

p-BLOCK ELEMENTS-II

NITROGEN FAMILY

GROUP 15 ELEMENTS (NITROGEN FAMILY)

The elements are : N, P [Non metal], As [Metalloid], 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 : $\frac{N < P}{\text{Non metal}} \quad \frac{\text{As} <}{\text{Metalloid}} \quad \frac{\text{Sb} < \text{Bi}}{\text{Metals}}$

(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.



- * 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 two P atoms bonded together the lesser tendency of elements of group 15 to show catenation in comparison 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) Valency and Oxidation Number :

(a) Gen. configuration : $ns^2 np^3$

Valency = 3

O.S. = - 3, + 3, + 5

P show O.S. = - 3, + 3

(b) P has two sleeping valency.

(c) **Sleeping Valency :** These electron of valency shell which does not take part in bonding.

(d) P in excited state show + 5 O.S.

So Hybridisation = sp^3d

Shape = Trigonal by pyramidal.

(e) P, As, Sb Show 3 & 5 both O.S.

N only 3, absence of d-orbital

Bi only 3, because of inert pair effect

(7) Reactivity :

- (a) \downarrow Decreases \therefore E.N. Decrease
(b) Least reactive in V group is N (due to triple bond formation of Bond Energy (\uparrow)
(c) Max. Reactive in V group is P.
(d) Order P > As > Sb > Bi > N

(8) Allotropic Forms : 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.

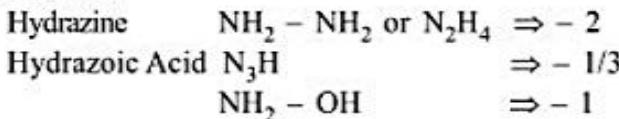
- * **Arsenic (As)** : It is the most poisonous element of Vth group.

ABNORMAL BEHAVIOUR OF NITROGEN

- (a) Nitrogen is a gas, while other elements are solids.
(b) Nitrogen molecule is diatomic (N_2) while molecules of P, As and Sb are tetra atomic (P_4 , As_4 , Sb_4) and that of Bi is mono atomic.
(c) Halides of nitrogen except NF_3 are highly explosive.
(d) N_2O_3 and N_2O_5 are monomeric while trioxides and pentoxides of P, As and Sb are dimeric.
(e) It is chemically inert due to the presence of triple bond other elements are highly reactive due to presence of single bond in their molecule.
(f) $N \equiv N$, $C = O$, $(C \equiv N)^-$ are isoelectronic species but $N \equiv N$ is less reactive due to nonpolar nature and high ionisation energy.
(g) N does not form sulphides.
(h) Nitrogen occurs in free state but others are not.

COMPOUNDS OF V-A GROUP**(I) FORMATION OF HYDRIDES**

- (a) Hydrides formed have YH_3 formula - { NH_3 , PH_3 , AsH_3 , SbH_3 , BiH_3 }
(b) Except NH_3 , all Hydrides are poisonous.
(c) NH_3 neutralises protic acids as well as aprotic acids (Lewis Acid) so ammonia is strong base.
(d) $PH_3 + HI \longrightarrow PH_4I$
Phosphene Phosphonium Iodide.
Phosphene is a weak base as compared to NH_3 and rest all have amphoteric nature.
(e) NH_3 will have high boiling point due to H-bond.
(f) Tendency of H-bonding and B.P.
 $NH_3 > PH_3 < AsH_3 < SbH_3 < BiH_3$.
(g) NH_3 cannot act as a reducing agent and BiH_3 is strongest reducing agent.
(h) Stability decreases from NH_3 to BiH_3 .
 \therefore Size increases and so bond strength decreases.
(i) Oxidation state :



- (j) Hydrazine is used as propellant for rocket fuels
 \therefore It undergoes combustion releasing large amount of energy.

(k) H_2O_2 also a better propellant than N_2H_4
 $\therefore \text{H}_2\text{O}_2$ provides nascent O which is more reactive than O_2 .

(l) N_3^- is called Azide Ion \longrightarrow Has 4 lone pair
 Eg. $\text{Ba}^{+2}\text{N}_3^- \longrightarrow$ Barium Azide $[\text{Ba}(\text{N}_3)_2]$.

(II) FORMATION OF HALIDES

(ii) Penta Halides :

- (1) Except N and Bi all forms pentahalides, N does not form due to absence of d-orbital Bi does not form due to inert pair effect.

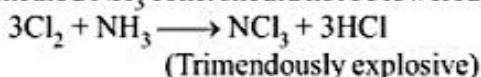
(2) PCl_5 acts as an effective chlorinating Agent so it decomposes into $\text{PCl}_5 \longrightarrow \text{PCl}_3 + \text{Cl}_2$

(III) NITROGEN (N_2)

Preparation of N₂:

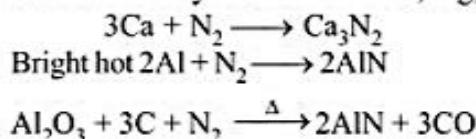


In this method NH₃ conc. should not be lowered down beyond a particular limit.



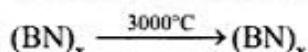
Properties of N₂:

- (i) It is inert due to high bond energy.
 - (ii) It is absorbed by hot metal like Ca, Mg, Al etc.

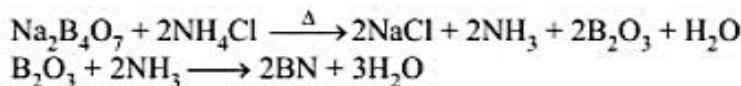


(BN)_x: Inorganic graphite

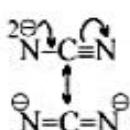
White slippery solid having 2D-sheet structure.



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



Cyanamide ion



- (iv)
$$\text{Ca}(\text{NCN}) + \text{C} + 3\text{H}_2\text{O} \longrightarrow \text{CaCO}_3 + 2\text{NH}_3 + \text{C}$$

↓ Slowly decomposes ↓

$\text{NH}_2-\text{CO}-\text{NH}_2$
(Intermediate 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 ($\text{M} = \text{Sc}, \text{Ti}, \text{Zr}, \text{Hf}, \text{La}$)

No. of metal atom per unit cell is equal to no. of octahedral voids per unit cell.

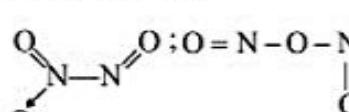
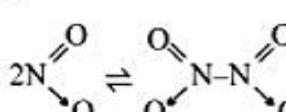
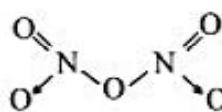
All the octahedral voids are occupied by nitrogen atoms. Hence the formula is MN_3 .

HCP: Hexagonal closed pack

ECC : Face centered cubic

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(IV) OXIDES OF NITROGEN

Oxides of nitrogen	Structure	Physical state	Colour of gas
N ₂ O	$\bar{N}=\overset{+}{N}=O$	Gas	Colourless
NO	$\ddot{N}=\ddot{O}$ or $:N\equiv O:$	Gas	Colourless
N ₂ O ₃			Blue liquid (-30°C)
NO ₂		Gas	Brown
N ₂ O ₅		Colourless solid	-(no existence in gas phase)

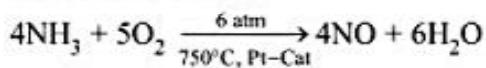
Preparations:

1. N₂O

- (i) $\text{NH}_4\text{NO}_3 \longrightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$
(ii) $(\text{NH}_4)_2\text{SO}_4 + \text{NaNO}_3 \longrightarrow \text{NH}_4\text{NO}_3 + \text{Na}_2\text{SO}_4$
 \downarrow
 $\text{N}_2\text{O} + 2\text{H}_2\text{O}$
- (iii) $\text{Zn} + \text{HNO}_3 \longrightarrow \text{Zn}(\text{NO}_3)_2 + \text{N}_2\text{O} + \text{H}_2\text{O}$
(dil. & cold)

2. NO

- (i) $\text{Cu} + \text{HNO}_3 \text{ (1 : 1)} \xrightarrow{\text{hot}} \text{Cu}(\text{NO}_3)_2 + \text{NO} + \text{H}_2\text{O}$
- (ii) $\text{KNO}_3 + \text{FeSO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + \text{NO} + \text{H}_2\text{O}$
 $\text{FeSO}_4 + \text{NO} \longrightarrow \text{FeSO}_4 \cdot \text{NO} \xrightarrow{\Delta} \text{FeSO}_4 + \text{NO} \uparrow$
- (iii) Oswald process—Restricted oxidation of NH₃.
Industrial process.

3. N₂O₃

- (i) $\text{HNO}_3 + \text{As}_2\text{O}_3 \longrightarrow \text{H}_3\text{AsO}_4 + \text{N}_2\text{O}_3$
- (ii) $\text{Cu} + \text{HNO}_3 \text{ (6M)} \longrightarrow \text{Cu}(\text{NO}_3)_2 + \underbrace{(\text{NO} + \text{NO}_2)}_{\substack{\downarrow \text{Cool}(-30^\circ\text{C}) \\ \text{Blueliq}(\text{N}_2\text{O}_3)}}$

- (i) $M(NO_3)_2 \xrightarrow{\Delta} MO + 2NO_2 + \frac{1}{2}O_2$
 $M = Pb, Cu, Ba, Ca$
- (ii) $(Cu, Pb, Ag) + HNO_3 \longrightarrow M\text{-nitrate} + NO_2 + H_2O$
(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) Decomposition Behaviour

- (i) $N_2O \xrightarrow{500^\circ C - 900^\circ C} 2N_2 + O_2$
- (ii) $2NO \xrightarrow{800^\circ C} N_2 + O_2$
- (iii) $N_2O_3 \xrightarrow{\text{Room temp.}} NO_2 + NO$
(Blue liq.) at ($-30^\circ C$)
- (iv) $2NO_2 \xrightarrow{620^\circ C} 2NO + O_2$
 $N_2O_4 \xrightarrow[\text{at } (-11^\circ C)]{\text{white solid}} \text{Brown gas}$
- (v) $\begin{matrix} N_2O_5 \\ \text{colourless} \end{matrix} \xrightarrow{30^\circ C} \begin{matrix} N_2O_5 \\ \text{yellow} \end{matrix} \xrightarrow{40^\circ C} 2NO_2 + \frac{1}{2}O_2$
solid liq.

(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 soln.	-----
(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	$NaNO_3$

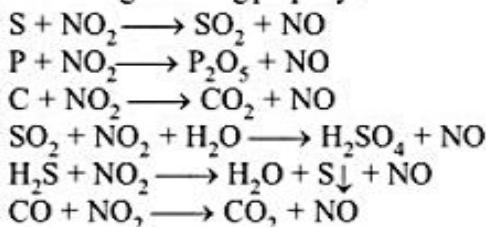
Other properties:

- N_2O : $2N_2O \longrightarrow 2N_2 + O_2$ $\left\{ \begin{matrix} \text{mixture contains} \\ 33\% O_2 \text{ compared} \\ \text{to 20\% in air} \end{matrix} \right.$
Hence it is better supporter for combustion
- $S + N_2O \longrightarrow SO_2 + N_2$
 $P + N_2O \longrightarrow P_2O_5 + N_2$
 $Mg + N_2O \longrightarrow MgO + N_2$
 $Na + N_2O \longrightarrow Na_2O + N_2$
 $Cu + N_2O \longrightarrow CuO + N_2$
 $H_2 + N_2O \longrightarrow H_2O + N_2$

- NO :** (i) It burns : $\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow \text{NO}_2$
- (ii) It supports combustion also for molten sulphur and hot phosphorous.
 $\text{S} + 2\text{NO} \rightarrow \text{SO}_2 + \text{N}_2$
 $2\text{P} + 5\text{NO} \rightarrow \text{P}_2\text{O}_5 + \frac{5}{2}\text{N}_2$
- (iii) It is being absorbed by FeSO_4 solution.
- (iv) It is having reducing property.
 $\text{KMnO}_4 + \text{NO} + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{HNO}_3 + \text{H}_2\text{O}$
 $\text{HOCl} + \text{NO} + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HCl}$
- (v) NO shows oxidising property also.
 $\text{SO}_2 + 2\text{NO} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{N}_2\text{O}$
 $\text{H}_2\text{S} + 2\text{NO} \rightarrow \text{H}_2\text{O} + \text{S} \downarrow + \text{N}_2\text{O}$
 $3\text{SnCl}_2 + 2\text{NO} + 6\text{HCl} \rightarrow 3\text{SnCl}_4 + 2\text{NH}_2\text{OH}$
(Used for NH_2OH preparation)
- (vi) NO combines with X_2 ($\text{X}_2 = \text{Cl}_2, \text{Br}_2, \text{F}_2$) to produce NO X
 $2\text{NO} + \text{X}_2 \rightarrow 2\text{NOX}$

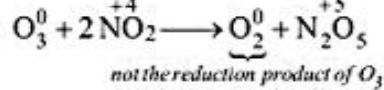
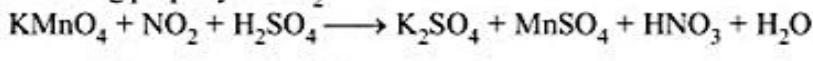
N_2O_3 : No more properties.

NO_2 : (1) It is having oxidising property.



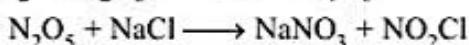
NO not formed : $2\text{KI} + 2\text{NO}_2 \rightarrow \text{I}_2 + 2\text{KNO}_2$

(2) Reducing property of NO_2 .



N_2O_5 : $\text{I}_2 + 5\text{N}_2\text{O}_5 \rightarrow \text{I}_2\text{O}_5 + 10\text{NO}_2$

I_2O_5 is used for the estimation of CO



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

Oxy acids of Nitrogen

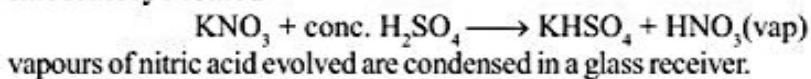
S.No.	Name of acids	Formula	Oxidation No. of N
1.	Hyponitrous acid	$\text{H}_2\text{N}_2\text{O}_2$ or HNO	+1
2.	Hydroxynitrous acid or Nitroxylic acid	$\text{H}_4\text{N}_2\text{O}_4$ or H_2NO_2	+2
3.	Nitrous acid	HONO or HNO_2	+3
4.	Pernitrous acid	HOONO	+4
5.	Nitric acid	HNO_3	+5
6.	Pernitric acid	HNO_4	+6

(V) NITRIC ACID (HNO_3)

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

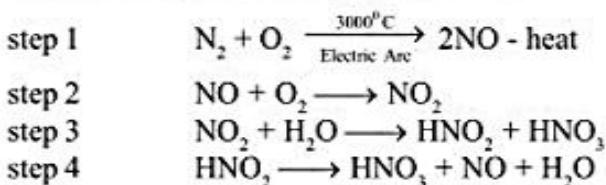
Preparation

(i) Laboratory Method

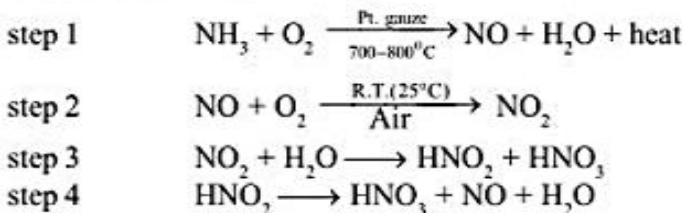


(ii) Industrial Preparation

(A) Birkeland Eyde Process or arc process



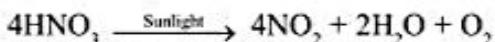
(B) Ostwald's Process



Properties

Physical

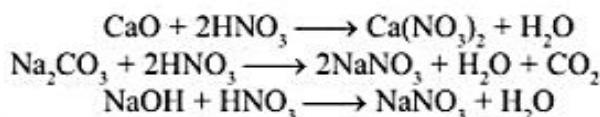
Nitric acid usually acquires yellow colour due to its decomposition by sunlight into NO_2 .



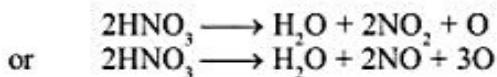
The yellow colour of the acid can be removed by warming it to $60-80^\circ\text{C}$ and bubbling dry air through it. It has extremely corrosive action on the skin and causes painful sores.

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.

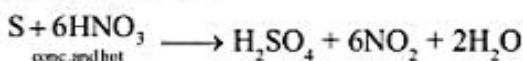


- (b) **Oxidising nature:** Nitric acid acts as a strong oxidising agent as it decomposes to give nascent oxygen easily.



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

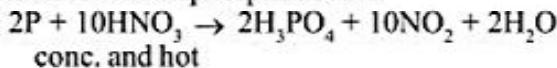
- (1) Sulphur is oxidised to sulphuric acid



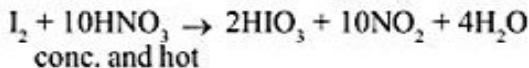
- (2) Carbon is oxidised to carbonic acid



- (3) Phosphorus is oxidised to orthophosphoric acid.

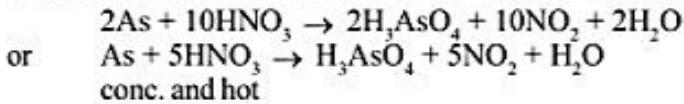


- (4) Iodine is oxidised to iodic acid

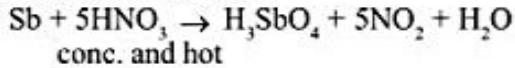


- (ii) **Oxidation of metalloids :** Metalloids like non-metals also form highest oxyacids

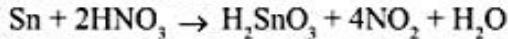
- (1) Arsenic is oxidised to arsenic acid



- (2) Antimony is oxidised to antimonic acid



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

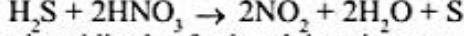


- (iii) **Oxidation of Compounds:**

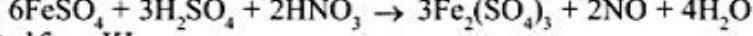
- (1) Sulphur dioxide is oxidised to sulphuric acid



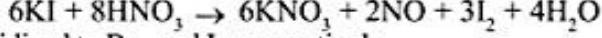
- (2) Hydrogen sulphide is oxidised to sulphur



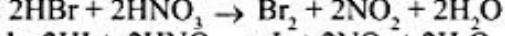
- (3) Ferrous sulphate is oxidised to ferric sulphate in presence of H_2SO_4



- (4) Iodine is liberated from KI.

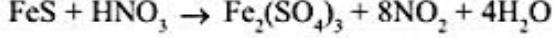


- (5) HBr, HI are oxidised to Br₂ and I₂, respectively.

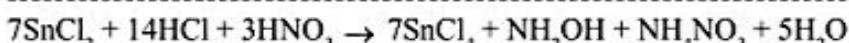
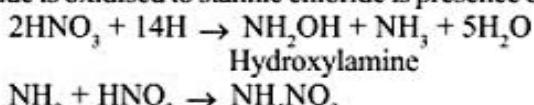


Similarly, $2\text{HI} + 2\text{HNO}_3 \rightarrow \text{I}_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$

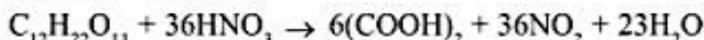
- (6) Ferrous sulphide is oxidised to ferrous sulphate



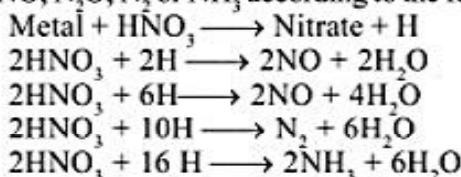
- (7) Stannous chloride is oxidised to stannic chloride in presence of HCl.



- (8) Cane sugar is oxidised to oxalic acid.



- (c) **Action on Metals:** Most of the metals will the exception 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:



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.

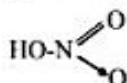
Concentration of nitric acid	Metal	Main Products
Very dilute HNO_3 (6%)	Mg, Mn	H_2 + Metal nitrate
	Fe, Zn, Sn	NH_4NO_3 + metal nitrate + H_2O
Dilute HNO_3 (20%)	Pb, Cu, Ag, Hg	$\text{NO} + \text{metal nitrate} + \text{H}_2\text{O}$
	Fe, Zn	$\text{N}_2\text{O} + \text{metal nitrate} + \text{H}_2\text{O}$
Conc. HNO_3 (70%)	Sn	$\text{NH}_4\text{NO}_3 + \text{Sn}(\text{NO}_3)_2$
	Zn, Fe, Pb, Cu, Ag	$\text{NO}_2 + \text{metal nitrate} + \text{H}_2\text{O}$
	Sn	$\text{NO}_2 + \text{H}_2\text{SnO}_3$ Metastannic acid

Action on Proteins

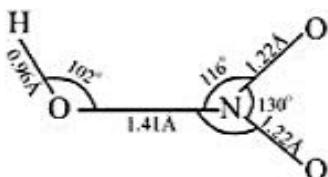
- (i) Nitric acid attacks proteins forming a yellow nitro compound called xanthoprotein. It, therefore, stains skin and renders wool yellow. This property is utilized for the test of proteins.
- (ii) **Oxidation** A number of organic compounds are oxidised. Sawdust catches fire when nitric acid is poured 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 acid is a planar molecule. The bond lengths and bond angles as present in the molecule are represented in the figure:

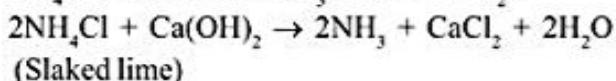
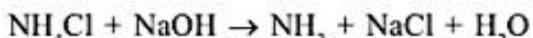


(VI) AMMONIA (NH_3)

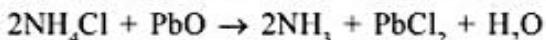
Discovery : - Berthelot, in 1788, pointed out that ammonia is a compound of nitrogen and hydrogen. In 1800, Davy established its formula NH_3 .

* **Preparation :**

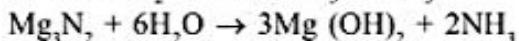
- (i) Ammonia is obtained on a small scale from ammonium salts which evolve it when heated with caustic soda or lime.



- (ii) Ammonia is formed when ammonium chloride is heated with litharge

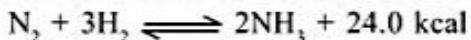


- (iii) By reacting nitrides with water, ammonia is obtained.



MANUFACTURE OF AMMONIA

- (i) **Haber's process : Principle :** Haber process is the most important industrial method of preparing ammonia. This method was discovered by a German chemist Fritz Haber. The method involves the direct combination of nitrogen and hydrogen according to the following reaction.



The reaction is reversible, exothermic and formation of NH_3 is followed by a decreased in volume. According to Le Chatelier's principle, the optimum conditions for the greater yield of ammonia are:

- (a) **High pressure :** Usually a pressure of 200 atmospheres is applied.

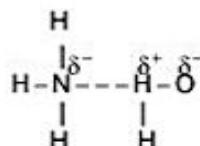
- (b) **Low temperature :** The working temperature of $450\text{--}550^\circ\text{C}$ is maintained.

- (c) **Catalyst :** At low temperature, although the yield of ammonia is more yet the reaction is very slow. In order to speed up the reaction, a catalyst is used. The following catalysts have been proposed for this purpose.
- Finely divided iron with some molybdenum as a promotor.
 - Finely divided nickel and sodalime deposited over pumice stone.

Raw materials : Nitrogen and hydrogen are the chief raw materials. Nitrogen is obtained from air by liquefaction followed by fractional evaporation of liquid air. Hydrogen is obtained by electrolysis of water.

Physical properties :

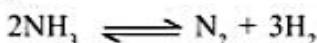
- Ammonia is a colourless gas with a characteristic pungent odour. It brings tears into the eyes.
- It is lighter than air.
- It is highly soluble in water. One volume of water dissolves 1300 volume of ammonia at 0°C and 1 atmosphere. The high solubility is due to the hydrogen bonding. The solubility of ammonia increases with increase of pressure and decreases with increase of temperature.



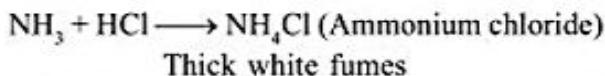
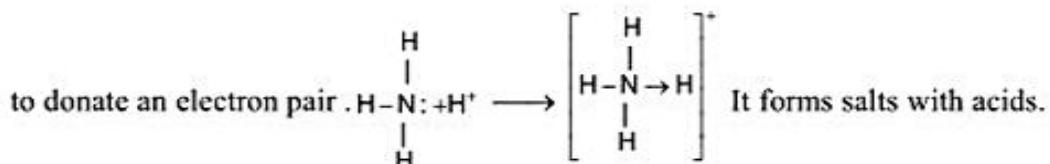
- It can be easily liquefied at room temperature by the application of pressure. The liquid ammonia is colorless and boils at -33°C. It freezes at -78°C. Liquid ammonia has a large heat of vaporization (327 cal/g.). It is, therefore, used in ice-plants.

* **Chemical Properties :**

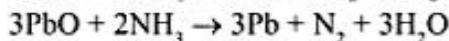
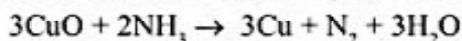
- Stability :** It is highly stable. It decomposes into nitrogen and hydrogen at red heat or when electric sparks are passed throughout it.



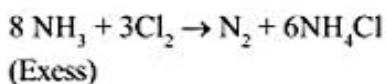
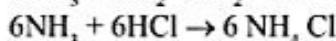
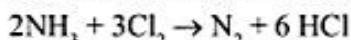
- Basic nature :** Ammonia is a Lewis base, accepting proton to form ammonium ion as it has tendency



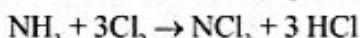
- Oxidation :** It is oxidised to nitrogen when passed over heated CuO or PbO.



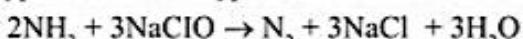
Both chlorine and bromine oxidise ammonia.



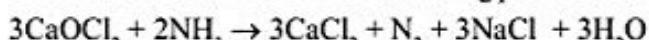
When chlorine is in excess an explosive substance nitrogen trichloride is formed.



Hypochlorites and hypobromite oxidise ammonia to nitrogen.



The oxidation of ammonia with bleaching powder occurs on warming.



Thus, ammonia acts as a reducing agent.

Uses :

- (i) Liquid ammonia is used in refrigeration on account of its large heat of evaporation.
- (ii) Ammonia is used in the form of ammonium hydroxide (aq. solution) in the laboratory in qualitative and quantitative analysis.
- (iii) Ammonia is used for making artificial silk.
- (iv) It is used as a cleansing agent for removing greases.

* Phosphorous :

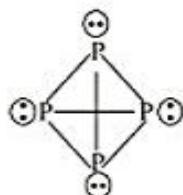
- (1) Phosphorous is largely used in match industry.
- (2) White phosphorous is used as a rat poison.

PHOSPHOROUS

TYPES OF PHOSPHOROUS

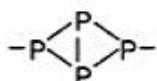
- (i) Yellow or white Phosphorous (ii) Red Phosphorous (iii) Black Phosphorous

(i) White P :



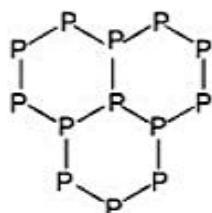
- (a) White P exist as discrete P_4 molecules. It has tetrahedral geometry. Bond angle is 60° instead of 109° . With this Bond angle white P is associated with strain and because it is less stable or more reactive.
- (b) Ignition temp of white P is 30°C . i.e. it is highly reactive and when it undergoes ignition, it releases large amount of energy and this energy is emitted in form of light which is called as Fluorescence. i.e. white P glows into dark.
- (c) Because of high reactivity of white P it is stored on H_2O .
- (d) White P slowly changes into Red P and it will get yellow colouration and finally Red.
- (e) If Red P has little % of white P in it as impurity then it is purified by adding NaOH white P undergoes reaction whereas red P not.
- (f) White P is highly poisonous.

(ii) Red P :

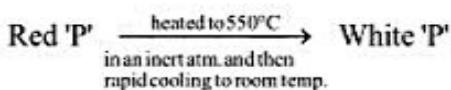
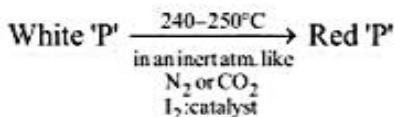
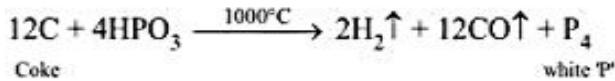
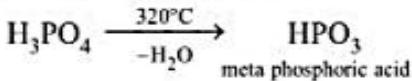
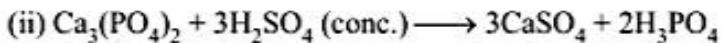
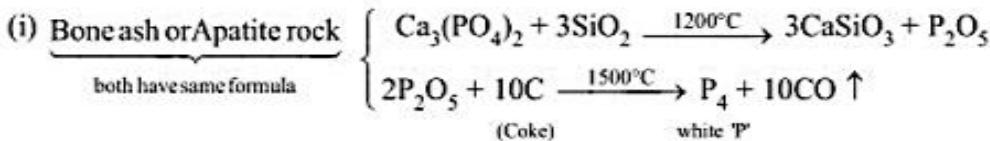


- (a) Formed from white P by breakage of one P – P bond and so chain of P_4 molecules is formed.
 (b) Long chain of P_4 molecules are formed and when compared with white P, red P has more density, less reactive with Breakage of P – P bond, strain related with P_4 molecules decreases.
 (c) Ignition temp of red P is above $230^\circ C$

(iii) Black P :



- (a) Exist in the form of Hexagonal layers like graphite.
 (b) It is least reactive and has maximum density.
 (c) Black P exist as solid of high density.
 (d) It is a conductor of electricity.

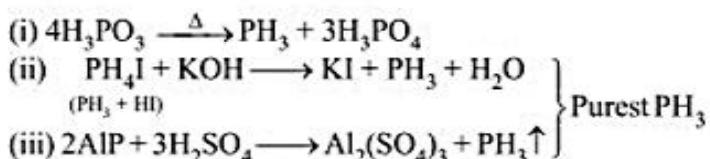
INTERCONVERSION OF WHITE 'P' & RED 'P'**Preparation of white 'P'**

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REACTIONS OF 'P'

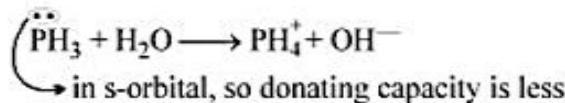
- * $P + H_2SO_4$ (hot & conc.) $\longrightarrow H_3PO_4 + SO_2 + H_2O$
- * $P + KIO_3 + H_2SO_4 \longrightarrow H_3PO_4 + I_2 + K_2SO_4$
- * Reaction with hot metal —
 - $3Na + P \longrightarrow Na_3P$
 - $3Mg + 2P \longrightarrow Mg_3P_2$
 - $3Ca + 2P \longrightarrow Ca_3P_2$
 - $2Cu + 2P \longrightarrow Cu_3P_2$
 - $Al + P \longrightarrow AlP$
 - $Ca_3P_2 + H_2O \longrightarrow M(OH)_n + PH_3$,
or Mg_3P_2 or AlP

PREPARATION OF PH_3 (PHOSPHINE GAS)



Physical Properties

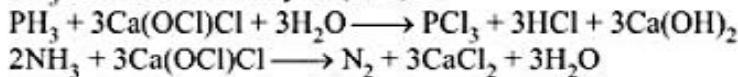
- (i) It is having 'rotten fish' smell
- (ii) It is soluble in CS_2 and insoluble in water.
(NH_3 is soluble in water)



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 $Ca(OCl)Cl$.

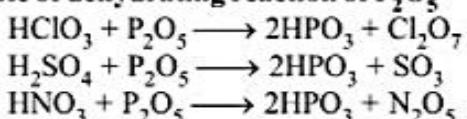


OTHER REACTIONS OF PH_3

- (i) $PH_3 + O_2 \xrightarrow{150^\circ} P_2O_5 + H_2O$
- (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) $2\text{PH}_3 + 3\text{CuSO}_4 \longrightarrow \text{Cu}_3\text{P}_2\downarrow + 3\text{H}_2\text{SO}_4$
 Detection of PH_3 Black ppt.
- (v) $\text{PH}_3 + 6\text{AgNO}_3 \longrightarrow [\text{Ag}_3\text{P} \cdot 3\text{AgNO}_3\downarrow] + 3\text{HNO}_3$
 yellow ppt.
 $\text{Ag}_3\text{P} \cdot 3\text{AgNO}_3 + 3\text{H}_2\text{O} \longrightarrow 6\text{Ag}\downarrow + 3\text{HNO}_3 + \text{H}_3\text{PO}_3$
 Black ppt.
- (vi) $\text{PH}_3 + 4\text{HCHO} + \text{HCl} \longrightarrow [\text{P}(\text{CH}_2\text{OH})_4]^+\text{Cl}^-$
 white/colourless solid
 which is used for making fire-proof cotton fabrics

Example of dehydrating reaction of P_2O_5



Illustration

Q.1 In P_4O_6 and P_4O_{10} , the number of oxygen atoms bonded to each phosphorus atoms are respectively -

- (A) 3 and 3 (B) 4 and 4 (C) 3 and 4 (D) 4 and 3

Ans. (C)

Sol. In P_4O_6 each phosphorus is linked to three oxygen atoms; whereas in P_4O_{10} each phosphorus atom is linked to four oxygen atoms.

Q.2 Choose the reactions which would liberate nitrogen gas?

- (A) $\text{Ca}(\text{OCl})\text{Cl} + \text{NH}_3 \xrightarrow[\text{medium}]{\text{aqueous}} ?$ (B) $\text{NH}_3 + \text{PbO} \xrightarrow{\Delta} ?$
 (C) NH_3 (excess) + $\text{Cl}_2 \xrightarrow{\Delta} ?$ (D) $\text{NH}_4\text{Cl} + \text{NaNO}_2 \xrightarrow{\Delta} ?$

Ans. (A, B, C, D)

Sol. (A) $3\text{Ca}(\text{OCl})\text{Cl} + 2\text{NH}_3 \xrightarrow[\text{medium}]{\text{aqueous}} 3\text{CaCl}_2 + \text{N}_2\uparrow + 3\text{H}_2\text{O}$
 (B) $2\text{NH}_3 + 3\text{PbO} \xrightarrow{\Delta} 3\text{Pb} + \text{N}_2 + 3\text{H}_2\text{O}$
 (C) 8NH_3 (excess) + $3\text{Cl}_2 \xrightarrow{\Delta} \text{N}_2\uparrow + 6\text{NH}_4\text{Cl}$
 (D) $\text{NH}_4\text{Cl} + \text{NaNO}_2 \xrightarrow{\Delta} \text{NH}_4\text{NO}_2 + \text{NaCl}$
 $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2\uparrow + 2\text{H}_2\text{O}$]

Exercise

Q.1 The correct sequence of decrease in the bond angle of the following hydrides is - :

- (A) $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$ (B) $\text{NH}_3 > \text{AsH}_3 > \text{PH}_3 > \text{SbH}_3$
 (C) $\text{SbH}_3 > \text{AsH}_3 > \text{PH}_3 > \text{NH}_3$ (D) $\text{PH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{SbH}_3$

Ans. (A)

OXYGEN FAMILY

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 (IE₁ 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 pπ – pπ overlap thus two O atoms form double bond O = O. The intermolecular forces in O₂ are weak VB forces. ∴ O₂ exist as gas. On the other hand, other elements of family do not form stable pπ – pπ bonds and do not exist as M₂ molecules. Other atoms are linked by single bonds and form poly atomic complex molecules for e.g. S – S₈, Se – S₈
- (7) **Allotropy :** All element exhibit allotropy for e.g.

Oxygen – O₂ and O₃
 Liquid O₂ - pale blue
 Solid O₂ - blue

Sulphur -

The main allotropic forms are

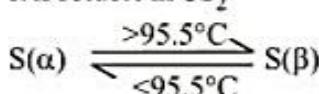
- (i) Rhombic sulphur (α sulphur)
- (ii) Monoclinic (β sulphur)
- (iii) Plastic sulphur (δ sulphur)

- (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 CS₂.

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

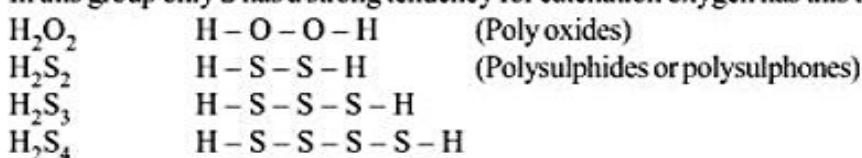
It is soluble in CS₂



- (iii) **Plastic Sulphur (δ sulphur)** It is insoluble in CS₂.

- (8) **Catenation**

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



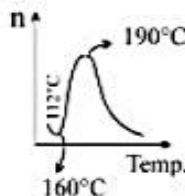
SULPHUR CHEMISTRY

- * **Allotropes:** (i) Rhombic or α -sulphur. } S(α) $\xrightleftharpoons[95.5^{\circ}\text{C}]{95.5^{\circ}\text{C}}$ S(β)
 (ii) Monoclinic or β -sulphur. } below 95.5°C above 95.5°C
 (iii) γ -Sulphur

Amorphous forms are

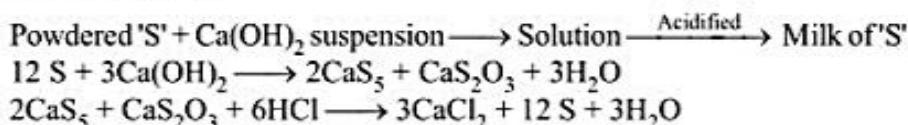
- (i) Plastic sulphur
- (ii) Milk of sulphur
- (iii) Colloidal sulphur

- * Viscosity of 'S' with temperature:
 m.p. of 'S' \rightarrow 112.8°C.



- (i) $> 112.8^{\circ}\text{C}$ to $160^{\circ}\text{C} \Rightarrow$ slow decreases due to S₈ rings slip and roll over one another easily.
- (ii) $> 160^{\circ}\text{C}$, increases sharply due to breaking of S₈ rings into chains and polymerases into large size chain.
- (iii) 190°C , again large chains are being broken into small chain.

- * **Milk of sulphur :**



- * **Colloidal Sulphur :** $\text{Na}_2\text{S}_2\text{O}_3 + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{SO}_2 + \text{S} \downarrow$
 $2\text{H}_2\text{S} + \text{SO}_2 \longrightarrow 3 \downarrow + 2\text{H}_2\text{O}$

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



(b) 'S' burns spontaneously in fluorine. $\text{S} + 3\text{F}_2 \longrightarrow \text{SF}_6$
 Cl_2 passed into liq. sulphur $\Rightarrow 2\text{ S} + \text{Cl}_2 \rightarrow \text{S}_2\text{Cl}_2$

(c) $\text{S} + 2\text{H}_2\text{SO}_4 \longrightarrow 3\text{SO}_2 + 2\text{H}_2\text{O}$
 $\text{S} + 2\text{HNO}_3 \longrightarrow \text{H}_2\text{SO}_4 + 2\text{NO}$

(d) $4\text{ S} + 6\text{ KOH} \longrightarrow 2\text{K}_2\text{S} + \text{K}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$
 (e) Burns in air : $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2$

FAMILY MEMBERS OF VITH GROUP

- * **Oxygen : (O)**

- (i) **Oxygen Molecule (O₂) :**

(1) In air as O₂ to the extent of 21% by volume or 23% by weight.

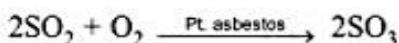
(2) Lab method to produce O₂ is.



(3) Air is liquefied by use of joule - Thomson effect {cooling by expansion of gas}.

(4) Reaction with compounds :

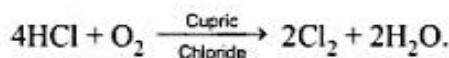
- (a) Contact Process :



- (b) Ostwald Process :



- (c) Deacon's Process :



(5) Uses :

- (a) Oxy-Acetylene flame is used for cutting process and welding process.
 (b) Liquid oxygen is a constituents of fuels used in rockets.

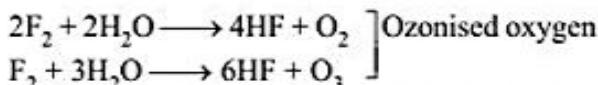
* **Oxides :**

A binary compound of oxygen with another element is called an oxide.

- (a) Oxygen combined nearly with all other elements except inert gases, noble metals and halogens.
 (b) The binary compounds of oxygen with other element are called oxides. Hence, the compounds of oxygen and fluorine (OF_2 , O_2 , F_2) are not called as oxides.

OZONE

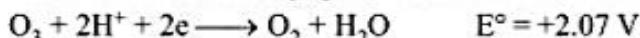
Unstable deep blue, diamagnetic gas, with fishy smell. Toxic enough (more toxic than KCN). It's intense blue colour is due to the absorption of red light.



These are separated by passing into spiral tube cooled into liquid air. Ozone condenses at -112.4°C .
 [b.p. of O_2 -183°C ; b.p. of liq. air is -190°C]

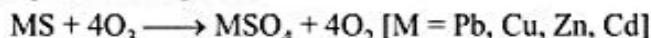
Oxidising property of O_3

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



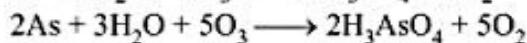
It is next to F_2 . [above 2.07 V, only F_2 , F_2O are there]

- (i) Metal Sulphides to Sulphates.



- (ii) $2\text{HX} + \text{O}_3 \longrightarrow \text{X}_2 + \text{H}_2\text{O} + \text{O}_2 \quad [\text{X} = \text{Cl, Br, I}]$

- (iii) Moist S, P, As + $\text{O}_3 \Rightarrow$



- (vi) alk. { $\text{KI} + 3\text{O}_3 \longrightarrow \text{KIO}_3 + 3\text{O}_2$ }
 { $\text{KI} + 4\text{O}_3 \longrightarrow \text{KIO}_4 + 4\text{O}_2$ }

- (v) Hg loses its fluidity (tailing of Hg)

$$2\text{Hg} + \text{O}_3 \longrightarrow \text{Hg}_2\text{O} + \text{O}_2$$

similarly $2\text{Ag} + \text{O}_3 \longrightarrow \text{Ag}_2\text{O} + \text{O}_2$

Brown

(vi) $\text{BaO}_2 + \text{O}_3 \rightarrow \text{BaO} + 2\text{O}_2$

$$\text{H}_2\text{O}_2 + \text{O}_3 \longrightarrow \text{H}_2\text{O} + 2\text{O}_2$$

$$\text{Na}_2\text{O}_2 + \text{O}_3 + \text{H}_2\text{O} \longrightarrow 2\text{NaOH} + 2\text{O}_2$$

Absorbent: (i) Turpentine oil

- (ii) Oil of cinnamon

Uses: (i) Sterilising water

(ii) Detection of no:

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

Classification of oxides

- (1) Acidic oxides $\rightarrow \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2\text{CO}_3$.
 e.g. CO_2 , B_2O_3 , SiO_2 , N_2O_3 , NO_2 , N_2O_5 , P_4O_6

Note: Mixed anhydrides → Those oxides which form two oxy acids.

- e.g. $2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3$
 $\text{P}_4\text{O}_8 + 6\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}_3 + 2\text{H}_3\text{PO}_4$
 $\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}$
salt water.

- ## (2) Basic oxides :

$$\text{Oxide} + \text{H}_2\text{O} \rightarrow \text{alkali} ; \text{e.g. } \text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$$

$$\text{Oxide} + \text{acid} \rightarrow \text{salt} + \text{H}_2\text{O}; \text{ e.g. CuO} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{H}_2\text{O}$$

Oxide + Acidic oxide \rightarrow salt ; e.g. $\text{PbO} + \text{SO}_3 \rightarrow \text{PbSO}_4$.

- ### (3) Neutral Oxide:

Oxide + Acid → No reaction

Oxide + Base → No reaction

- e.g. CO, H₂O, N₂O, NO etc.

- (4) **Amphoteric oxides** → React with acid & base both to form salts.

- e.g. ZnO, Al₂O₃, BeO, Sb₂O₃, Cr₂O₃, PbO, PbO₂, etc.

$$\text{ZnO} + 2\text{NaOH} \rightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2\text{O}; \text{ZnO} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2\text{O}$$

$$\text{Al}_2\text{O}_3 + 2\text{NaOH} \rightarrow 2\text{NaAlO}_2 + \text{H}_2\text{O}; \text{Al}_2\text{O}_3 + 6\text{HCl} \rightarrow 2\text{AlCl}_3 + 3\text{H}_2\text{O}$$

$$\text{PbO} + 2\text{NaOH} \rightarrow \text{Na}_2\text{PbO}_2 + \text{H}_2\text{O}; \quad \text{PbO} + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + \text{H}_2\text{O}$$

$$\text{Cr}_2\text{O}_3 + 2\text{NaOH} \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O}; \text{Cr}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O}$$

- (5) **Compound or mixed oxides** → Oxides which behaves as mixture of two simple oxides.

- e.g. Pb_3O_4 ($2\text{PbO} + \text{PbO}_2$)

$$\text{Fe}_3\text{O}_4 \quad (\text{FeO} + \text{Fe}_2\text{O}_3)$$

$$\text{Mn}_2\text{O}_4 \quad (2\text{MnO} + \text{MnO}_2)$$

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- (6) **Peroxides** → Oxides + dil acids → H_2O_2
e.g. $Na_2O_2 + H_2SO_4(\text{dil}) \rightarrow Na_2SO_4 + H_2O_2$
 $BaO_2 + H_2SO_4(\text{dil}) \rightarrow BaSO_4 + H_2O_2$
- (7) **Dioxides** → Like peroxides, these also contain excess of oxygen but do not form H_2O_2 with dilute acids. They evolve chlorine with conc. HCl and oxygen with conc. H_2SO_4 .
e.g. → PbO_2, MnO_2
 $MnO_2 + 4HCl \text{ conc.} \rightarrow MnCl_2 + Cl_2 + 2H_2O$
 $2MnO_2 + 2H_2SO_4 \text{ (conc.)} \rightarrow 2MnSO_4 + O_2 + 2H_2O$
- (8) **Suboxides** → The oxides which contain less oxygen than expected from the normal valency of the elements are termed sub-oxides.
e.g. Carbon suboxide - C_3O_2
Lead suboxide - Pb_3O
Nitrous oxides - N_2O
- (9) **Superoxides** → These oxides contain O_2^- ion.
e.g. KO_2, RbO_2, CsO_2
These react with water to give hydrogen peroxide and oxygen.
 $2KO_2 + 2H_2O \rightarrow 2KOH + H_2O_2 + O_2$

* **Sulphur (S) :**

Atomic Number : 16

Outer electronic configuration : $3s^2 3p_x^2 3p_y^1 3p_z^1$

Number of unpaired electrons : 2

Covalency : 2

Oxidation States : -2, 0, +2, +4, +6

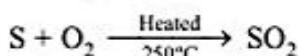
Occurrence : Sulphur is one of the widely occurring element. It constitutes about 0.1 percent of the earth's crust. It is found in free (native) as well as combined state. In the combined state it occurs as sulphides and sulphates.

1. **As sulphides :** Cinnabar (HgS), Galena (PbS), Zinc blende (ZnS), Copper pyrites ($CuFeS_2$)
2. **As Sulphates :** Gypsum ($CaSO_4 \cdot 2H_2O$), barytes ($BaSO_4$), epsomite ($MgSO_4 \cdot 7H_2O$). Organic substances such as eggs, proteins onions, garlic, mustard, hair and wool contain sulphur.

Properties

* **Physical Properties :**

1. Sulphur is a pale yellow, crystalline, brittle solid. It is odourless and tasteless.
2. It has no physiological action on human beings as it is poisonous to lower organisms.
3. It is poor conductor of heat and a bad conductor of electricity. Hence sulphur is a very good insulator.
4. It is insoluble in water but soluble in carbon disulphide, sparingly soluble in alcohol and ether.
5. Burning : When heated to about $250^\circ C$ sulphur burns in air with a pale blue flame forming mainly



(air)

USES :

1. For vulcanization of rubber.
2. In match industry and fireworks.
3. As a disinfectant for houses, for destroying bacteria, fungi, insects, etc.
4. For the manufacture of SO_2 , CS_2 , H_2SO_4 etc.
5. In manufacture of sulphur dyes.
6. In skin medicines.
7. For preparing gun powder (a mixture of charcoal, sulphur and potassium nitrate).
8. Po is radioactive element

*** Allotropic forms of Sulphur :**

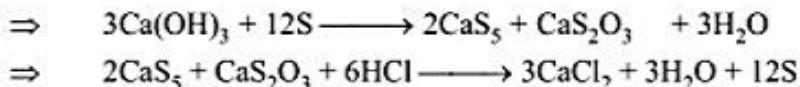
(i) **Rhombic octahedral or α -sulphur :**

(ii) **Monoclinic Prismatic or β -sulphur :**

- (a) These two sulphur are called as enantiotropic substances
 α - sulphur \rightleftharpoons β - sulphur.
- (b) α and β sulphur are crystalline and rest being amorphous and exist as S_8 cyclic molecule.

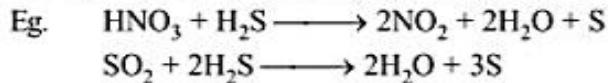
(iii) **Plastic or γ sulphur :** It is obtained by quenching of boiling sulphur in a thin stream to cold water.

(iv) **Milk of sulphur :** It is obtained by boiling milk of lime with sulphur and decomposing the products with HCl.



Milk of sulphur is soluble in CS_2 and is mainly used in medicine

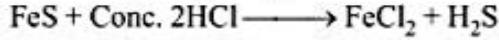
(v) **Colloidal or δ -sulphur :** It is prepared by passing H_2S through a solution of an oxidising agent

*** Uses of Sulphur :**

- (a) In manufacture of H_2SO_4 , CS_2 gun powder etc.
- (b) Vulcanisation of rubber.

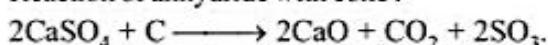
COMPOUNDS OF SULPHUR**Hydrogen sulphide (H_2S) :**

- (i) Also known as sulphurated hydrogen.
- (ii) Lab method : Kipps apparatus



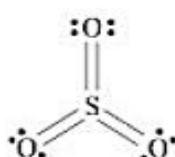
In this reaction conc. HNO_3 cannot be employed because HNO_3 is a oxidising agent and converts H_2S into colloidal sulphur.

(3) Reaction of anhydride with coke :



(iv) Physical Properties :

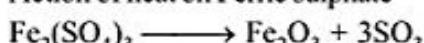
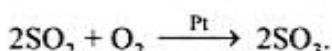
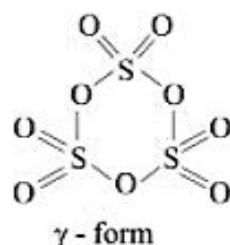
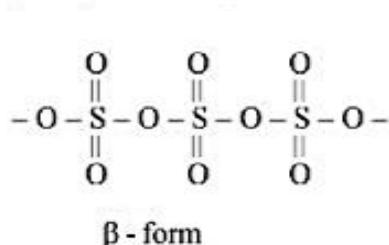
(1) It is pungent smelling suffocating gas

(2) It is soluble in H_2O * Sulphur trioxide (SO_3) :

triagonal planar molecule.

(1) Preparation :

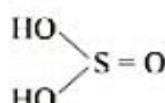
1. Action of heat on Ferric sulphate

2. Commercial Method : By the oxidation of dry SO_2 with dry oxygen. SO_2 and O_2 are first dried by passing through conc. H_2SO_4 and then passed over heated (400°C) platinised asbestos contained in a hard glass tube.(2) Physical Properties : It exists in atleast three forms α - SO_3 , β - SO_3 and γ - SO_3 The structure of solid SO_3 is complex. It possesses cyclic trimer (α form) structure.(a) α form: It is branched and sheet like structure(b) β and γ forms : It possesses an infinite helical chain made up of linked SO_4 tetrahedron.

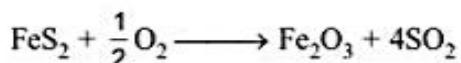
(3) Chemical Reactions :

1. It dissolves in conc. H_2SO_4 to form pyrosulphuric acid (oleum)2. $\text{SO}_3 + 2\text{HBr} \longrightarrow \text{H}_2\text{O} + \text{Br}_2 + \text{SO}_2$. In this SO_3 is used as an oxidising agent.

* Oxy Acids of Sulphur :

(a) Sulphurous Acid (H_2SO_3) :Structure of Sulphurous Acid (H_2SO_3)(b) Sulphuric Acid (H_2SO_4) or oil of vitrol :

Preparation : Mainly two process used

(A) Lead Chamber Process :**Note :**

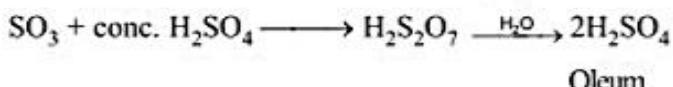
1. NO (Nitric Oxide) produced takes oxygen from air and gets converted back to nitrogen dioxide. Thus oxide of nitrogen take oxygen from air and pass it to SO_2 and thus act as oxygen carriers.



2. It is seen that in the presence of an insufficient quantity of steam or water spray, lead chamber crystals of the composition $SHSO_4 \cdot NO$ are obtained.

(B) Contact Process :

Initially Pt. was employed as catalyst but now V_2O_5 is used because Pt is poisonous.



- (1) To get the appropriate amount of H_2SO_4 contact process is utilised.
- (2) If bottle of H_2SO_4 is opened, it absorbs unlimited amount of moisture and H_2SO_4 overflows to conc. H_2SO_4 is deliquescent liquid which is highly viscous and has high density.
- (3) When H_2SO_4 is done dilute by adding water the reaction being highly exothermic so temperature increases to $120^\circ C$ and thus along with water vapour the energy released when conc. H_2SO_4 is contacted with skin, causing burning.
- (4) Conc. $H_2SO_4 + \text{Glucose} \longrightarrow 6C + 6H_2O$

The white sugar changes to black and this is called charring of sugar (Blackening of sugar). This is the conformation test of H_2SO_4 .

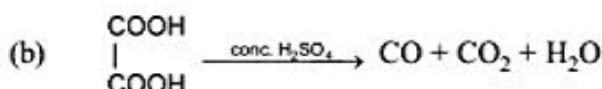
*** Chemical Reaction of H_2SO_4 :**

- (1) It has greater affinity for water. Hence is used for drying of all gases except ammonia. It is also employed as dehydrating agent.

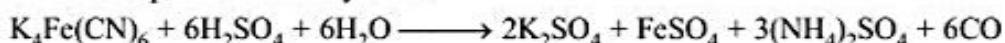
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This called as charring of sugars.



(2) Action with potassium ferrocyanide:



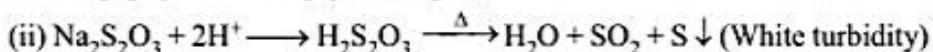
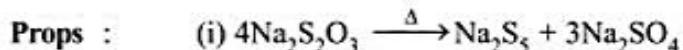
Uses :

- (a) It is regarded as king of chemical.
- (b) In manufacture of explosives (T.N.T, gun cotton) etc.
- (c) As a pickling agent : Pickly is an industrial process for removing layers of basic oxides from metals like Fe and Cu. Before electroplating, galvanizing and soldering.

SODIUM THIOSULPHATE

Prepⁿ.:

- (i) $\text{Na}_2\text{SO}_3 \text{ soln.} + \text{S (powder)} \xrightarrow{\text{boiling}} \text{Na}_2\text{S}_2\text{O}_3 \xrightarrow{\text{evaporation}} \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, monoclinic crystal
- $\nearrow \text{SO}_2$ $\left\{ \begin{array}{l} \text{Na}_2\text{CO}_3 + 2\text{SO}_2 + \text{H}_2\text{O} \longrightarrow 2\text{NaHSO}_3 + \text{CO}_2 \\ 2\text{NaHSO}_3 + \text{Na}_2\text{CO}_3 \longrightarrow \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} + \text{CO}_2 \end{array} \right.$
- Na_2CO_3
excess
- (ii) $\text{Na}_2\text{SO}_4 \text{ Salt cake} + 4\text{C Coke} \xrightarrow{\text{roasting}} \text{Na}_2\text{S} + 4\text{CO}$
- ↓
 $\text{SO}_2 \text{ passed into it}$
- $\text{Na}_2\text{S}_2\text{O}_3 [3\text{SO}_2 + 2\text{Na}_2\text{S} \longrightarrow 2\text{Na}_2\text{S}_2\text{O}_3 + \text{S}]$
- (iii) $2\text{Na}_2\text{S} + \text{Na}_2\text{CO}_3 + 4\text{SO}_2 \longrightarrow 3\text{Na}_2\text{S}_2\text{O}_3 + \text{CO}_2$
- (iv) $6\text{NaOH} + 4\text{S} \longrightarrow \text{Na}_2\text{S}_2\text{O}_3 + 2\text{Na}_2\text{S} + 3\text{H}_2\text{O}$
 $3\text{Ca}(\text{OH})_2 + 12\text{S} \longrightarrow \text{CaS}_2\text{O}_3 + 2\text{CaS}_5 + 3\text{H}_2\text{O}$
- (v) $\text{Na}_2\text{SO}_3 + \text{Na}_2\text{S} + \text{I}_2 \longrightarrow \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaI}$
- (vi) $2\text{Na}_2\text{S} + 2\text{O}_2 + \text{H}_2\text{O} \longrightarrow \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaOH}$ [Na₂S is readily oxidised in air giving rise to Na₂S₂O₃]



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Reaction: (i) $\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$

$+ \text{Cl}_2 - \text{water} \longrightarrow \text{SO}_4^{2-} + \text{S} + 2\text{HCl}$

$+ \text{Br}_2 - \text{water} \longrightarrow \text{SO}_4^{2-} + \text{S} + 2\text{HBr}$

$+ 4\text{OI}^- + 2\text{OH}^- \longrightarrow 2\text{SO}_4^{2-} + 4\text{I}^- + \text{H}_2\text{O}$

$+ 4\text{Cl}_2 + 5\text{H}_2\text{O} \xrightarrow{\text{excess}} \text{Na}_2\text{SO}_4 + 8\text{HCl} + \text{H}_2\text{SO}_4$

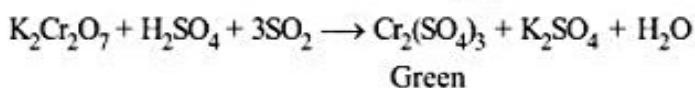
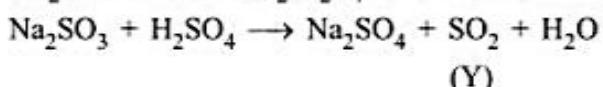
Illustration

- Q.1** Compounds A and B are treated with dilute HCl separately. The gases liberated are Y and Z respectively. Y turns acidified $K_2Cr_2O_7$ paper green while Z turns lead acetate paper black. The compounds A and B are respectively -

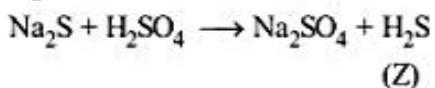
- (A) Na_2S and Na_2SO_3 (B) Na_2SO_3 and Na_2S
 (C) NaCl and Na_2CO_3 (D) Na_2SO_3 and Na_2SO_4

Ans. (B)

Sol. SO_2 turns acidified $\text{K}_2\text{Cr}_2\text{O}_7$ paper green.



H_2S turns lead acetate paper black.



Exercise

- Q.1** The correct order of decreasing stability of hexafluorides of group 16 members is -

- (A) $\text{SF}_6 > \text{SeF}_6 > \text{TeF}_6$ (B) $\text{TeF}_6 > \text{SeF}_6 > \text{SF}_6$
 (C) $\text{SF}_6 > \text{TeF}_6 > \text{SeF}_6$ (D) $\text{TeF}_6 > \text{SF}_6 > \text{SeF}_6$

Ans. (A)

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HALOGEN FAMILY

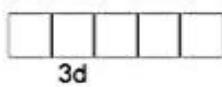
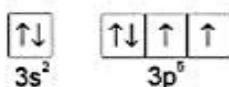
Element	Atomic no.	Outer shell configuration
F	9	He $2s^22p^5$
Cl	17	Ne $3s^23p^5$
Br	35	Ar $3d^{10}4s^24p^5$
I	53	Kr $4d^{10}5s^25p^5$
At	85	Xe $4f^{14}5d^{10}6s^26p^5$

- **HALO : Sea Salts :** Generally they are called halogen because they are sea salts forming elements.
- **Important point :** At (astatine) is a radioactive element.
- **General Properties :**
- * **State and Nature :**
 - (a) F and Cl are Gas.
 - (b) Br : Liquid
 - (c) I, At is solid
 - (d) All are non metallic
 - (e) Metallic character down the group (F → I) non metallic character decreases
 - (f) I has metallic lustre on heating and its show's sublimation property
- * **Atomic Radii, Ionic Radii, Boiling point and Melting point, Density :** All these character increases down the group
- * **Ionisation potential and Electronegativity :** Down the group atomic size increases so IP and EN decreases down the group
- * **Electron Affinity (E.A.) :** Cl > F > Br > I. Generally down the group electron affinity decreases but the electron affinity of Cl is more than F because due to the small size and high electron density of F the incoming electron is not easily enters as comparison Cl because it's size not as small as size of F and not large as Br and I.
- * **Colour properties :**
 - (a) F : Pale yellow. Cl : Greenish yellow Br : Red I : Violet purple.
 - (b) Outermost electronic configuration is to $ns^2 np^5$ due to the presence of unpaired electron they absorb visible light and reflect complementary light and exhibit colour.
 - (c) F absorbs violet colour light and appears yellow. It will absorbs yellow coloured light and appears violet.
 - (d) Astatine being stable could have absorbed orange or red light and would have exhibited indigo or bluish colour.
- * **Valency and Oxidation state :**
 - (a) ns^2np^5
 - (b) valency = 1

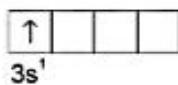
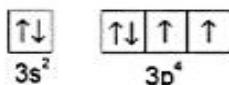
if Halogens combines with more E.N. elements then O.S. = + 1.

(c) For Cl. Ground State :

Valency = 1



1st excited state



* **Bond Energy :**

F – F bond dissociation energy is less than that of Cl – Cl and Br – Br. It is due to larger inter electronic (electron - electron) repulsion between the non bonding electrons in the 2p orbitals of fluorine atom, then these in the 3p orbitals of chlorine atoms.

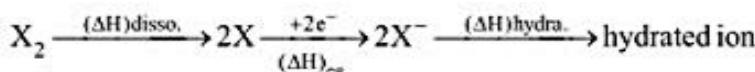
F – F	Cl – Cl	Br – Br	I – I
38 kcal/mol	57 kcal/mol	45.5 kcal/mol	35.6 kcal/mol
$Cl_2 > Br_2 > F_2 > I_2$			

* **Oxidising Power :**

The electron affinity, or tendency to gain electrons reaches a maximum at chlorine. Oxidation may be regarded as the removal of electron so that an oxidising agent gains electrons.

Thus the halogens act as oxidizing agents.

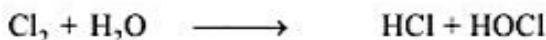
The strength of an oxidising agent (i.e. oxidation potential) depends upon several energy terms and represented by following diagram.



ΔH (reduction potential) = ΔH (dissociation energy) + ΔH (electron gain enthalpy) + ΔH (hydration energy)

Element	ΔH (reduction potential)
F_2	- 186.5
Cl_2	- 147.4
Br_2	- 136.4
I_2	- 122.4

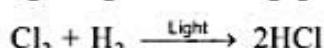
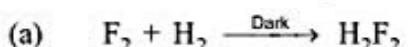
Thus oxidising powers decrease on descending in group VII. Fluorine is so strong oxidising agent that H oxidizes water to oxygen. The oxidation of H_2O by Cl_2 is thermodynamically possible but since the energy of activation is high this reaction does not occur.



Iodine is even weaker oxidising agent and the free energy change indicate that energy would have to be supplied to make it oxidise water.

CHEMICAL PROPERTIES

* **Reaction with H₂** : All halogens reacts with H to form hydrogen halides.



(b) Reactivity of Halogens $F > Cl > Br > I$

(c) HCl in gaseous state is hydrogen chloride. While HCl in aqueous solution is hydrochloric acid.

(d) HCl, HBr, HI acts as reducing agent.

(e) H_2F_2 cannot decompose into H_2 and F_2 and so its can never acts as reducing agent.

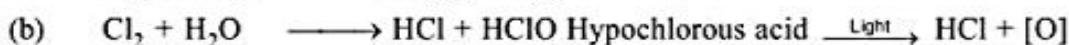
(f) H_2F_2 has highest boiling point and exist in liquid state.

(g) HCl , HBr and HI exist on gaseous state.

(h) HCl b.p. is very low and after HCl b.p. increases because Vanderwaals forces increases (\uparrow) and so b.p. (\uparrow).

* **Reaction With H₂O** :

(a) H₂O acts as reducing Agent only with F.

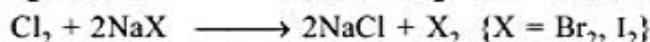
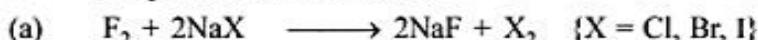


So Cl_2 in presence of moisture acts as bleaching agent.

(c) $H_2O + I_2 \longrightarrow$ No Reaction.

(d) All these halogen are soluble in water except I_2 when KI solution is added I_2 will also dissolve because adsorption of I_2 molecule on the surface of iodide ion KI_3 is formed which is a highly ionic compound.

* **Displacement Reaction** :



So order of displacement $[F_2 > Cl_2 > Br_2 > I_2]$

(b) If Halogen is in -ve O.S. then it is replaced by more E.N. element.

(c) If Halogen is +ve O.S. then it is replaced by less E.N. element.

* **Reaction with Metals** : Metal halides are formed $F > Cl > Br > I$

* **Reaction with Non Metals** : Non metallic halides are formed. Eg. NF_3 , PCl_3 etc.

* **Reaction with NH_3 :**

- (a) $3\text{F}_2 + \text{NH}_3 \longrightarrow \text{NF}_3 + 3\text{HF}$
- (b) $3\text{Cl}_2 + \text{NH}_3 \longrightarrow \text{NCl}_3 + 3\text{HCl}$
- (c) I_2 is less reactive and so remains same and Ammoniated compound will form.
 $3\text{I}_2 + 2\text{NH}_3 \longrightarrow \text{NI}_3 \cdot \text{NH}_3 + 3\text{HI}$

* **Reaction with NaOH :**

- (a) $\text{F}_2 + \text{NaOH}$ (dil.) $\longrightarrow 2\text{NaF} + \text{OF}_2 + \text{H}_2\text{O}$
- (b) $2\text{F}_2 + 4\text{NaOH}$ (conc.) $\longrightarrow 4\text{NaF} + 2\text{H}_2\text{O} + \text{O}_2$

They are both redox reactions.

- (c) $\text{Cl}_2 + \text{NaOH} \longrightarrow \text{NaCl} + \text{NaClO}_3 + \text{H}_2\text{O}$
- (d) $\text{Br}_2 + \text{NaOH} \longrightarrow \text{NaBr} + \text{NaBrO}_3 + \text{H}_2\text{O}$

* **Formation of Oxides :**

- (a) No oxides of F because of its maximum E.N. character.
- (b) Rest forms

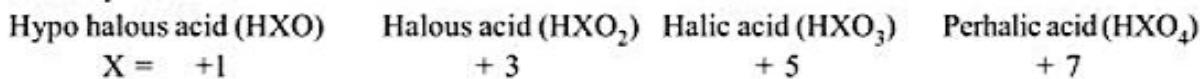
	X_2O	X_2O_3	X_2O_5	X_2O_7
	+ 1	+ 3	+ 5	+ 7
Eg.	Cl_2O	Cl_2O_3	Cl_2O_5	Cl_2O_7

Molecular formula	Structures
Cl_2O	
Cl_2O_3	
Cl_2O_5	
Cl_2O_7	

- (c) All these oxides are acidic
- (d) Acidity decreases down the group and maximum active oxide is Cl_2O_7

* **Formation of Oxyacids :**

- (a) F does not form any oxyacid because High E.N.
- (b) Rest oxyacids are



- (c) All these oxy acids are acidic
- (d) Acidity and thermal stability decreases down the group and maximum acidity and thermal stability will be of HClO_4 .
- (e) Thermal stability of acids increases with the increasing O.S. of the halogens or with increase in the no. of oxygen atom.

(f) Oxidising Power :

- (i) All these oxyacids acts as strong oxidizing agents.
- (ii) Stability of anions increases from ClO^- to ClO_4^- , the oxidising power decreases from ClO^- to ClO_4^-
- (iii) Order of oxidising agent $\text{HClO} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$

* Miscellaneous Reaction :

- (a) $\text{I}_2 + \text{Na}_2\text{S}_2\text{O}_3$ (Hypo) $\longrightarrow 2\text{NaI}$ (Colourless) + $\text{Na}_2\text{S}_4\text{O}_6$
This reaction is employed for identification of I_2 .
- (b) Dry $\text{Cl}_2 + \text{Ca}(\text{OH})_2(\text{s}) \longrightarrow \text{CaOCl}_2$ (Bleaching Powder) + H_2O

* Inter Halogens :

Product obtained by uniting two halogen compounds :



Where A = less E.N. Halogen

B = More E.N. Halogen

Eg.	ClF	ClF_3	BrF_5	IF_7
	BrCl	BrCl_3	ICl_5	
	IBr	IBr_3		

These inter halogens have polarity because of different E.N.

Note : Abnormal Behaviour of Fluorine as Compared to Other Members :

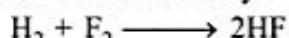
Fluorine differs considerably from other halogens due to -

- (i) Small size
 - (ii) High electronegativity.
 - (iii) Non availability of d - orbitals in its valency shell.
 - (iv) Low bond dissociation energy of F – F bond.
- (a) Boiling point of HF is the highest and for other increases down the group.

Comparison of $[\text{Cl}_2, \text{Br}_2$ and $\text{I}_2]$

S.No.	Property	Chlorine	Bromine	Iodine
1.	Physical State	Gas	Liquid	Solid
2.	Colour of Vapour	Greenish Yellow	Dark Red	Violet
3.	Action of H_2O	Decomposes into HCl & O_2	Decomposes Slowly in Presence of Light	No action
4.	Oxidising Action	Strong	Good	Weak
5.	Bleaching Action	Moist Cl_2 is a Good Bleaching Agent	Moist Br_2 is a good Bleaching Agent	No Bleaching
6.	Action of Halides	Displaces Br_2 & I_2	Displaces I_2	No Action
7.	Combination with H_2	Explosive in Light Slow in Dark	Only on Heating	Heating + Catalyst

- (b) Due to hydrogen bonding HF is a liquid while HCl, HBr and HI are gases.
 (c) Fluorine, being the most electronegative gives SF₆ while other member do not form hexahalides with sulphur.
 (d) It exhibits oxidation state of only -1.
 (e) It is the strongest oxidising agent.
 (f) It liberates oxygen as well as ozone with water.
 (g) HF does not ionize while HCl, HBr and HF ionize in aqueous solution.
 (h) Solubility of salts :
 (i) AgF is soluble in water while AgCl, AgBr and AgI are insoluble.
 (j) It combines with hydrogen with explosion at a low temperature and even in the dark. No other halogens combines so readily.



- (k) It liberates oxygen as well as ozone with water.



FAMILY MEMBERS OF HALOGEN

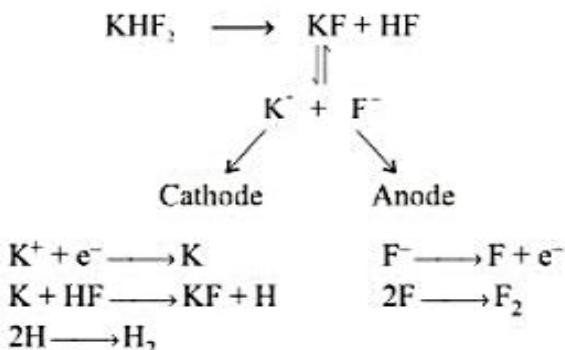
* Fluorine (F₂) :

Modern method of Isolation :

In this method F₂ is prepared by the electrolysis of fused fluoride, (KHF₂) potassium hydrogen fluoride.

* The electrolytic cells are made of Cu, Ni or monel metal.

Reaction in the electrolytic cell :



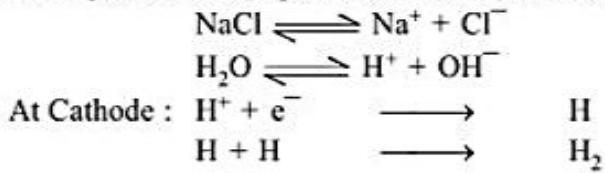
(i) Uses : It is used in the preparation of fluorine compound such as.

- (a) Freon : Fereon - 12 i.e. CF₂Cl₂ as used in refrigeration and air conditioning in place of NH₃ and SO₂.
 (b) Teflon : (-F₂C - CF₂)_n It is a new plastic.

* Chlorine (Cl₂) :

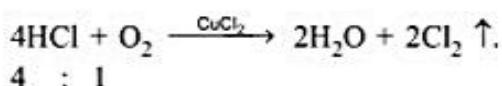
(i) Preparation :

- (a) By the electrolysis of brine (Aq. solution of NaCl) in nelson cell. This is the cheapest method





(b) Decon's Process :



Chlorine gas thus obtained contains N₂ and O₂ and is used for the manufacture of bleaching powder by hansenlever's process



(ii) Properties :

Bleaching:



Coloured matter + [O] → Colourless matter.

(iii) Uses :

- (a) As a Germicide and disinfectant.
- (b) Domestic antiseptic solution (NaOCl)
- (c) In Mfg of bleaching powder, D.D.T etc.
- (d) In warfare gases such as phosgene CaOCl₂, tear gas (CCl₃.NO₂) and mustard gas (ClC₂H₄ – S – C₂H₄Cl)

* **Bromine (Br₂) :**

(i) Preparation :

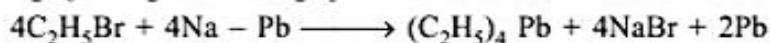
Bittern : Mother liquor contains about 0.25% of bromine or MgBr₂ and is known as bittern.

Bittern is treated with Chlorine gas.



(ii) Uses :

it is used in preparation of ethyl bromide which is used in the mfg of tetraethyl lead (TEL) as an important anti - knock compound in the petroleum industry.



* **Iodine (I₂) :**

(i) I₂ is the rarest of all the halogens. Its main source is kelp (varee).

(ii) Properties :

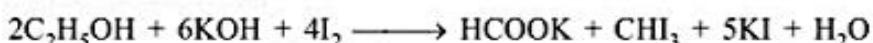
- (a) It is only sparingly soluble in water but readily soluble in Na or K iodide due to formation of triiodide.



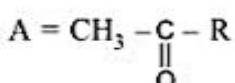
However, this solution behaves as a simple mixture of KI and free I₂.

Note : Tincture of iodine contains $\frac{1}{2}$ ounce I₂, $\frac{1}{4}$ ounce KI and 1 pinch of rectified spirit.

- (b) Iodoform Reaction :



Iodoform or Haloform reaction show by following -



When R = H, CH₃, C₂H₅,

R = Benzyl and its derivatives

R = Every 2-Alcohol (not secondary)

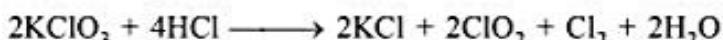
R = C₂H₅OH (only Ethyl Alcohol in Primary)

R = No. tertiary Alcohol.

COMPOUNDS OF DIFFERENT MEMBERS

* Potassium Chlorate (KClO₃)

- (i) On heating with conc. HCl, KClO₃ gives a mixture of chlorine and chlorine dioxide known as exchlorine.



- (ii) Uses : In mfg. of matches, fire works and photographic flash powders.

PSEUDOHALIDES AND PSEUDOHALOGENS

A few ions are known, consisting of two or more electronegative atoms of which at least one is nitrogen, that have properties similar to those of halide ions. These ions are called pseudohalide ions, Pseudohalide ions are univalent and these form salts resembling halide salts.

The pseudohalide ions are :

Cyanide ions (CN ⁻)	:	Isocyanide ion (NC ⁻)
Cyanate ion (OCN ⁻)	:	Fulminate ion (ONC ⁻)
Thiocyanate ions (SCN ⁻)	:	Iothiocyanate ion (NCS ⁻)
Selenocyanate ion (SeCN ⁻)	:	Tellurocyanate ion (TeCN ⁻)
Azide ion (N ₃ ⁻)	:	Azido carbon disulphide ion (SCSN ₃ ⁻)

As the dimers of halide ions are called halogens, the covalent dimers of the pseudohalide ions are called halogens or halogenoids. The pseudohalogens known are :

Cyanogen (CN) ₂	:	Oxycyanogen (OCN) ₂
Thiocyanogen (SCN) ₂	:	Selenocyanogen (SeCN) ₂
Tellurocyanogen (TeCN) ₂	:	Azido carbon disulphide (SCSN ₃) ₂

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The best known pseudohalide is CN^- . This resembles Cl^- , Br^- and I^- in the following respects:

- It forms an acid, HCN .
- It can be oxidised to $(\text{CN})_2$ molecule.
- It forms insoluble salts with Ag^+ , Pb^{2+} and Hg_2^{2+} .
- It forms large number of complexes similar to halide complexes, e.g.
 $[\text{Cu}(\text{CN})_4]^{2-}$ and $[\text{CuCl}_4]^{2-}$. $[\text{Co}(\text{CN})_6]^{3-}$ and $[\text{CoCl}_6]^{3-}$
- Inter-pseudohalogen compounds ClCN , BrCN and ICN can be formed.
- AgCN is insoluble in water but soluble in ammonia like AgCl .

Oxy acids of Halogens

Oxidation state of halogens	Chlorine	Bromine	Iodine	Name of acid	Name salt	
+1	HClO	HBrO	HIO	Hypohalous	Hypohalite	Stability and acidity increases but oxidising power decreases
+3	HClO_2	-	-	Halous	Halite	
+5	HClO_3	HBrO_3	HIO_3	Halic	Halate	
+7	HClO_4	HBrO_4	HIO_4	Perhalic	Perhalate	

OXY ACIDS OF HALOGENS

- Fluorine does not form any oxy-acids because it is more electronegative than oxygen.
- Other halogens form four series of oxy acids with formulae
 $\text{HXO} \rightarrow$ Hypohalous
 $\text{HXO}_2 \rightarrow$ Halous
 $\text{HXO}_3 \rightarrow$ Halic
 $\text{HXO}_4 \rightarrow$ Perhalic acids or Halic (I), Halic (III), Halic (V) and Halic (VII)

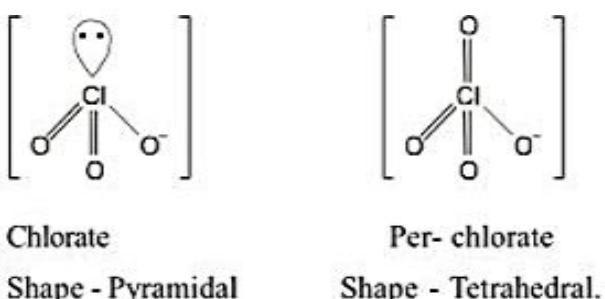
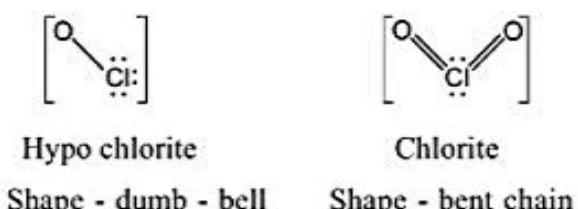
* Some important general trends in Oxy-acids of Halogens

- In oxy-acids, hydrogen is present as $-\text{OH}$ group
- All the hypohalous acids (HXO) are unstable and readily form HXO_3 . Among these the relative order of stability is $\text{HClO} > \text{HBrO} > \text{HIO}$
- In halic acids (HXO_3), iodic acid is the most stable.
- Thermal stability -

Thermal stability \propto oxidation state of halogens & No. of oxygen atoms.

- The thermal stability of both the acids and their salts increases with the increasing oxidation state of the halogen or with the increase in the number of oxygen atoms i.e. stability of the oxy halide anion increases from ClO^- , ClO_2^- , ClO_3^- , ClO_4^- .

- (b) This is due to the fact with the increasing number of oxygen atoms in the series, the no. of electron involved in forming σ and π bonds increases.
- (c) Thus in the most stable perchlorate ion, ClO_4^- , all the valence orbitals and electron of chlorine atom are involved in the formation of bonds.
- (d) The stability of perchlorate ion, ClO_4^- may also be said due to greater multiplicity of the Cl-O bond.



- (5) Oxidising power -
 ClO^-
 \downarrow Stability increases and oxidising power decreases
 ClO_4^-
Hypochlorites are the strongest oxidising agents.
- (6) Relative acidity \propto oxidation no.
 $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$

Note : (i) In all these acids and salts halogen is in sp^3 hybridised state.

(ii) Stronger the acid, the weaker will be its conjugate base and vice-versa.
 $\text{ClO}_4^- < \text{ClO}_3^- < \text{ClO}_2^- < \text{ClO}^-$ (relative basic character)
Thus ClO_4^- is the weakest base and HClO_4 (conjugate acid of ClO_4^-) is the strongest acid.

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

Relative stability of Cl–O bonds

Illustration

Q.1 Which of the following is the strongest oxidant –

- (A) F_2 (B) Cl_2 (C) Br_2 (D) I_2

Ans. (A)

Sol. F_2 is strongest oxidant, because (i) F_2 has exceptionally low dissociation energy of F-F bond. (ii) F^- has high energy of hydration due to small size of the F^- ion.

Exercise

Q.1 Solid Cl_2O_6 exists as -

- (A) ClO_2^+ , ClO_4^- (B) Covalent species (C) $(\text{ClO}_3)_2$ (D) None

Ans. (A)

O.2 Fluorine does not show positive oxidation states because -

- (A) It is most electronegative element
 - (B) It forms only anions in ionic compounds
 - (C) It cannot form multiple bonds
 - (D) It shows non-bonded electron pair repulsion due to small size

Ans. (A)

INERT GAS FAMILY

Element	Atomic no.	Outer shell configuration
He	2	$1s^2$
Ne	10	$He\ 2s^22p^6$
Ar	18	$Ne\ 3s^23p^6$
Kr	36	$Ar\ 3d^{10}4s^24p^6$
Xe	54	$Kr\ 4d^{10}5s^25p^6$
Rn	86	$Xe\ 4f^{14}5d^{10}6s^26p^6$

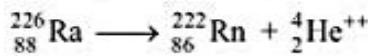
RARE GASES OR NOBLE GASES

These are found in atmosphere to very less extent so named rare gases and form very few compounds so termed noble gases.

Important point

All have octet configuration except He having duplet configuration.

- (i) They exist in gaseous state.
(ii) Rn is produced by the disintegration of radium and is radioactive itself.



-
- (iii) Ramsay was the discoverer of these gases.
 - (iv) First inert gas which was discovered by ram say firstly i.e. argon.
 - (v) All except Rn occur in atmosphere almost 1% by volume in which argon is the major constituent.

ISOLATION

Except He, non-radioactive noble gases are commercially isolated from air by two method.

(i) Fractional Distillation of Liquid air (Claude's Method) :

Due to difference in b.p. the various constituents of air are separated from each other.

(ii) Dewar's Coconut Charcoal Adsorption Method :

- (a) O₂ and N₂ are removed by means of compound formation.
- (b) The principle of this method is that the adsorption capacity of these gases at low temperature by coconut charcoal increases with increase in their atomic weights.
- (c) Thus He has the lowest and Xe has the maximum adsorption capacity.

GENERAL PROPERTIES

(i) Atomic Radii, Melting point and Boiling Point, Density :

- (a) All increases down the group.
- (b) He is the only element having two boiling point i.e. 4.2 K and 2.5 K.
- (c) It is [He] only element which exist in two liquid phases i.e. He and He₂.
- (d) They are colorless, odourless and tasteless.

(ii) Ionisation Energy :

- (a) They possess very high ionisation energy.
- (b) Ionisation energy of Xe is nearly equal to that of molecular oxygen.

(iii) Electron Affinity :

Due to complete octet, noble gas atoms are unable to take extra electron.

(iv) Monatomicity :

Due to very high I.E. and nearly zero E.A. noble gas atoms are not capable of combine and their value of $\gamma = \frac{C_p}{C_v}$ is close to 1.66.

(v) Force of attraction between atoms of Noble Gases :

Vander Walls force between the atoms increases from He to Xe.

(vi) Solubility in Water :

Slightly soluble in water and solubility in water increases with increase in atomic number.

(vii) Chemical Nature :

- (a) Noble gases are almost chemically inert.
 - (b) But Kr, Xe and Rn are slightly reactive because of relatively low IP of gases.
-

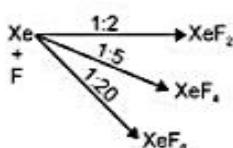
(viii) Adsorption of Inert Gases :

- (a) Done on coconut. Gas particles are adsorbed in surface of coconut charcoal
 (b) Larger the size, more will be the adsorption so maximum adsorption of Xe at highest temp.

- (ix)** (a) First gas discovered was Argon. (Ar gas Lazy)
 (b) Other inert gas isolated was Neon.
 (c) Other inert gas remaining hidden gas krypton (Kryptos = Hidden)
 (d) Then Xenon (Xenon = stranger)
 (e) Rn emits α , β , γ radiations.
 (f) He has unusual property of diffusion through lab material like Rubber, Glass, Plastic.

FAMILY MEMBERS OF NOBLE GASES*** Xenon (Xe) :**

It is the only element that forms true compounds.



- (i) XeF_2 :**

$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\quad	\quad	\quad	\quad
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5s 5p 5d
 sp^3d
 Linear Geometry

- (ii) XeF_4 :**

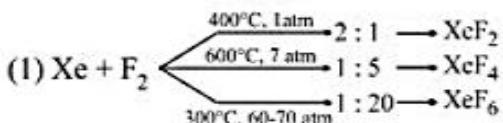
$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\uparrow	\quad	\quad	\quad
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5s 5p 5d
 sp^3d^2
 Square Planar

- (iii) XeF_6 :**

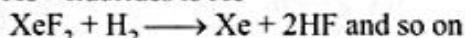
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sp^3d^3
 Distorted octahedral

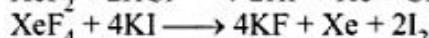
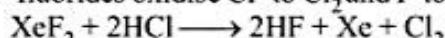
(iv) Xe – COMPOUNDS**Xenon Fluorides:-**

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(2) H_2 reduces Xe – fluorides to Xe

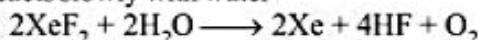


(3) Xe - fluorides oxidise Cl^- to Cl_2 and I^- to I_2

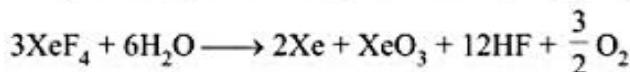


(4) Hydrolysis

XeF_2 reacts slowly with water

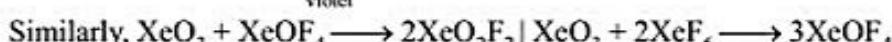
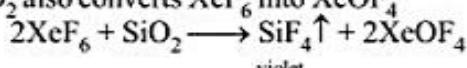


XeF_4 and XeF_6 react violently with water giving XeO_3

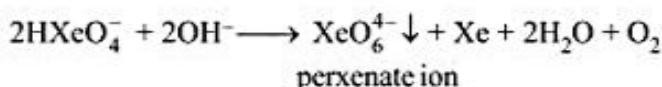
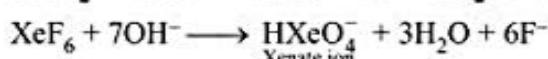


↓
(explosive, white hygroscopic solid)

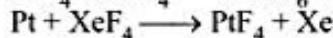
(5) SiO_2 also converts XeF_6 into XeOF_4



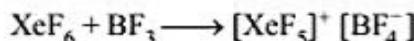
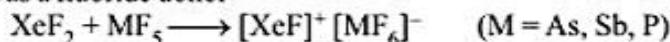
(6) Xe-fluorides are also hydrolysed in alkaline medium



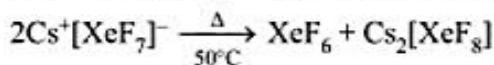
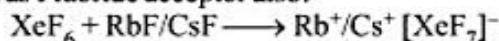
(7) They are used as fluorinating agent



(8) Act as a fluoride donor



(9) Act as Fluoride acceptor also:



(alkali metals fluoride)

* Neon and Argon :

- (i) Gets trapped in the interstitial spaces of H_2O or alcohols and this type of mixture resulted is called as clatharate compound.
- (ii) These compounds are not formed by He.,

USES

- (i) Noble gases are widely used to provide inert atmospheres in metallurgical process.
- (ii) He is used as a cooling medium in gas cooled atomic reaction because of its high thermal conductivity, low viscosity and low density.
- (iii) Liquid He is used in gas thermometer required for low temperature measurement.
- (iv) Neon in neon lamps.
- (v) Neon in neon tubes for rectifiers, voltage regulators etc.
- (vi) Argon is filling in incandescent lamps.
- (vii) Xe is used in discharge tube for quick photography.
- (viii) Rn is used in treatment of cancer (Radiotherapy)

Illustration

Q.1 Noble gases can be separated by –

- (A) Passing them through some solution
- (B) Electrolysis of their compounds
- (C) Adsorption and desorption on coconut charcoal
- (D) None

Ans. (C)

Sol. Coconut charcoal possess characteristic property for adsorbing different noble gases at different temperatures.

Q.2 Which of the following noble gases does not form clathrates?

- (A) He
- (B) Br₂
- (C) Ar
- (D) Xe

Ans. (A)

Sol. Due to small size of He it does not form clathrates.

Exercise

Q.1 The first compound of noble gases prepared by N-Bartlett was -

- (A) Xe⁺[Pt F₆]⁻
- (B) XeF₄
- (C) XeF₆
- (D) XeOF₄

Ans. (A)

SOLVED EXAMPLES

Q.1 Pick out the incorrect statement.

- (A) central oxygen in O_3 is sp^2 hybridised (B) the two O—O bonds in O_3 are equal
 (C) with BaO_2 , O_3 reacts to produce H_2O , (D) O_3 causes tailing of mercury

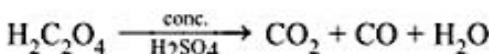
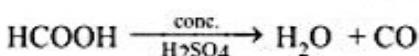
Ans. (C)

Sol. Only (c) is wrong because $\text{BaO}_2 + \text{O}_2 \rightarrow \text{BaO} + 2\text{O}_2$. The rest of the alternatives are correct.

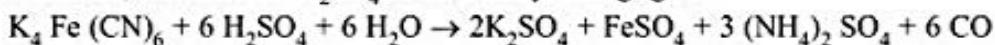
Q.2 Carbon monoxide is formed by the action of concentrated H_2SO_4 on

Ans. (D)

Sol. The reaction of concentrated H_2SO_4 on all the compounds is as follows



In these reactions, concentrated H_2SO_4 acts as a dehydrating agent.

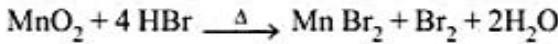
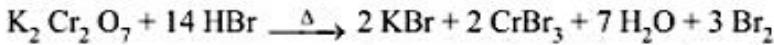
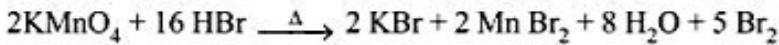


Q.3 Bromine is formed when concentrated HBr is heated with

- (A) KMnO_4 (B) $\text{K}_2\text{Cr}_2\text{O}_7$ (C) MnO_2 (D) All of these

Ans. (D)

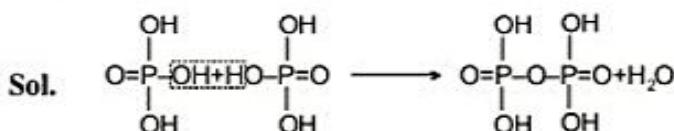
Sol. Concentrated HBr reacts with these compounds as follows:



Q.4 Pick out out incorrect statement -

- (A) Orthophosphorus acid can be obtained by reacting P_4O_6 with H_2O
 - (B) Orthophosphoric acid can be obtained by reacting P_4O_{10} with H_2O
 - (C) Pyrophosphoric acid can be obtained by heating orthophosphorous acid
 - (D) Metaphosphoric acid is obtained by the dehydration of orthophosphoric acid at $316^{\circ}C$.

Ans. (C)

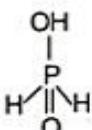


Q.5 Hypophosphorus acid H_2PO_3 is –

- (A) Tribasic acid (B) Dibasic acid (C) Monobasic acid (D) Not acidic at all

Ans. (C)

Sol. Structure of Hypophosphorous acid. As it contains only one replaceable H atom, it is mono basic.



Q.6 Maximum covalency of sulphur is –

- (A) 2 (B) 4 (C) 6 (D) -2

Ans. (C)

Sol. Sulphur atom in ground state

3s	3p	3d
↓↑	↓↑↑↑	

sulphur atom in excited state

3s	3p	3d
↑	↑ ↑ ↑	↑ ↑

Due to presence of six unpaired electrons, it can form maximum of six bonds, so covalency is six.

Q.7 The formula of sulphur molecule is –

- (A) S₂ (B) S₁ (C) S₃ (D) S₀

Ans (D)

Sol. Sulphur atom in S_8 molecule is in sp^3 hybridization state and involves both bonding and non bonding pairs of electrons.

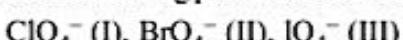
Q.8 Which of the following is a false statement-

- (A) Halogens are strong oxidizing agent (B) Halogens show only (-1) oxidation state
(C) HF molecules form intermolecular H-bonds (D) Fluorine is highly reactive

Ans. (B)

Sol. Fluorine, being most electronegative element, always show the oxidation state of -1. Other halogens can show higher positive oxidation state in addition to negative oxidation of -1

Q.9 Consider the following perhalate ion in acidic medium

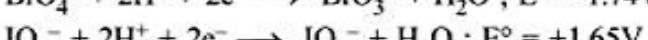
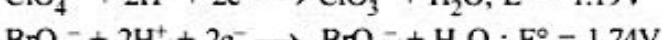
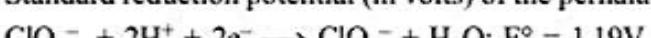


Arrange these in the decreasing order of oxidizing power

- (A) I \geq II \geq III (B) I \geq III \geq II (C) II \geq I \geq III (D) II \geq III \geq I

Ans. (D)

Sol. Standard reduction potential (in volts) of the perhalate ions are given as below –



more the standard reduction potential, the more is tendency of perhalite ion to undergo reduction and more stronger it will be an oxidizing agent.

- Q.10** Which of the following reactions will give bleaching powder –
 (A) $\text{CaCl}_2 + \text{H}_2\text{O}$ (B) $\text{CaO} + \text{HCl}$ (C) $\text{Ca}(\text{OH})_2 + \text{Cl}_2$ (D) $\text{ClO}_2 + \text{Ca}(\text{OH})_2$

Ans. (C)

Sol. $\text{Ca}(\text{OH})_2 + \text{Cl}_2 \rightarrow \text{CaOCl}_2 + \text{H}_2\text{O}$
 Slaked lime

- Q.11** The boiling point and melting point of inert gases are –
 (A) Low (B) High (C) Very high (D) Very low

Ans. (D)

Sol. Due to very weak, Vander Waals forces.

- Q.12** The ease of liquefaction of noble gases increases in the order –
 (A) $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$ (B) $\text{Xe} < \text{Kr} < \text{Ne} < \text{Ar} < \text{He}$
 (C) $\text{Kr} < \text{Xe} < \text{He} < \text{Ne} < \text{Ar}$ (D) $\text{Ar} < \text{Kr} < \text{Xe} < \text{Ne} < \text{He}$

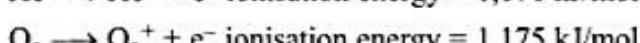
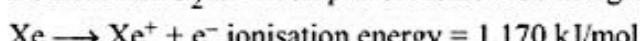
Ans. (A)

Sol. As size increases, Vander Waals forces also increases.

- Q.13** The statement, which prompted Neil Bartlett to prepare the first noble gas compound was -
 (A) Xe-F bond has high bond energy
 (B) F_2 has exceptionally low bond energy
 (C) PtF_6 is a strong oxidant
 (D) O_2 molecule and Xe atom have very similar ionization energies.

Ans. (D)

Sol. Both Xe and O_2 have comparable ionisation energies.



- Q.14** Which of the following halides is most acidic ?

- (A) PCl_3 (B) SbCl_3 (C) BiCl_3 (D) CCl_4

Ans. (A)

Sol. In CCl_4 , carbon atom does not have d-orbitals to accommodate a lone pair of electrons and hence is not a lewis acid. In PCl_3 , SbCl_3 , BiCl_3 centre atom has empty d-orbitals but electronegativity of P is maximum, hence PCl_3 is strongest acid.

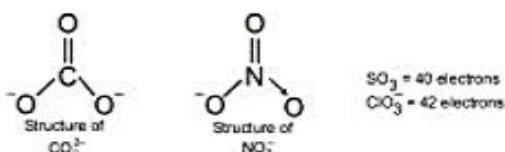
- Q.15** Which of the following are isoelectronic and isostructural ?

- (A) NO_3^- , CO_3^{2-} , (B) SO_3 , NO_3^- (C) ClO_3^- , CO_3^{2-} (D) CO_3^{2-} , SO_3

Ans. (A)

Sol. NO_3^- and CO_3^{2-} both have same number of electrons (32 electrons) and central atom in each being sp^2 hybridized.

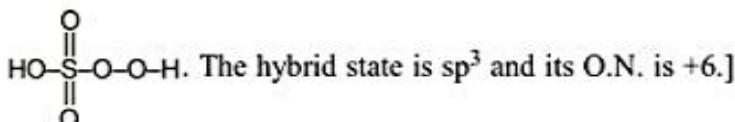
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- Q.16** What is the hybrid state and oxidation state of sulphur in Caro's acid ?
 (A) sp^2 , +10 (B) sp^3 , +10 (C) sp^2 , +6 (D) sp^3 , +6

Ans. (D)

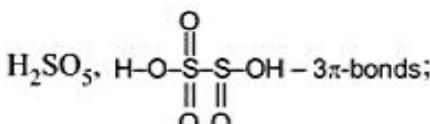
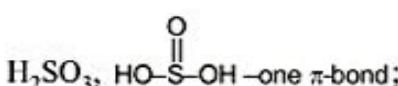
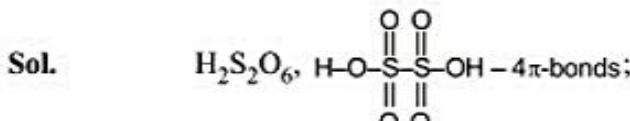
Sol. The structure of Caro's acid is



- Q.17** Identify the correct sequence of increasing number of π -bonds in structures of the following molecules –

- (i) $\text{H}_2\text{S}_2\text{O}_6$ (ii) H_2SO_3 (iii) $\text{H}_2\text{S}_2\text{O}_5$
 (A) I, II, III (B) II, III, I (C) II, I, III (D) I, III, II

Ans. (B)

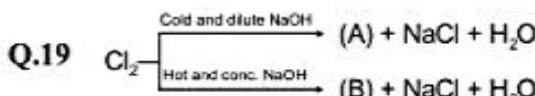
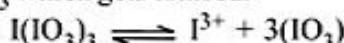


- Q.18** I_4O_9 is an –

- (A) covalent bond (B) coordinate compound
 (C) ionic compound (D) double salt

Ans. (C)

Sol. I_4O_9 is actually $\text{I}(\text{IO}_3)_3$ which gets ionised.



Compounds (A) and (B) are -

- (A) NaClO_3 , NaClO (B) NaOCl_2 , NaOCl (C) NaClO_4 , NaClO_3 (D) NaOCl , NaClO_3

Ans. (D)



Cold and dil. (A)



Hot and conc. (B)

- Q.20** When chlorine water is added to an aqueous solution of sodium iodide in the presence of chloroform, a violet colouration is obtained. On adding more of chlorine water and vigorous shaking, the violet colour disappears. This shows the conversion of.....into.....

(A) I_2 , HIO_3 (B) I_2 , HI (C) HI , HIO_3 (D) I_2 , HIO

Ans. (A)

Sol. $Cl_2 + 2NaI \rightarrow 2NaCl + I_2$

(Violet colouration in chloroform)



colourless

- Q.21** A greenish yellow gas reacts with an alkali hydroxide to form a halate which can be used in fireworks and safety matches. The gas and the halate are –

(A) Br_2 , $KBrO_3$ (B) Cl_2 , $KClO_3$ (C) I_2 , $NaIO_3$ (D) I_2 , KIO_3

Ans. (B)

Sol. The halate used in fireworks and safety matches is $KClO_3$. Thus, the gas is Cl_2 .



greenish

yellow gas

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