms adduct

Quick lime is used for this purpose

$CaO + H_2O \longrightarrow Ca(OH)_2$ (base)
NH_3 (base)
} *Hence no interaction*

Properties :

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

Eg. : K in liq $NH_3 \Rightarrow$ (i) Blue in colour
(ii) Conducts electricity
(iii) having reducing property

$$K \longrightarrow K^+ + e^-$$

$K^+ \,(NH_3)_n$

$e(NH_3)_x$ solvated e^-] It is the cause for above property

$$\underset{\text{Square planar complex}}{K_2[Ni(CN)_4]} \xrightarrow[NH_3]{K\text{ in liq}} \underset{\text{Tetrahedral complex}}{K_4[Ni(CN)_4]}$$

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

Residue AgCl | Filtrate $Ba(NO_3)_2$

AgCl $\xrightarrow{\text{liq } NH_3}$ $Cl^- + [Ag(NH_3)_2]^+$

$\downarrow$ $Ba(NO_3)_2$ crystal

$BaCl_2\downarrow + [Ag(NH_3)_2]^+ + NO_3^-$

(iii) CH_3COOH is strong acid in liq. NH_3 while in water is weak acid.

$AcOH \rightleftharpoons Ac\bar{O} + H^+$

$NH_3 + H^+ \longrightarrow NH_4^+$ $\qquad H_2O + H^+ \longrightarrow H_3O^+$

Basisity order $NH_3 > H_2O$

more solvation of H^+ in NH_3.

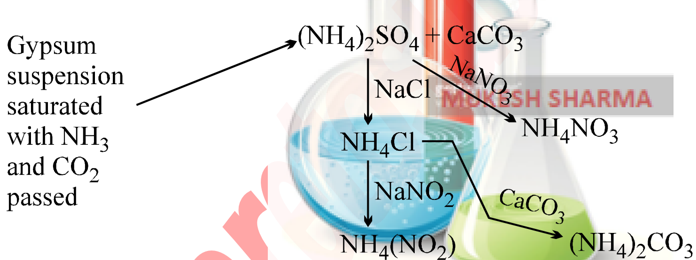
(iv) Hydrolysis and Ammonolysis occurs is a same way.

$SiCl_4 + 4H_2O \longrightarrow 4HCl + Si(OH)_4 \xrightarrow{\Delta} SiO_2 + 2H_2O$

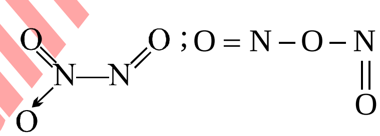
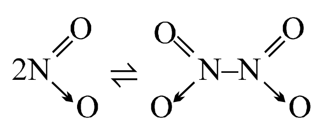
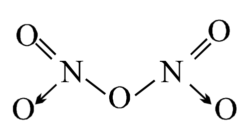
$SiCl_4 + 8NH_3 \longrightarrow 4NH_4Cl + Si(NH_2)_4 \xrightarrow{\Delta} Si_3N_4 + NH_3\uparrow$

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

NH_4^+ – Salts Preparation



OXIDES OF NITROGEN

Oxides of nitrogen	*Structure*	*Physical state*	*Colour of gas*
N_2O	$\bar{N}=\overset{+}{N}=O$	Gas	Colourless
NO	:N̈=Ö: or :N≡O:	Gas	Colourless
N_2O_3			Blue liquid (–30°C)
NO_2		Gas	Brown
N_2O_5		Colourless solid	–(no existance in gas phase)

Preparations:

1. **N_2O**

(i) $NH_4NO_3 \longrightarrow N_2O + H_2O$

(ii) $(NH_4)_2SO_4 + NaNO_3 \longrightarrow NH_4NO_3 + Na_2SO_4$

$$NH_4NO_3 \downarrow N_2O + 2H_2O$$

(iii) $Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + N_2O + H_2O$
(dil.& cold)

2. **NO**

(i) $Cu + HNO_3\ (1:1) \longrightarrow Cu(NO_3)_2 + NO + H_2O$
hot

(ii) $KNO_3 + FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + K_2SO_4 + NO + H_2O$

$FeSO_4 + NO \longrightarrow FeSO_4 . NO \xrightarrow{\Delta} FeSO_4 + NO\uparrow$

(iii) Oswald process–Restricted oxidation of NH_3.
Industrial process.

$$4NH_3 + 5O_2 \xrightarrow[750°C,\ Pt-Cat]{6\ atm} 4NO + 6H_2O$$

3. **N_2O_3**

(i) $HNO_3 + As_2O_3 \longrightarrow H_3AsO_4 + N_2O_3$

(ii) $Cu + HNO_3(6M) \longrightarrow Cu(NO_3)_2 + (NO + NO_2)$ $\xrightarrow{Cool(-30°C)}$ Blueliq(N_2O_3)

4. **NO_2**

(i) $M(NO_3)_2 \xrightarrow{\Delta} MO + 2NO_2 + \frac{1}{2}O_2$

M = Pb, Cu, Ba, Ca

(ii) $(Cu, Pb, Ag) + HNO_3 \longrightarrow$ M-nitrate $+ NO_2 + H_2O$
(hot & conc.)

5. **N_2O_5**

(i) $2HNO_3 + P_2O_5 \longrightarrow 2HPO_3 + N_2O_5$

(ii) $4AgNO_3 + 2Cl_2(\text{dry gas}) \longrightarrow 4AgCl + 2N_2O_5 + O_2$

Properties:

(I) Decoposition Behaviour

(i) $N_2O \xrightarrow{500°C-900°C} 2N_2 + O_2$

(ii) $2NO \xrightarrow{800°C} N_2 + O_2$

(iii) $N_2O_3 \xrightarrow{Room\ temp.} NO_2 + NO$
(Blue liq.) at (–30°C)

(iv) $2NO_2 \xrightarrow{620°C} 2NO + O_2$

N_2O_4 (white solid) at (–11°C) $\xrightarrow{-11°C}$ $2NO_2$ Brown gas

(v) N_2O_5 colourless solid $\xrightarrow{30°C}$ N_2O_5 yellow liq. $\xrightarrow{40°C} 2NO_2 + \frac{1}{2}O_2$

(II) Reaction with H_2O & NaOH

		H_2O	NaOH
(i)	N_2O :	Fairly soluble in water and produces neutral solution	-------
(ii)	NO :	Sparingly soluble in water and produces neutral sol^n.	-------
(iii)	N_2O_3:	$2HNO_2$ Hence it is known as anhydride of HNO_2	$NaNO_2$
(iv)	NO_2:	$HNO_2 + HNO_3$ called as mixed anhydride	$NaNO_2 + NaNO_3$
(v)	N_2O_5:	$2HNO_3$ called as anhydride of HNO_3	$NaNO_3$

Other properties:

N_2O : $2N_2O \longrightarrow 2N_2 + O_2$

Hence it is better supporter for combustion { mixture contains 33% O_2 compared to 20% in air

$S + N_2O \longrightarrow SO_2 + N_2$

$P + N_2O \longrightarrow P_2O_5 + N_2$

$Mg + N_2O \longrightarrow MgO + N_2$

$Na + N_2O \longrightarrow Na_2O + N_2$

$Cu + N_2O \longrightarrow CuO + N_2$

$H_2 + N_2O \longrightarrow H_2O + N_2$

NO : (i) It burns : $NO + \frac{1}{2}O_2 \longrightarrow NO_2$

(ii) It supports combustion also for molten sulphur and hot phosphorous.

$S + 2NO \longrightarrow SO_2 + N_2$

$2P + 5NO \longrightarrow P_2O_5 + \frac{5}{2}N_2$

(iii) It is being absorbed by $FeSO_4$ solution.

(iv) It is having reducing property.

$KMnO_4 + NO + H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + HNO_3 + H_2O$

$HOCl + NO + H_2O \longrightarrow HNO_3 + HCl$

(v) NO shows oxidising property also.

$SO_2 + 2NO + H_2O \longrightarrow H_2SO_4 + N_2O$

$H_2S + 2NO \longrightarrow H_2O + S\downarrow + N_2O$

$3SnCl_2 + 2NO + 6HCl \longrightarrow 3SnCl_4 + 2NH_2OH$

(Used for NH_2OH preparation)

(vi) NO combines with X_2 (X_2= $Cl_2Br_2F_2$) to produce NO X

$2NO + X_2 \longrightarrow 2NOX$

N_2O_3 : No more properties.

NO_2 : (1) It is having oxidising property.

$S + NO_2 \longrightarrow SO_2 + NO$

$P + NO_2 \longrightarrow P_2O_5 + NO$

$C + NO_2 \longrightarrow CO_2 + NO$

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

$H_2S + NO_2 \longrightarrow H_2O + S\downarrow + NO$

$CO + NO_2 \longrightarrow CO_2 + NO$

NO not formed : $2KI + 2NO_2 \longrightarrow I_2 + 2KNO_2$

(2) Reducing property of NO_2.

$KMnO_4 + NO_2 + H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + HNO_3 + H_2O$

$$\overset{0}{O_3} + 2\overset{+4}{NO_2} \longrightarrow \underset{\text{not the reduction product of } O_3}{\overset{0}{O_2}} + \overset{+5}{N_2O_5}$$

N_2O_5 :

$I_2 + 5N_2O_5 \longrightarrow I_2O_5 + 10NO_2$

I_2O_5 is used for the estimation of CO

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

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

$N_2O_5 + NaCl \longrightarrow NaNO_3 + NO_2Cl$

This likes proves that N_2O_5 is consisting of ion pair of NO_2^+ & NO_3^-

Oxyacids of N :

HNO_2 :

Preparation

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

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

Properties

(i) Oxidising property of HNO_2

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

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

$SO_2 + HNO_2 + H_2O \longrightarrow H_2SO_4 + NO$

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

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

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

(ii) Reducing property of HNO_2

$KMnO_4 + HNO_2 + H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + HNO_3 + H_2O$

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

$H_2O_2 + HNO_2 \longrightarrow H_2O + HNO_3$

HNO_2 + urea $\longrightarrow$

+ thiourea $\longrightarrow$

+ sulphamic acid $\longrightarrow$

$+ NH_3 \longrightarrow NH_4NO_2$

$+ C_2H_5NH_2 \longrightarrow C_2H_5OH + N_2$

$+ Ph{-}NH_2 \xrightarrow{<5°C} PhN_2^+X^-$

Nitric acid (HNO_3)

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

Preparation

(i) 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.

(ii) Industrial Preparation

(A) Birkeland Eyde Process or arc process

step 1 $N_2 + O_2 \xrightarrow[\text{Electric Arc}]{3000^0 C} 2NO - \text{heat}$

step 2 $NO + O_2 \longrightarrow NO_2$

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

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

(B) Ostwald's Process

step 1 $NH_3 + O_2 \xrightarrow[700-800^0 C]{\text{Pt. gauze}} NO + H_2O + \text{heat}$

step 2 $NO + O_2 \xrightarrow[\text{Air}]{\text{R.T.}(25°C)} NO_2$

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

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

PROPERTIES

Physical

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

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

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

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

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

(b) 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 $$2HNO_3 \longrightarrow H_2O + 2NO + 3O$$

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

(1) Sulphur is oxides to sulphuric acid

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

(2) Carbon is oxidised to carbonic acid

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

(3) Phosphorus is oxidised to orthophosphoric acid.

$$2P + 10HNO_3 \rightarrow 2H_3PO_4 + 10NO_2 + 2H_2O$$

conc. and hot

(4) Iodine is oxidised to iodic acid

$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$$
conc. and hot

(ii) Oxidation of metalloids

Metalloids like non-metals also form highest oxyacids

(1) Arsenic is oxidised to arsenic acid

$$2As + 10HNO_3 \rightarrow 2H_3AsO_4 + 10NO_2 + 2H_2O$$
or $$As + 5HNO_3 \rightarrow H_3AsO_4 + 5NO_2 + H_2O$$
conc. and hot

(2) Antimony is oxidised to antimonic acid

$$Sb + 5HNO_3 \rightarrow H_3SbO_4 + 5NO_2 + H_2O$$
conc. and hot

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

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

(iii) Oxidation of Compounds:

(1) Sulphur dioxide is oxidised to sulphuric acid

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

(2) Hydrogen sulphiode is oxidised to sulphur

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

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

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

(4) Iodine is liberated from KI.

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

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

$$2HBr + 2HNO_3 \rightarrow Br_2 + 2NO_2 + 2H_2O$$
Similarly, $2HI + 2HNO_3 \rightarrow I_2 + 2NO_2 + 2H_2O$

(6) Ferrous sulphide is oxidised to ferrous sulphate

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

(7) Stannous chloride is oxidised to stannic chloride is presence of HCl.

$$2HNO_3 + 14H \rightarrow NH_2OH + NH_3 + 5H_2O$$
Hydroxylamine

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

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

(8) Cane sugar is oxidised to oxalic acid.

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

(c) Action on Metals: Most of the metals will the exveption of noble metals like gold and platinum are attacked by Nitric acid plays a double role in the action of metals, i,e, it acts as an acid as well as an oxidising agent. ARmstrong postulated that primary action of nitric acid is to produce hydrogen in the nascent form. Before this hydrogen is allowed to escape, it reduces the nitric acid into number of products like NO_2, NO, N_2O, N_2 or NH_3 according to the following reactions:

$$Metal + HNO_3 \longrightarrow Nitrate + H$$
$$2HNO_3 + 2H \longrightarrow 2NO + 2H_2O$$
$$2HNO_3 + 6H \longrightarrow 2NO + 4H_2O$$
$$2HNO_3 + 10H \longrightarrow N_2 + 6H_2O$$
$$2HNO_3 + 16H \longrightarrow 2NH_3 + 6H_2O$$

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	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	NO_2 + metal nitrate + H_2O
	Sn	NO_2 + H_2SnO_3 Metastannic acid

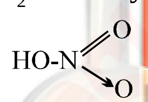
Action on Proteins

(i) 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.

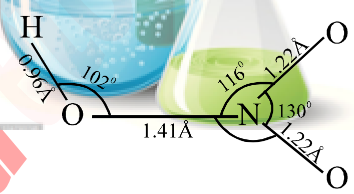
(ii) **Oxidation** A number of organic compounds are oxidised.
Sawdust catches fire when nitric acid is poured on it. Turpentine oil bursts into flames when treated with fuming nitric acid. Cane sugar is oxidised to oxalic acid. Toluene is oxidised to benzoic acid with dil. HNO_3.

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



PHOSPHOROUS

INTERCONVERSION OF WHITE 'P' & RED 'P'

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

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

PREPRATION OF WHITE 'P'

(i) Bone ash or Apatite rock (both have same formula)

$$Ca_3(PO_4)_2 + 3SiO_2 \xrightarrow{1200°C} 3CaSiO_3 + P_2O_5$$

$$2P_2O_5 + \underset{(Coke)}{10C} \xrightarrow{1500°C} \underset{\text{white 'P'}}{P_4} + 10CO\uparrow$$

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

$$H_3PO_4 \xrightarrow[-H_2O]{320°C} \underset{\text{meta phosphoric acid}}{HPO_3}$$

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

REACTIONS OF 'P'

* $P + H_2SO_4 \text{ (hot \& conc.)} \longrightarrow H_3PO_4 + SO_2 + H_2O$

$P + KIO_3 + H_2SO_4 \longrightarrow H_3PO_4 + I_2 + K_2SO_4$

* Reaction with hot metal —

$3Na + P \longrightarrow Na_3P$

$3Mg + 2P \longrightarrow Mg_3P_2$

$3Ca + 2P \longrightarrow Ca_3P_2$

$2Cu + 2P \longrightarrow Cu_3P_2$

$Al + P \longrightarrow AlP$

$Ca_3P_2 + H_2O \longrightarrow M(OH)_n + PH_3$

or Mg_3P_2

or AlP

PREPARATION OF PH_3 (PHOSPHINE GAS)

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

(ii) $\underset{(PH_3 + HI)}{PH_4I} + KOH \longrightarrow KI + PH_3 + H_2O$

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

} Purest PH_3 [(ii) and (iii)]

PHYSICAL PROPERITIES

(i) It is having 'rotten fish' smell

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

(NH_3 is soluble in water)

$NH_4^+ + OH^-$

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

→ in s-orbital, so donating capacity is less

PH_4^+ is formed with acids

(iii) 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.

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

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

OTHER REACTIONS OF PH_3

(i) $PH_3 + O_2 \xrightarrow{150°} P_2O_5 + H_2O$

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

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

(iv) $2PH_3 + 3CuSO_4 \longrightarrow Cu_3P_2\downarrow + 3H_2SO_4$

Detection of PH_3 Black ppt.

(v) $PH_3 + 6AgNO_3 \longrightarrow [Ag_3P \cdot 3AgNO_3\downarrow] + 3HNO_3$

yellow ppt.

$Ag_3P \cdot 3AgNO_3 + 3H_2O \longrightarrow 6Ag\downarrow + 3HNO_3 + H_3PO_3$

Black ppt.

(vi) $PH_3 + 4HCHO + HCl \longrightarrow [P(CH_2OH)_4]^+Cl^-$

white/colourless solid which is used for making fire-proof cotton fabrics

EXAMPLE OF DEHYDRATING REACTION OF P_2O_5

$HClO_3 + P_2O_5 \longrightarrow 2HPO_3 + Cl_2O_7$

$H_2SO_4 + P_2O_5 \longrightarrow 2HPO_3 + SO_3$

$HNO_3 + P_2O_5 \longrightarrow 2HPO_3 + N_2O_5$

Group 16 Elements (Oxygen family)

The Elements are O, S, Se, Te, Po (Chalcogens)

Atomic and Physical Properties

(1) ***Atomic radii and Ionic radii***

Covalent radius : O < S < Se < Te

(2) ***Ionization Enthalpies***

O > S > Se > Te > Po (IE_1 values)

(3) ***Melting and Boiling points***

M.P. : Te > Po > Se > S > O

B.P. Te > Po > Se > S > O

(4) ***Electronegativity***

O > S > Se > Te

(5) ***Metallic Character***

O < S < Se < Te < Po

(6) ***Elemental State***

Oxygen exist as diatomic molecular gas in this case there is $p\pi - p\pi$ overlap thus tow O atoms form double bond O = O. The intermolecular forces in O_2 are weak VB forces. ∴ O_2 exist as gas . On the other bond, other elements of family do not form stable $p\pi - p\pi$ bonds and do not exist as M_2 molecules. Other atoms are linked by single bonds and form poly atomic complex molecules for eg. S – S_8, Se – S_8

(7) ***Allotropy***

All element exhibit allotropy for e.g.

Oxygen – O_2 and O_3
Liquid O_2 - pale base
Solid O_2 - blue

Sulphur -

The main allotropic forms are

(i) Rhombic sulphur (α sulphur) (ii) Monoclinic (β sulphur) (iii) Plastic sulphur (δ sulphur)

(i) ***Rhombic Sulphur (α sulphur)***

This allotrope is yellow in colour (m.p. 385.8 K).
It is insoluble in water but readily soluble in CS_2.

(ii) ***Monoclinic Sulphur (β sulphur)***

It is soluble in CS_2

$$S(\alpha) \underset{<95.5^\circ C}{\overset{>95.5^\circ C}{\rightleftharpoons}} S(\beta)$$

(iii) ***Plastic Sulphur (δ sulphur)*** It is insoluble in CS_2.

(8) ***Catenation***

In this group only S has a strong tendency for catenation oxygen has this tendency to a limited extent.

H_2O_2	H – O – O – H	(Poly oxides)
H_2S_2	H – S – S – H	(Polysulphides or polysulphones)
H_2S_3	H – S – S – S – H	
H_2S_4	H – S – S – S – S – H	

SULPHUR CHEMISTRY

* **Allotropes:** (i) Rhombic or α-sulphur.
(ii) Monoclinic or β-sulphur.
(iii) γ-Sulphur

$$S(\alpha) \underset{\text{below } 95.5^\circ C}{\overset{95.5^\circ C}{\rightleftharpoons}} S(\beta) \quad \text{above } 95.5^\circ C$$

Amorphous forms are

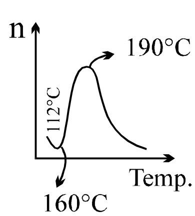
(i) Plastic sulphur
(ii) Milk of sulphur
(iii) Colloidal sulphur

* Viscosity of 'S' with temperature:

m.p. of 'S' ⟶ 112.8°C.

(i) > 112.8°C to 160°C ⇒ slow decreases due to S_8 rings slip and roll over one another easily.

(ii) > 160°C, increases sharply due to breaking of S_8 rings into chains and polymerses into large size chain.



(iii) 190°C, again large chains are being broken into small chain.

* **Milk of sulphur :**

Powdered 'S' + $Ca(OH)_2$ suspension $\longrightarrow$ Solution $\xrightarrow{\text{Acidified}}$ Milk of 'S'

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

$2CaS_5 + CaS_2O_3 + 6HCl \longrightarrow 3CaCl_2 + 12\,S + 3H_2O$

* **Colloidal Sulphur :** $Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2 + S\downarrow$

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

Props. of 'S' : (a) Thin Cu-strip catches fire in sulphur vapour.

$Cu + S \longrightarrow CuS.$

(b) 'S' burns spontaneously in fluorine. $S + 3F_2 \longrightarrow SF_6$

Cl_2 passed into liq. sulphur $\Rightarrow 2\,S + Cl_2 \rightarrow S_2Cl_2$

(c) $S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$

$S + 2HNO_3 \longrightarrow H_2SO_4 + 2NO$

(d) $4\,S + 6\,KOH \longrightarrow 2K_2S + K_2S_2O_3 + 3H_2O$

(e) Burns in air : $S + O_2 \longrightarrow SO_2$

H_2S :

Prep^n.: $FeS + \text{dil. } H_2SO_4 \longrightarrow FeSO_4 + H_2S$

$FeS + \text{dil. } HCl \longrightarrow FeCl_2 + H_2S$

$Sb_2S_3 + (\text{conc.})6HCl \longrightarrow 2SbCl_3 + 3H_2S$

* Drying agent for this gas : fused $CaCl_2$, Al_2O_3 (dehydrated) P_2O_5 etc. But not H_2SO_4, because

$H_2SO_4 + H_2S \longrightarrow 2H_2O + SO_2 + S$

Reducing property of H_2S :

$Cl_2 + H_2S \longrightarrow 2HCl + S$

$I_2 + H_2S \longrightarrow 2HI + S$

$H_2O_2 + H_2S \longrightarrow 2H_2O + S$

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

$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S$

** $4H_2O + 4Cl_2 + H_2S \longrightarrow H_2SO_4 + 8HCl$

$KMnO_4 + H_2S + H_2SO_4 \longrightarrow S + Mn^{2+}$

$H_2Cr_2O_7 + H_2S + H_2SO_4 \longrightarrow Cr^{3+} + S +$

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

<u>With metal (hot)</u>

$2Na + H_2S \longrightarrow Na_2S + H_2$

$Cu + H_2S \longrightarrow CuS + H_2$

$Pb + H_2S \longrightarrow PbS + H_2$

<u>With metal oxide (hot)</u>

$CaO + H_2S \longrightarrow CaS + H_2O$

$ZnO + H_2S \longrightarrow ZnS + H_2O$

Metal ion + $H_2S \longrightarrow$ M-Sulphides

** (i) Alkali-sulphide $\longrightarrow$ water soluble

(ii) Alkaline earth–sulphide $\longrightarrow$ sparingly soluble

(iii) Al_2S_3 & $Cr_2S_3 + 6H_2O \longrightarrow Al(OH)_3$ or $Cr(OH)_3 + 3H_2S$

Test :

(i) Smell $\Rightarrow$ rotten egg.

(ii) Pb– Acetate paper–black

(iii) Purple colour when alk. Nitropruside + H_2S

Absorbent : NaOH, KOH, $PbNO_3$ solution

$Pb(NO_3)_2 + H_2S \longrightarrow 2HNO_3 + PbS$ (Black)

$\underline{SO_2}$

Prep^n.:

Industrial : $4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

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

Lab prep^n.: $Cu + 2H_2SO_4$ (conc.) $\longrightarrow CuSO_4 + 2H_2O + SO_2$

$Hg + H_2SO_4 \longrightarrow HgSO_4 + H_2O + SO_2$

$2Ag + H_2SO_4 \longrightarrow Ag_2SO_4 + H_2O + SO_2$

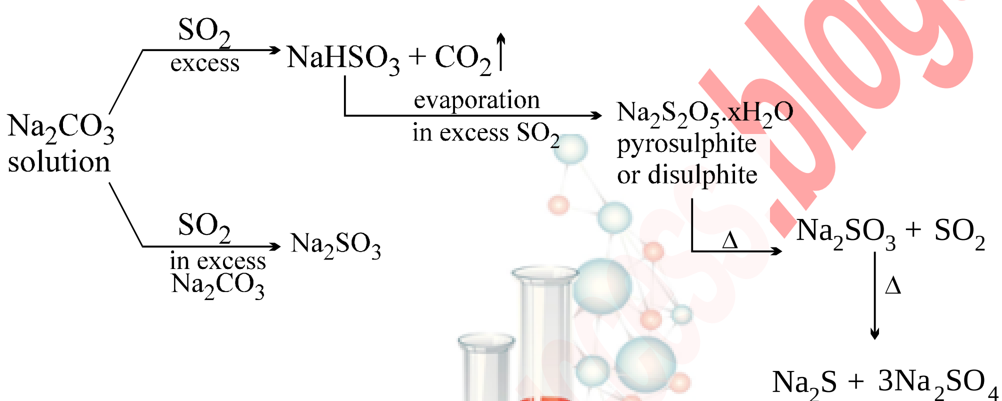
$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$

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

$NaHSO_3 + H_2SO_4 \longrightarrow NaHSO_4 + H_2O + SO_2$

Props: (i) Incombustible gas, but heated K burns in SO_2

$4K + 3SO_2 \longrightarrow K_2SO_3 + K_2S_2O_3$



Reducing Prop.: (Revise from acid radical)

(i) $FeCl_3 + SO_2 \longrightarrow FeCl_2 + H_2SO_4$

$FeCl_2 \xrightarrow{\text{Add HCl to make strongly acidic and } SO_2 \text{ passed}} FeCl_3$

$4FeCl_2 + SO_2 + 4HCl \longrightarrow 4FeCl_3 + H_2O + S$

$6SnCl_2 + 2SO_2 + 8HCl \longrightarrow 5SnCl_4 + 4H_2O + SnS_2\downarrow$(Yellow solid)

(ii) $SO_2 + 2H_2SO_3 \xrightarrow[\text{sealed tube}]{150°C} 2H_2SO_4 + S$

* $FeSO_4 \longrightarrow Fe_2O_3 + SO_2 + SO_3$

$Fe_2(SO_4)_3 \longrightarrow Fe_2O_3 + 3SO_3$

H_2SO_4 & SO_3 :

$\overset{\text{Both gas}}{SO_2 + Cl_2} \longrightarrow SO_2Cl_2$

$H_2SO_4 + 2PCl_5 \longrightarrow .... \longrightarrow SO_2Cl_2 + 2POCl_3 + 2HCl$

Use of H_2SO_4 as nitrating mixture: (SO_2Cl_2 ↓ good chlorinating agent)

** P_2O_5 is stronger dehydrating agent than H_2SO_4 : $H_2SO_4 + P_2O_5 \longrightarrow 2HPO_3 + SO_3$

Properties of H_2SO_4 :

(a) Dissociation : At 444°C. $H_2SO_4 \rightleftharpoons H_2O + SO_3$

(b) Acidic nature : $NaOH + H_2SO_4 \rightleftharpoons NaHSO_4 + H_2O \xrightleftharpoons{NaOH} Na_2SO_4 + H_2O$

(c) $CO_3^{2-} + H_2SO_4 \longrightarrow SO_4^{2-} + H_2O + CO_2$

$HCO_3^- + H_2SO_4 \longrightarrow H_2SO_4^- + H_2O + CO_2$

} *Carbonates or bicarbonates are getting decomposed*

(d) $Zn / Fe + H_2SO_4 \longrightarrow ZnSO_4$ & $FeSO_4 + H_2$

where as

$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

$2Ag + 2H_2SO_4 \longrightarrow Ag_2SO_4 + SO_2 + 2H_2O$

$Hg + 2H_2SO_4 \longrightarrow HgSO_4 + SO_2 + 2H_2O$

(e)

$NaCl$		HCl
$Ca_3(PO_4)_2$		H_3PO_4
FeS		H_2S
CH_3CO_2Na	$+ H_2SO_4 \longrightarrow$	$AcOH$
$NaNO_3$		HNO_3
CaF_2		HF
$NaNO_2$		HNO_2

(f) **Oxidising Prop.:**

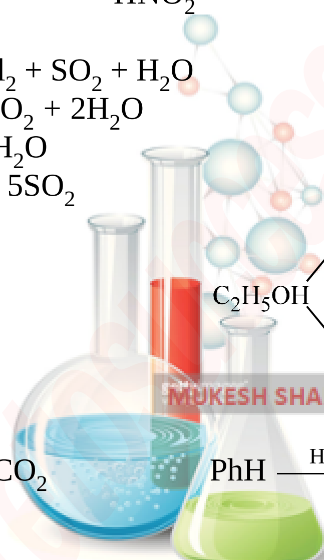
$HBr / HI + H_2SO_4 \longrightarrow I_2/Cl_2 + SO_2 + H_2O$

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

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

$2P + 5H_2SO_4 \longrightarrow H_3PO_4 + 5SO_2$

(g) Dehydrating agent:



$C_{12}H_{22}O_{11} \xrightarrow[-11H_2O]{H_2SO_4} 12\ C$

$C_2H_5OH \xrightarrow[H_2SO_4]{140°C} C_2H_5O{-}C_2H_5$

$C_2H_5OH \xrightarrow{180°C} C_2H_4$

$C_6H_{12}O_6 \xrightarrow[-6H_2O]{H_2SO_4} 6C$

$(COOH)_2 \xrightarrow[-H_2O]{H_2SO_4} CO + CO_2$

$PhH \xrightarrow{H_2SO_4} Ph{-}SO_3H$

$HCO_2H \xrightarrow[-H_2O]{} CO$

SODIUM THIOSULPHATE

Prep^n.:

(i) Na_2SO_3 sol^n. + S (powder) $\xrightarrow{boiling} Na_2S_2O_3 \xrightarrow{eavporation} Na_2S_2O_3.5H_2O$, monoclinic crystal

Na_2CO_3 excess $\xrightarrow{SO_2 \text{ passed}}$ $\begin{cases} Na_2CO_3 + 2SO_2 + H_2O \longrightarrow 2NaHSO_3 + CO_2 \\ 2NaHSO_3 + Na_2CO_3 \longrightarrow Na_2SO_3 + H_2O + CO_2 \end{cases}$

(ii) $\underset{\text{Salt cake}}{Na_2SO_4} + \underset{\text{Coke}}{4C} \xrightarrow{roasting} Na_2S + 4CO$

$\downarrow$ SO_2 passed into it

$Na_2S_2O_3$ [$3SO_2 + 2Na_2S \longrightarrow 2Na_2S_2O_3 + S$]

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

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

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

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

(vi) $2Na_2S + 2O_2 + H_2O \longrightarrow Na_2S_2O_3 + 2NaOH$ [Na_2S is readily oxidised in air giving rise to $Na_2S_2O_3$]

Props : (i) $4Na_2S_2O_3 \xrightarrow{\Delta} Na_2S_5 + 3Na_2SO_4$

(ii) $Na_2S_2O_3 + 2H^+ \longrightarrow H_2S_2O_3 \xrightarrow{\Delta} H_2O + SO_2 + S\downarrow$ (White turbidity)

Reaction: (i) $Na_2S_2O_3 + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

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

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

$+ 4OI^- + 2OH^- \longrightarrow 2SO_4^{2-} + 4I^- + H_2O$

$+ \underset{\text{excess}}{4Cl_2} + 5H_2O \longrightarrow Na_2SO_4 + 8HCl + H_2SO_4$

OZONE

⇒ 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.

⇒ $2F_2 + 2H_2O \longrightarrow 4HF + O_2$
$F_2 + 3H_2O \longrightarrow 6HF + O_3$
] Ozonised oxygen] is separated by passing into spiral tube cooled by liq. air. Ozone condenses at –112.4°C. [b.p. of O_2 –183°C ; b.p. of liq. air is –190°C]

⇒ ***Oxidising property of O_3***

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

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

It is next to F_2. [above 2.07 V, only F_2, F_2O are there]

(i) Metal Sulphides to Sulphates.

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

(ii) $2HX + O_3 \longrightarrow X_2 + H_2O + O_2$ [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) Moist S, P, As + O_3 ⇒

$S + H_2O + 3O_3 \longrightarrow H_2SO_4 + 3O_2$

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

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

(v) Moist $I_2 \longrightarrow HIO_3$ whereas dry iodine $\longrightarrow I_4O_9$ (yellow)

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

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

(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)(a) 2KI (acidified) + O_3 + 2HCl $\longrightarrow I_2 + 2KCl + H_2O + O_2$

(b) 2KI (neutral) + $O_3 + H_2O \longrightarrow I_2 + 2KOH + O_2$

$KI + KOI + 2HCl \longrightarrow 2KCl + I_2 + H_2O$ (KI+KOI)

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

} O_3 estimated by this reaction

(c) alk. { $KI + 3O_3 \longrightarrow KIO_3 + 3O_2$
$KI + 4O_3 \longrightarrow KIO_4 + 4O_2$ }

(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) $BaO_2 + O_3 \rightarrow BaO + 2O_2$

$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$

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

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

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

(i) $3SO_2 + O_3 \longrightarrow 3SO_3$

(ii) $3SnCl_2 + 6HCl + O_3 \longrightarrow 3SnCl_4 + 3H_2O$

Absorbent : (i) Turpentine oil

(ii) Oil of cinnamon

Uses: (i) Sterilising water

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

H_2O_2

Method of preparation:

(i) $Na_2O_2 + H_2O$ (ice cold water) $\longrightarrow 2NaOH + H_2O_2$

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

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.

$3BaO_2 + 2H_3PO_4 \rightarrow Ba_3(PO_4)_2 + 3H_2O_2$ and $Ba_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3BaSO_4 + 2H_3PO_4$ (reused again)

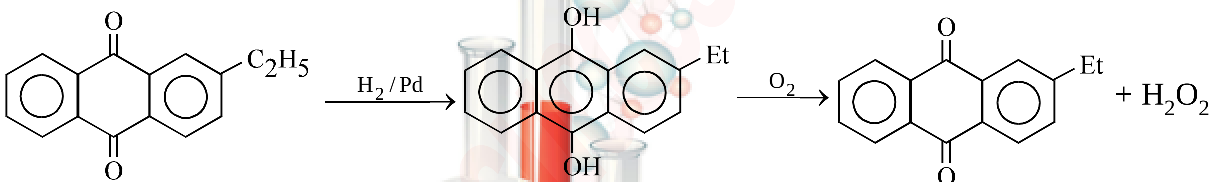
(iii) Electrolysis of 50% H_2SO_4 using high current density.

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

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

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

(iv)



Properties:

(i) Colourless, odourless liquid (b.p.152°)

(ii) Acidic nature: $H_2O_2 + 2NaOH \longrightarrow Na_2O_2 + H_2O$

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

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

(iii) It is oxidant as well as reductant.

$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$ [reaction in acidic medium]

$H_2O_2 + 2e \rightarrow 2OH^-$ [rxn^n in alkali medium]

Oxidising Properties:

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

(ii) $NaNO_2 + H_2O_2 \longrightarrow NaNO_3 + H_2O$

$Na_2SO_3 + H_2O_2 \longrightarrow Na_2SO_4 + H_2O$

$Na_3AsO_3 + H_2O_2 \longrightarrow Na_3AsO_4 + H_2O$

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

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

[$X_2 + H_2O_2 \longrightarrow 2HX + O_2$ X = Cl, Br.
S.R.P order of $Cl_2 > Br_2 > H_2O_2 > I_2$]

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

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

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

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

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

$Mn^{+2} + OH^- + H_2O_2 \longrightarrow MnO_2 + 2H_2O \Rightarrow$ This reaction can be utilised to detect NH_3

Reducing properties:

(a) $Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$

(b) $O_3 + H_2O_2 \longrightarrow H_2O + 2O_2$

(c) $MnO_2 + H_2O_2 + H_2SO_4 \rightarrow MnSO_4 + 2H_2O + O_2$

(d) $PbO_2 + H_2O_2 \rightarrow PbO + H_2O + O_2$

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

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

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

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

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

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

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

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

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

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

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

(i) $NaOCl + H_2O_2 \longrightarrow NaCl + H_2O + O_2$

(j) $NaIO_4 + H_2O_2 \longrightarrow NaIO_3 + H_2O + O_2$

Uses: (i) As a rocket propellant:

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

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

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

Group -17 Elements (Halogens Family)

Method of Prep^n :

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

$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

$HF + KF \longrightarrow KHF_2$

{*KF decreases the m.p. of the mix. depending upon the composition.*}

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

Cl_2 : (i) By electrolysis of aq. NaCl :

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

(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 Brine water (contains 65 ppm of Br^-)

$Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2$ (Br_2 is volalite 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

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

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^-.

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

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

Q. Liquid I_2 conducts electricity. Explain

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

Q. $X_2 + OH^- \longrightarrow X^- + OX^- + H_2O$

$\longrightarrow X^- + XO_3^- + H_2O$

$X_2 = Cl_2, Br_2, I_2$. But For F_2

$2F_2 + 2NaOH \rightarrow 2NaF + F_2O + H_2O$
$F_2O + 2NaOH \rightarrow 2NaF + O_2 + H_2O$

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

but on acidification the disproportionated product gives back the same element.

i.e. $X^- + OX^- + 2H^+ \longrightarrow X_2 + H_2O$
$5X^- + XO_3^- + 6H^+ \longrightarrow 3X_2 + 3H_2O$
[X = Cl, Br, I]

HALOGEN ACID:

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

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

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

If SiO_2 present as impurity

$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$
$SiF_4 + 2HF \longrightarrow H_2[SiF_6]$

} Hence presence of one molecule SiO_2 consumes 6 molecule of HF

Q. HF can not be stored in glass vessel. Explain– same reason.

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

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

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

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

[NH_4HSO_4 intermediate is water soluble and easy to handle]

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

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

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

Ans. 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. $NaBr + H_3PO_4 \longrightarrow NaH_2PO_4 + HBr$

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

Q. Boiling point order of HX : HF > HI > HBr > HCl
↓ (HF) Due to H-bonding

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

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

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

HO X:

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

$HOF + F_2 \longrightarrow F_2O + HF$

$HOF + H_2O \longrightarrow H_2O_2 + HF$

$\left.\begin{matrix} HOCl \\ HOBr \\ HOI \end{matrix}\right\} X_2 + H_2O \longrightarrow HOX + HX$

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

X = Cl, Br, I

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

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

(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:

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

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

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

Prep[n]**:**

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

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

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

$Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$ (recycled)

$NaClO_3 + KCl \longrightarrow KClO_3\downarrow + NaCl$ [$KClO_3$ prep.^{n}] on cooling

$NaClO_3 + BaCl_2 \longrightarrow Ba(ClO_3)_2 + NaCl\downarrow$ first

$Ba(ClO_3)_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow HClO_3$

Properties :

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

* $IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$

$ClO_3^- + 3SO_3^{2-} \longrightarrow Cl^- + 3SO_4^{2-}$ } Oxidising property

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

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

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 { A : $ClO_3^- + H_2O \longrightarrow ClO_4^- + 2H^+ + 2e$

C : $2H^+ + 2e \longrightarrow H_2$

$\xrightarrow{KCl} KClO_4 \xrightarrow{H_2SO_4} HClO_4$

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

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

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

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 CHLORINE

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

Prep^n.: Cl_2 does not combine directly to produce its oxides but indirect methods are there.

Cl_2O: $2Cl_2$ (dry) $+ 2HgO(s)$ (in cooled tube) $\longrightarrow HgO.HgCl_2$ (Basic Hg(II) chloride) $+ Cl_2O\uparrow$ (Brownish yellow gas) → Condensed to orange liq.

Props.:

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

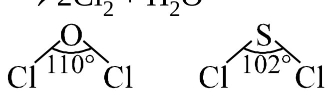
(ii) Explodes violently with NH_3.

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

(iii) It is oxidising agent

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

(iv) Structures.



{ Back bonding

(II) **ClO_2: Prep^n.:**

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

(ii) $2HClO_3 + H_2C_2O_4 \xrightarrow{60°C} 2H_2O + 2ClO_2 + 2CO_2$

(iii) $2AgClO_3 + Cl_2 \xrightarrow{90°C} 2AgCl + 2ClO_2 + O_2$ [By this reaction pure ClO_2 obtained]

ClO_2 dissolves in water producting 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 a mixture of chlorite and chlorate.

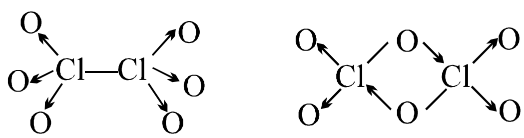
$$2ClO_2 + 2NaOH \longrightarrow NaClO_2 + NaClO_3 + H_2O$$

where $2ClO_2 + 2NaOH + H_2O_2 \longrightarrow 2NaClO_2 + O_2 + 2H_2O$
used in bleaching textles and paper.

* ClO_2 does not dimerise because odd e' 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 $\rightarrow$ dark red
Solid $\rightarrow$ Yellow

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

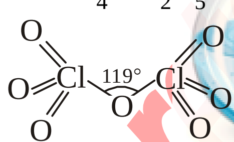
Prep^n.: $2ClO_2 + 2O_3 \xrightarrow{0°C} Cl_2O_6 + 2O_2$
$Cl_2O_6 \rightleftharpoons 2ClO_3$ (monomer is paramagnetic)

Reactions :
$Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$
$Cl_2O_6 + NaOH \longrightarrow NaClO_3 + NaClO_4 + H_2O$
$Cl_2O_6 + HF \longrightarrow ClO_2F + HClO_4$
$Cl_2O_6 + NO_2 \longrightarrow ClO_2 + [NO_2]^+ [ClO_4]^-$

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

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

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 type halogens in a molecule.
* 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 more atoms around it.
* The interhalogens are generally more reactive than the halogens (except F_2) due to weaker A–X bonds compared to X–X bond.

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

$$\left.\begin{array}{l} BrF_5 + 3H_2O \longrightarrow HBrO_3 + 5HF \\ IF_5 + 3H_2O \longrightarrow HIO_3 + 5HF \\ IF_7 + H_2O \longrightarrow IOF_5 + 2HF \text{ less} \\ \quad 4H_2O \longrightarrow HIO_4 + 7HF \end{array}\right\}$$

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

Parallel reaction

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

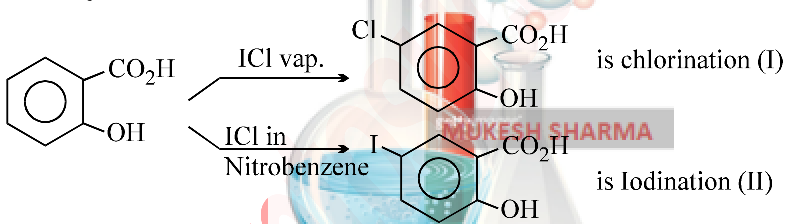
$6ClF + 2Al \longrightarrow 2AlF_3 + 3Cl_2$

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

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

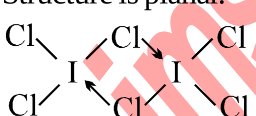
$ClF + SF_4 \longrightarrow SF_5Cl$

One pecularity with ICl :



In II[nd] case, the attacking species is I^+ which has been supporetd by the formation of I^+ in fused state as follows : $3ICl \longrightarrow [I_2Cl]^+ + [ICl_2]^-$

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



(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) $ICl_3 + KCl \longrightarrow K^+[ICl_4]^-$

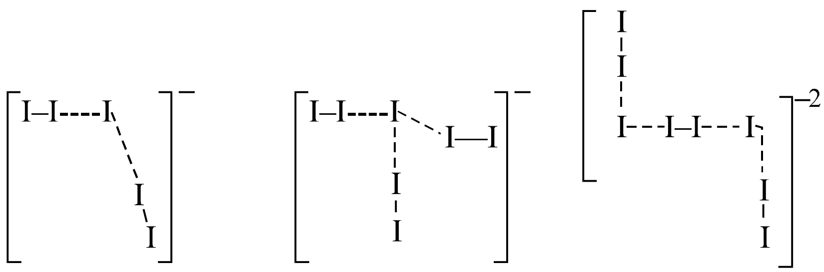
(iv) $IF_5 + CsF \longrightarrow Cs^+[IF_6]^-$

(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. $Cs_2\ I_3 - I_2 - I_3$]

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 properties 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 similarites with Cl^-, Br^-, I^-

(i) froms HCN

(ii) forms$(CN)_2$

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

(iv) Interpseudo 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. $[Cu(CN)_4]^{3-}$ & $[CuCl_4]^{-3}$
$[Co(CN)_6]^{-3}$ & $[CoCl_6]^{-3}$

- * I.E. order : He > Ne > Ar > Kr > Xe > Rn
- * M.P. order : He < Ne < Ar < Kr < Xe < Rn ↓
- * B.P. order : (–269°C) same order
- * Atomic radius order : Same order
- * Density order : Same order
- * Relative abundance : Ar is highest (Ne, Kr, He, Rn)
- * "He" (helium) has the lowest b.p (–269°C) 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_2 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 same metals.
- * He liquid can exist in two forms. I-form when changes to II-form at λ-point temperature many physical properties change abruptly.

  e.g.

  (i) Sp. heat changes by a factor of 10

  (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?

eg. $Xe \cdot 6H_2O$, $Ar \cdot 6H_2O$, $Kr \cdot 6H_2O$ } formed only when water freezes at high pressure together with noble gas

Xe – COMPOUNDS

Xenon Fluorides:–

(1) $Xe + F_2$

- $\xrightarrow{400°C,\ 1atm}$ 2 : 1 $\longrightarrow XeF_2$
- $\xrightarrow{600°C,\ 7\ atm}$ 1 : 5 $\longrightarrow XeF_4$
- $\xrightarrow{300°C,\ 60\text{-}70\ atm}$ 1 : 20 $\longrightarrow XeF_6$

(2) H_2 reduces Xe – fluorides to Xe

$$XeF_2 + H_2 \longrightarrow Xe + 2HF \text{ and so on}$$

(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

$$3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12HF + \frac{3}{2}O_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

↓ (explosive, white hygroscopic solid)

(5) SiO_2 also converts XeF_6 into $XeOF_4$

$$2XeF_6 + SiO_2 \longrightarrow SiF_4\uparrow + 2XeOF_4$$

violet

Similarly, $XeO_3 + XeOF_4 \longrightarrow 2XeO_2F_2$ | $XeO_3 + 2XeF_6 \longrightarrow 3XeOF_4$

(6) Xe-fluorides are also hydrolysed in alkaline medium

$$2XeF_2 + 4OH^- \longrightarrow 2Xe + 4F^- + 2H_2O + O_2$$

$$XeF_6 + 7OH^- \longrightarrow \underset{\text{Xenate ion}}{HXeO_4^-} + 3H_2O + 6F^-$$

$$2HXeO_4^- + 2OH^- \longrightarrow XeO_6^{4-}\downarrow + Xe + 2H_2O + O_2$$

perxenate ion

(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

$$XeF_2 + MF_5 \longrightarrow [XeF]^+ [MF_6]^- \quad (M = As, Sb, P)$$

$$XeF_6 + BF_3 \longrightarrow [XeF_5]^+ [BF_4^-]$$

$$XeF_6 + HF \longrightarrow [XeF_5]^+ [HF_2]^-$$

(9) Act as Fluoride acceptor also:

$$XeF_6 + RbF/CsF \longrightarrow Rb^+/Cs^+ [XeF_7]^-$$

$$2Cs^+[XeF_7]^- \xrightarrow[50°C]{\Delta} XeF_6 + Cs_2[XeF_8]$$

$$XeF_4 + MF \longrightarrow M^+ + XeF_5^-$$

(alkali metals fluoride)