



## p-Block Elements (Nitrogen and Oxygen Family)

**Section (A) : General facts, Based on trend, Chemical Bonding, Preparation & Properties of group 15 elements**

**Group 15 Elements : The nitrogen family**

### 1. Occurrence :

Element	Occurrence
Nitrogen	78 % of earth's atmosphere by mass, essential constituent of proteins and amino acids.
Phosphorus	About 60% of bones and teeth are $\text{Ca}_3(\text{PO}_4)_2$ or $[\text{3}(\text{Ca}_3(\text{PO}_4)_2).\text{CaF}_2]$ . Nucleic acid such as DNA and RNA are made up of polyester chains of phosphates and sugars with organic bases.

### 2. Atomic & physical properties :

#### ATOMIC & PHYSICAL PROPERTIES

Element		N	P	As	Sb	Bi
Atomic Number		7	15	33	51	83
Atomic Mass		14.01	30.97	74.92	121.76	208.98
Electronic configuration		$[\text{He}] 2s^2 2p^3$	$[\text{Ne}] 3s^2 3p^3$	$[\text{Ar}] 3d^{10} 4s^2 4p^3$	$[\text{Kr}] 4d^{10} 5s^2 5p^3$	$[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^3$
Covalent Radius/pm		70	110	120	140	150
Ionic Radius/pm $a = \text{M}^{3-}$ , $b = \text{M}^{+3}$		171 <sup>a</sup>	212 <sup>a</sup>	222 <sup>a</sup>	76 <sup>b</sup>	103 <sup>b</sup>
Ionization enthalpy (kJ mol <sup>-1</sup> )	I	1402	1012	947	834	703
	II	2856	1903	1798	1595	1610
	III	4577	2910	2736	2443	2466
Electronegativity		3.0	2.1	2.0	1.9	1.9

Group 15 includes nitrogen phosphorus, arsenic, antimony and bismuth. As we go down the group, there is a shift from non-metallic to metallic through metalloid character.

**Nitrogen**  
**Phosphorus**

**Non metals**

**Arsenic**  
**Antimony**

**Metalloid**

**Bismuth {Typical metal}**

- (i) **Electronic Configuration** : The valence shell electronic configuration of these element is  $ns^2np^3$ . The s orbital in these element is completely filled and p orbitals are half- filled, making their electronic configuration extra stable.
- (ii) **Atomic and Ionic Radii** : Covalent and ionic (in a particular state) radii increase in size down the group. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled d and / or f orbitals in heavier members.
- (iii) **Ionisation Enthalpy** :
  - Ionisation enthalpy decreases down the group due to gradual increase in atomic size because of the extra stable half- filled p-orbital electronic configuration and smaller size.
  - The ionisation enthalpy of the group 15 element is much greater than of group 14 elements in the corresponding periods. The order of successive ionisation enthalpies, as expected is  $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$
- (iv) **Electronegativity** : The electronegativity value, in general, decreases down the group with increasing atomic size. However, amongst the heavier elements, the difference is not that much pronounced.



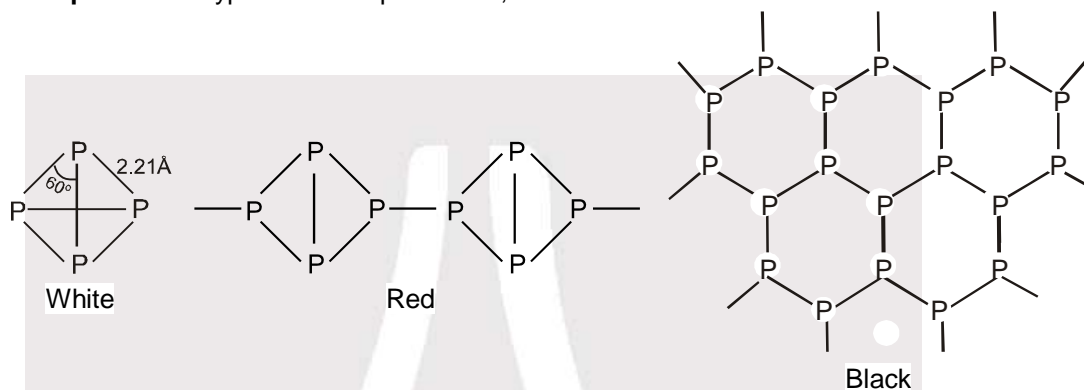
**(v) Physical Properties :**

- All the elements of this group are polyatomic. Dinitrogen is a diatomic gas while all others are solids.
- Metallic character increases down the group.
- The boiling points, in general, increase from top to bottom in the group but the melting point increases upto arsenic and then decreases upto bismuth.
- Except nitrogen, all the elements show allotropy.

**3. Allotropy**

**3.1. Nitrogen :** does not show allotropy

**3.2. Phosphorus :** 3 types of allotropes: white, red and black.



Properties	White-P	Red-P
Physical state	Soft waxy solid	Brittle powder
Colour	White when pure. Attains yellow colour on standing	Red
Odour	Garlic	Odourless
Melting point	44°C	Sublimes in absence of air at 290°C
Physiological Action	Highly Poisonous	Non-Poisonous
Solubility in water	Insoluble	Insoluble
Solubility in CS <sub>2</sub>	Soluble	Insoluble
Chemical activity	Very active	Less active
Stability	Unstable	Stable
Phosphorescence	Glow in dark	Does not glow in dark
Burning in air	Forms P <sub>4</sub> O <sub>10</sub>	From P <sub>4</sub> O <sub>10</sub>
Reaction with NaOH	Evolves phosphine	No action
Reaction with hot HNO <sub>3</sub>	Forms H <sub>3</sub> PO <sub>4</sub>	Forms H <sub>3</sub> PO <sub>4</sub>

**White Phosphorus :**

The P<sub>4</sub> molecule is tetrahedral in shape.

It remains in both liquid and gaseous states.

It is quite reactive due to bond angle strain and ring strain.

It is stored under water.

Above 800°C it dissociates to P<sub>2</sub>.

Due to slow oxidation in dark it glows. This phenomenon is known as **phosphorescence**.

Thermodynamically it is the least stable allotrope of phosphorus. It is highly toxic.

**Red Phosphorus :**

It is made by heating white phosphorus to about 250°C for several hours in inert atmosphere using iodine as catalyst or at a lower temperature in presence of sun light.



It consists of long chains of phosphorus atoms which are covalently bonded forming a giant molecule. Due to this highly polymerised structure red phosphorus is less reactive and less volatile.

### Black Phosphorus :

It has two forms (i)  $\alpha$ -black phosphorus (ii)  $\beta$ -black phosphorus

#### $\alpha$ -black phosphorus

It is obtained by dissolving red phosphorus in fused lead or bismuth at 803K in a sealed tube for a long time and cooling. Lead or bismuth are separated by dissolving in dilute nitric acid.

It has opaque monoclinic or rhombohedral crystals

It is very stable chemically inert and cannot be oxidised by air unless heated very strongly.

It is non-conductor.

#### $\beta$ -black phosphorus

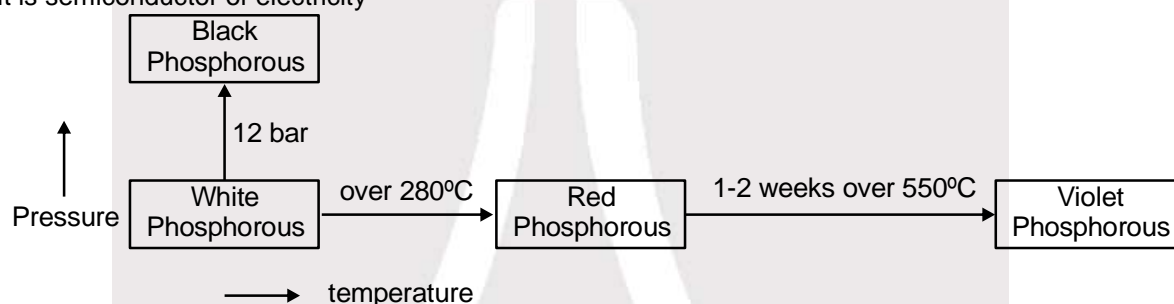
It is obtained by heating white phosphorus at 473K and at very high pressure (12000 atm)

It is inert and has a layered structure. Each phosphorus atom is bonded with three other atoms.

The PPP angle is  $99^\circ$  and P-P bond length is 218 pm.

Distance between adjacent layers is 388 pm.

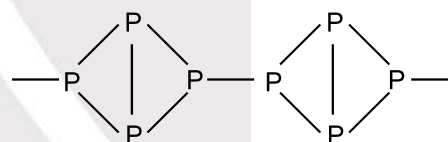
It is semiconductor of electricity



## Solved Examples

**Ex-1.** Explain the high reactivity of white phosphorus as compared to red phosphorus.

**Sol.** The high reactivity of white phosphorus is due to an unusual bonding that produces considerable strain in the  $P_4$  molecule. The  $P_4$  molecule exists as a discrete molecule whereas the red phosphorus is a polymeric substance in which the tetrahedral,  $P_4$  units are held by covalent bonds as shown in the following structure.



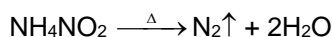
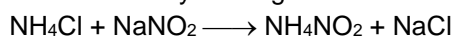
## Preparation & Properties of elements

### 4. Preparation of Elements :

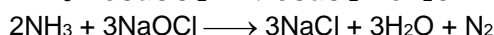
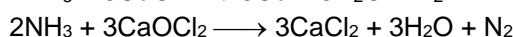
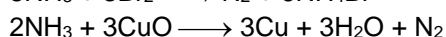
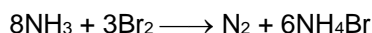
#### 4.1 Nitrogen :

##### (a) Lab preparation :

(i) It can be obtained by making ammonium nitrite and then warming it



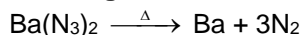
(ii) It is also obtained by oxidizing  $NH_3$  with calcium hypochlorite, bromine water or  $CuO$ .



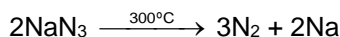
(b) **Industrial preparation :**

(i) **From liquified air by fractional distillation:** The boiling point of  $N_2$  is  $-196^\circ C$  and that of oxygen is  $-183^\circ C$  and hence they can be separated by distillation using fractional column.

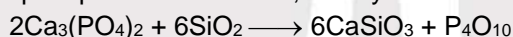
(ii) **From producer gas from furnaces:** Producer gas is a mixture of CO and  $N_2$ . When the mixture of CO and  $N_2$  is passed over heated CuO, the CO gas is oxidized to  $CO_2$  which is absorbed in alkalis &  $N_2$  remains which is collected in gas cylinders.

(c) **Very pure nitrogen :**

Small quantities of very pure  $N_2$  may be obtained by carefully warming sodium azide  $NaN_3$  to about  $300^\circ C$ .

4.2. **Phosphorous :**

It is obtained by reduction of calcium phosphate with C in an electric furnace at  $1400-1500^\circ C$ . Sand (silica  $SiO_2$ ) is added to remove the calcium as fluid slag (calcium silicate) and to drive off phosphorous as  $P_4O_{10}$ . The  $P_4O_{10}$  is reduced to phosphorous by C. At this temperature, gaseous phosphorous distills off, mainly as  $P_4$  but with some  $P_2$ .

**Physical Properties of Nitrogen & Phosphorus**

Element	Physical Properties
<b>Nitrogen</b>	<ul style="list-style-type: none"> <li>Colourless, odourless, tasteless, diamagnetic gas.</li> <li>Insoluble in water and is neither combustible nor a supporter of combustion.</li> <li>Inert at room temperature, though it does react with Li, forming the nitride <math>Li_3N</math>.</li> </ul>
<b>Phosphorus</b>	<ul style="list-style-type: none"> <li>Solid at room temperature, soft, waxy and reactive.</li> <li>Reacts with moist air and give out light (chemiluminescence).</li> <li>Ignites spontaneously in air at about <math>35^\circ C</math> and is stored under water to prevent this.</li> <li>Exists as tetrahedral <math>P_4</math> molecules and tetrahedral structure remains in the liquid and gaseous states.</li> <li>Above <math>800^\circ C</math>, <math>P_4</math> begin to dissociate in to <math>P_2</math> molecule.</li> </ul>

**Solved Examples**

**Ex-2.** Write the reaction of thermal decomposition of sodium azide.

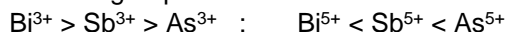
**Sol.** Thermal decomposition of sodium azide gives dinitrogen gas.  $2NaN_3 \longrightarrow 2Na + 3N_2$ .

**Section (B) : General trends & Chemical Properties of group 15 elements**5. **General trends and Chemical properties :**(i) **Oxidation States and trends in a chemical reactivity :**

The common oxidation states of these elements are  $-3$ ,  $+3$  and  $+5$ .

The tendency to exhibit  $-3$  oxidation state decreases down the group.

The stability of  $+5$  oxidation state decreases and that of  $+3$  state increases (due to inert pair effect) down the group.



• The only well characterised Bi (V) compound is  $BiF_5$ .

• Apart from these oxidation states nitrogen exhibits a large number of oxidation states from  $-3$  to  $+5$ .

-3	-2	-1	-1/3	0	+1	+2	+3	+4	+5
$NH_3$	$N_2H_4$	$NH_2OH$	$N_3H$	$N_2$	$N_2O$	$NO$	$N_2O_3$	$NO_2/N_2O_4$	$N_2O_5$

• Phosphorus also shows  $+1$  and  $+4$  oxidation states in some oxoacids.



- In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution.

For example,  $3 \text{HNO}_2 \longrightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2 \text{NO}$

- Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and -3 both in alkali and acid medium. However +3 oxidation state in case of arsenic, antimony and bismuth become increasingly stable with respect to disproportionation.
- Nitrogen is restricted to a maximum covalency of 4 since only four (one s and three p) orbitals are available for bonding.
- The heavier elements have vacant d orbitals in the outermost shell which can be used for bonding (covalency) and hence, expand their covalence as in  $\text{PF}_6^-$ .

## (ii) Reactivity towards hydrogen (hydrides) :

All the elements of Group 15 form hydrides of the type  $\text{EH}_3$  where E = N, P, As, Sb or Bi.

All these hydrides are colourless poisonous gases. The poisonous nature increases from  $\text{NH}_3$  to  $\text{BiH}_3$ .

**Table : Properties of Hydrides of Group 15 Elements**

Property	$\text{NH}_3$	$\text{PH}_3$	$\text{AsH}_3$	$\text{SbH}_3$	$\text{BiH}_3$
m.p./K	195.2	139.5	156.7	185	-
b.p./K	238.5	185.5	210.6	254.6	290
H-E distance/pm	101.7	141.9	151.9	170.7	-
HEH angle ( $^\circ$ )	107.8	93.6	91.8	91.3	-
$\Delta_f H^\circ/\text{kJ mol}^{-1}$	-46.1	13.4	66.4	145.1	278
$\Delta_{\text{diss}} H (\text{H-E})/\text{kJ mol}^{-1}$	389	322	297	255	-

The vanderwaals' forces in bigger Stibine molecules dominate the weaker hydrogen bonding in ammonia. **The order of boiling points is:**  $\text{PH}_3 < \text{AsH}_3 < \text{NH}_3 < \text{SbH}_3 < \text{BiH}_3$

**The order of melting points is:**  $\text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{NH}_3$

**The order of volatility is:**  $\text{PH}_3 > \text{AsH}_3 > \text{NH}_3 > \text{SbH}_3$

**The order of basic nature:**  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$

**The order of stability:**  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$

**The order of reducing nature:**  $\text{SbH}_3 > \text{AsH}_3 > \text{PH}_3 > \text{NH}_3$

**The order of covalent character:**  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{BiH}_3$

## (iii) Reactivity towards oxygen :

- All these elements form two types of oxides :  $\text{E}_2\text{O}_3$  and  $\text{E}_2\text{O}_5$ .
- The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state.
- Their acidic character decreases down the group.
- The oxides of the type  $\text{E}_2\text{O}_3$  of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and that of bismuth is predominantly basic.
- The oxides in lower oxidation state (i.e. +3) will act as reducing reagents and their reduction power decreases from nitrogen to bismuth.
- The oxides in higher oxidation state (i.e. +5) will act as oxidising agents and their oxidation power should increase from nitrogen to bismuth as their stability of +5 oxidation state decreases from nitrogen to bismuth but N (V) and Bi (V) are strong oxidising agents than the intervening three elements.
- The solubility of oxides in water decreases from nitrogen to bismuth.

**Table : Oxides of the group 15 elements**

Element	Trioxide	Pentoxide
Nitrogen	$\text{N}_2\text{O}_3$	$\text{N}_2\text{O}_5$
Phosphorus	$\text{P}_4\text{O}_6$	$\text{P}_4\text{O}_{10}$
Arsenic	$\text{As}_4\text{O}_6$	$\text{As}_4\text{O}_{10}$
Antimony	$\text{Sb}_4\text{O}_6$	$\text{Sb}_4\text{O}_{10}$
Bismuth	$\text{Bi}_2\text{O}_3$	—

**(iv) Reactivity towards halogens :**

- These elements react to form two series of halides :  $EX_3$  and  $EX_5$
- Nitrogen does not form pentahalide due to non-availability of the d-orbitals in its valence shell.
- Pentahalides are more covalent than trihalides.
- All the trihalides of these elements except those of nitrogen are stable. In case of nitrogen, only  $NF_3$  is known to be stable.  $NCl_3$  is explosive,  $NBr_3$  and  $NI_3$  are known only as their unstable ammoniates  $NBr_3 \cdot 6NH_3$  and  $NI_3 \cdot 6NH_3$ .
- For a given element of group 15 the stability of halides will be in the order  
Fluoride > Chloride > Bromide > Iodide.
- Only  $BiF_3$  is ionic and all other halides are covalent.
- $PCl_5$  is less stable than  $PCl_3$ .
- Trihalides are pyramidal and pentahalides are trigonal bipyramidal.
- Reducing nature of trihalides :  $PI_3 > PBr_3 > PCl_3 > PF_3$

**Table : Halides of the group 15 elements**

Element	Trihalides	Pentahalides
Nitrogen	$NF_3, NCl_3, NBr_3, NI_3$	—
Phosphorus	$PF_3, PCl_3, PBr_3, PI_3$	$PF_5, PCl_5, PBr_5$
Arsenic	$AsF_3, AsCl_3, AsBr_3, AsI_3$	$AsF_5, (AsCl_5)$
Antimony	$SbF_3, SbCl_3, SbBr_3, SbI_3$	$SbF_5, SbCl_5$
Bismuth	$BiF_3, BiCl_3, BiBr_3, BiI_3$	$BiF_5$

**(v) Reactivity towards metals :**

These elements react with metals to form their binary compounds exhibiting  $-3$  oxidation state, such as,  $Ca_3N_2$  (calcium nitride)  $Ca_3P_2$  (calcium phosphide),  $Na_3As_2$  (sodium arsenide),  $Zn_3Sb_2$  (zinc antimonide) and  $Mg_3Bi_2$  (magnesium bismuthide).

**(vi) Anomalous properties of nitrogen :**

- Nitrogen differs from the rest of the members of this group due to :  
(i) Smaller size (ii) high electronegativity (iii) high ionisation enthalpy (iv) non-availability of d orbitals.
- Nitrogen can form  $p\pi-p\pi$  multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C, O).
- Heavier elements of this group do not form  $p\pi-p\pi$  bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping. Thus, nitrogen exists as a diatomic molecule with a triple bond (one s and two p) between the two atoms.
- However, the single N–N bond is weaker than the single P–P bond because of high interelectronic repulsion of the non-bonding electrons, owing to the small bond length. As a result the catenation tendency is weaker in nitrogen. Another factor which affects the chemistry of nitrogen is the absence of d orbitals in its valence shell.
- Besides restricting its covalency to four, nitrogen cannot form  $d\pi-p\pi$  bonds just like the heavier elements of the same group  
e.g.,  $R_3P=O$  or  $R_3P=CH_2$  (R = alkyl group).
- Phosphorus and arsenic can form  $d\pi-p\pi$  bond also with transition metals when their compounds like  $P(C_2H_5)_3$  and  $As(C_6H_5)_3$  act as ligands.
- Phosphorus, arsenic and antimony form metallic bonds in elemental state.

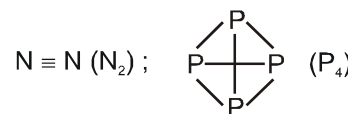




## Solved Examples

**Ex-3.** Give reason(s) why elemental nitrogen exists as diatomic molecule whereas elemental phosphorus is a tetra-atomic molecule.

**Sol.** In the form of elemental nitrogen it exists as a diatomic molecule ( $N_2$ ). This is due to the fact that nitrogen can form  $p\pi-p\pi$  multiple bond ( $N \equiv N$ ) because of small size of nitrogen atom. Heavier elements of this group do not form  $p\pi-p\pi$  bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping. Further P-P single bond is stronger than N-N single bond. Hence phosphorus has tendency to under go catenation.



**Ex-4.** Why does nitrogen show catenation properties less than phosphorus?

**Sol.** Because single P-P bond is stronger than single N-N bond.

**Ex-5.** Why does  $R_3P = O$  exist but  $R_3N = O$  does not (R = alkyl group) ?

**Sol.** Because of inability of nitrogen to expand its covalency beyond 4.

**Ex-6.** Why are penta halides more covalent than trihalides ?

**Sol.** Higher the positive oxidation state of central atom more will be its polarising power which in turn increases the covalent character of bond formed between the central atom and the other atom.

**Ex-7.** Explain why  $NH_3$  is basic while  $BiH_3$  is only feebly basic ?

**Sol.** Lone pair of electrons is present in more concentrated spherical non directional s-orbital in  $BiH_3$  whereas it is present in  $sp^3$  hybrid orbital which is directional; due to decrease in bond (E-H) dissociation enthalpy down the group,  $BiH_3$  acts as acid rather than a base.

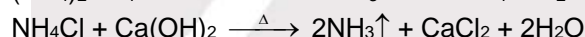
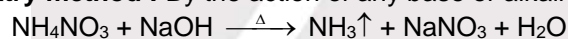
## Section (C) : Compounds of Nitrogen (Hydrides, Oxides & Oxyacids)

### 6. Hydrides :

#### 6.1. Ammonia ( $NH_3$ )

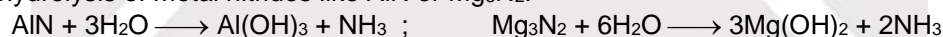
##### 6.1.1 PREPARATION:

(i) **Laboratory method :** By the action of any base or alkali on any ammonium salt :

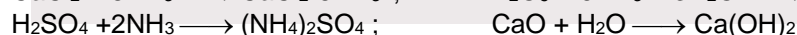
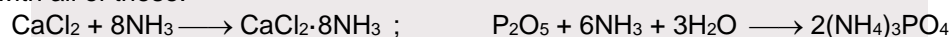


**This is a general method and is used as a test for ammonium salts.**

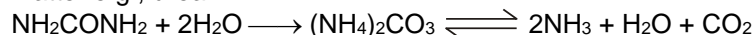
(ii) By the hydrolysis of metal nitrides like  $AlN$  or  $Mg_3N_2$ .



(iii) The ammonia evolved is passed through quick lime to dry it and collected by the downward displacement of air. Ammonia cannot be dried using  $CaCl_2$ ,  $P_2O_5$  or concentrated  $H_2SO_4$  because  $NH_3$  reacts with all of these.

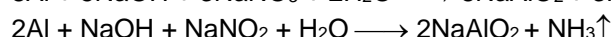
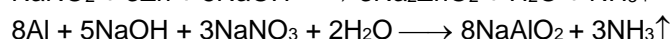
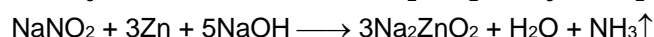
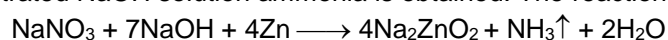


(iv) Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.



(v) **Quantitative estimation of nitrogen :**

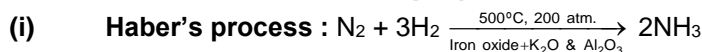
From nitrates and nitrites: When a metal nitrate or nitrite is heated with zinc powder or aluminium and concentrated  $NaOH$  solution ammonia is obtained. The reactions are



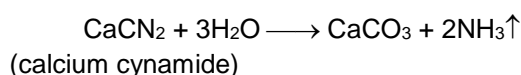
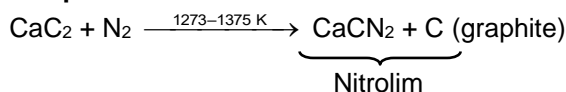


Thus a nitrite or a nitrate can be identified by this reaction but this test cannot make distinction between them.

### Industrial methods of preparation :



(ii) **Cyanamide process** :



(iii) **From destructive distillation of coal** : When coal is heated at a high temperature in an iron retort and the distillate is bubbled in water, three substances are obtained :

(a) Tarry black pitch, (b) Liquor ammonia & (c) Coal gas

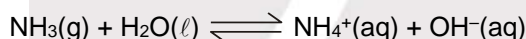
The liquor ammonia is a concentrated solution of ammonia and ammonium salts. When heated it gives out ammonia. When all the free  $\text{NH}_3$  is obtained, the residual liquid is heated with  $\text{Ca(OH)}_2$  when ammonium salts get decomposed to liberate further quantity of ammonia.

### 6.1.2. Physical properties :

(i) Ammonia is a colourless gas with a pungent odour. Its freezing point and boiling point are 195.2 K and 238.5 K respectively.

(ii) In the solid and liquid states, it is associated through hydrogen bonds as in the case of water and that accounts for its higher melting and boiling points than expected on the basis of its molecular mass.

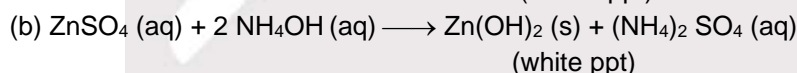
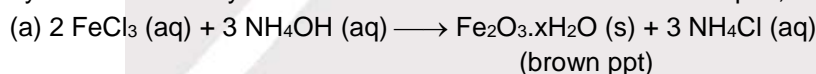
(iii) Ammonia gas is highly soluble in water. Its aqueous solution is weakly basic due to the formation of  $\text{OH}^-$  ions.



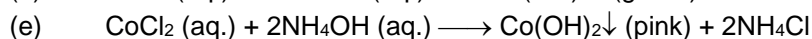
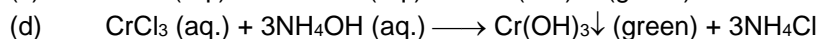
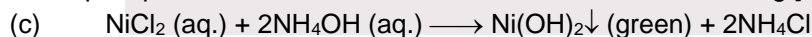
### 6.1.3. Chemical properties :

(i)  **$\text{NH}_3$  as weak base** :

It forms ammonium salts with acids, e.g.,  $\text{NH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{SO}_4$  etc. As a weak base, it precipitates the hydroxides of many metals from their salt solutions. For example ,



White precipitate is soluble in excess of ammonia solution forming  $[\text{Zn(NH}_3)_4]^{2+}$ , soluble complex.

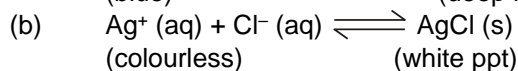
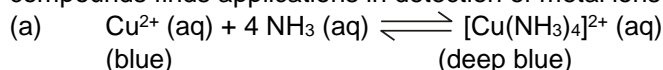


$\text{Cr(OH)}_3$  (precipitate) is partially soluble in excess ammonia whereas

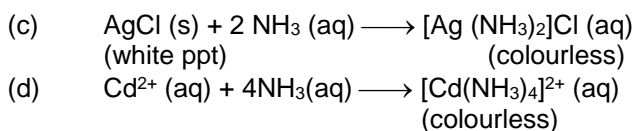
$\text{Ni(OH)}_2$  (precipitate),  $\text{Co(OH)}_2$  (precipitate) are soluble in excess of ammonia forming soluble complex.

(ii) **Complex formation by  $\text{NH}_3$**  :

The presence of lone pair of electrons on the nitrogen atoms of the ammonia molecule makes it a Lewis base. It donates the electrons pair and forms linkage with metal ions and the formation of such complex compounds finds applications in detection of metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ;  $\text{Cd}^{2+}$  :

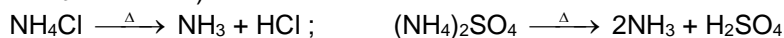






(iii) **Thermal decomposition of ammonium salts :**

Ammonium salts decompose quite readily on heating. If the anion is not particularly oxidising (e.g.  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$  or  $\text{SO}_4^{2-}$ ) then ammonia is evolved.

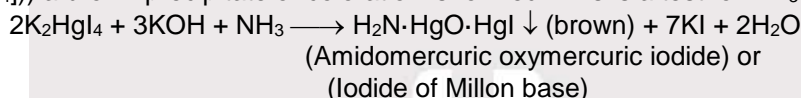


If the anion is more oxidising (e.g.  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ) then  $\text{NH}_4^+$  is oxidised to  $\text{N}_2$  or  $\text{N}_2\text{O}$ .



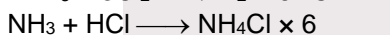
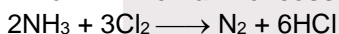
(iv) **Test of Ammonia and Ammonium salts :**

When  $\text{NH}_3$  gas is passed into the colourless solution of Nessler's reagent (Alkaline solution of  $(\text{K}_2[\text{HgI}_4])$ ) a brown precipitate or coloration is formed. This is a test for  $\text{NH}_3$  gas.

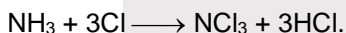


(v) **Reaction with Halogens :**

**When Ammonia in excess :** The products are nitrogen and ammonium chloride.



**When chlorine in excess :** The products are nitrogen trichloride and HCl.



**6.1.4. USES OF  $\text{NH}_3$  :**

- Used as a refrigeration fluid.
- For the production of nitrogenous fertilizers such as ammonium sulphate, ammonium phosphate, ammonium nitrate, urea etc.
- For removing grease because  $\text{NH}_4\text{OH}$  dissolves grease.
- For manufacture of  $\text{HNO}_3$  by the Ostwald process.
- As a laboratory reagent.
- In the production of artificial rayon, silk, nylon etc. in the form of tetraamine copper(II) sulphate (Schweitzer's reagent)

## Solved Examples

**Ex-8.** What happens when:

- (a)  $\text{NH}_4\text{Cl}$  &  $\text{NaNO}_3$  is heated strongly. (b)  $(\text{NH}_4)_2\text{CO}_3$  is heated. (c)  $\text{NH}_4\text{NO}_2$  is heated.

**Sol.** (a)  $\text{NH}_4\text{Cl} + \text{NaNO}_3 \longrightarrow \text{NH}_4\text{NO}_3 + \text{NaCl}$ ;  $\text{NH}_4\text{NO}_3 \xrightarrow{\Delta} \text{N}_2\text{O} + 2\text{H}_2\text{O}$

(b)  $(\text{NH}_4)_2\text{CO}_3 \xrightarrow{\Delta} 2\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}$  (c)  $\text{NH}_4\text{NO}_2 \xrightarrow{\Delta} \text{N}_2 + 2\text{H}_2\text{O}$

## 7.1. Oxides of nitrogen

S.N. / Compounds	Preparation	Properties
1. <b><math>\text{N}_2\text{O}</math></b> (Nitrous Oxide)	$\text{NH}_4\text{NO}_3 \xrightarrow{280^\circ\text{C}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$	Stable, relatively unreactive, colourless gas and a neutral oxide. Used as an anaesthetic and called laughing gas.
2. <b><math>\text{NO}</math></b> (Nitric)	<b>Laboratory method:</b> (i) $3\text{Cu} + 8\text{HNO}_3 \rightarrow 2\text{NO} + 3\text{Cu}(\text{NO}_3)_2 + 4\text{H}_2\text{O}$	Colourless gas, an important intermediate in manufacturing of nitric acid by Ostwald process. Neutral oxide, not an acid anhydride.



<b>Oxide)</b>	(ii) $2\text{HNO}_2 + 2\text{I}^- + 2\text{H}^+ \rightarrow 2\text{NO} + \text{I}_2 + 2\text{H}_2\text{O}$	Reacts instantly with $\text{O}_2$ to give $\text{NO}_2$ $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ $3\text{NO} \xrightarrow[30 - 50^\circ\text{C}]{\text{High pressure}} \text{N}_2\text{O} + \text{NO}_2$
<b>3.</b> <b><math>\text{N}_2\text{O}_3</math></b> <b>[Dinitrogen trioxide]</b>	By condensing equimolar amounts of $\text{NO}$ and $\text{NO}_2$ together or by reacting $\text{NO}$ with appropriate amount of $\text{O}_2$ . $\text{NO} + \text{NO}_2 \rightarrow \text{N}_2\text{O}_3$ $4\text{NO} + \text{O}_2 \rightarrow 2\text{N}_2\text{O}_3$	Blue solid, acidic oxide and anhydride of $\text{HNO}_2$ . With alkali forms nitrites $\text{N}_2\text{O}_3 + \text{NaOH} \rightarrow 2\text{NaNO}_2 + \text{H}_2\text{O}$ $\text{N}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{HNO}_2$
<b>4.</b> <b>[Nitrogen dioxide]</b> <b>and</b> <b><math>\text{N}_2\text{O}_4</math></b>	Laboratory method: $2\text{Pb}(\text{NO}_3)_2 \rightarrow 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$ $\text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$ (conc.) $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ Paramagnetic Brown      Diamagnetic colourless	Red-brown poisonous gas, very reactive, dimerizes into colourless $\text{N}_2\text{O}_4$ . Mixed anhydride as it reacts with water to give nitric and nitrous acids. $\text{N}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_2$ $\text{NO}_2$ – $\text{N}_2\text{O}_4$ system is a strong oxidizing agent
<b>5.</b> <b><math>\text{N}_2\text{O}_5</math></b> <b>(Dinitrogen pentoxide)</b>	Prepared by carefully dehydrating $\text{HNO}_3$ with $\text{P}_2\text{O}_5$ at low temperature $4\text{HNO}_3 + \text{P}_4\text{O}_{10} \rightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$	Colourless deliquescent solid, highly reactive, strong oxidizing agent Anhydride of $\text{HNO}_3$ . In gas phase, decomposes into $\text{NO}_2$ , $\text{NO}$ and $\text{O}_2$

**Table : Structures of Oxides of Nitrogen**

Lewis dot main resonance structures and bond parameters of oxides are given in Table.

Formula	Resonance Structures	Bond Parameters
$\text{N}_2\text{O}$	$\ddot{\text{N}} \equiv \text{N}=\text{O} \longleftrightarrow :\text{N} \equiv \text{N}-\ddot{\text{O}}:$	$\text{N}-\text{N}-\text{O}$ 113pm 119pm Linear
$\text{NO}$	$:\text{N}=\ddot{\text{O}}: \longleftrightarrow :\ddot{\text{N}}=\ddot{\text{O}}:$	$\text{N}-\text{O}$ 115pm
$\text{N}_2\text{O}_3$		
$\text{NO}_2$		
$\text{N}_2\text{O}_4$		
$\text{N}_2\text{O}_5$		



## Solved Examples

**Ex-9.** (A) Colourless salt + NaOH  $\xrightarrow{\Delta}$  (B) gas + (C) alkaline solution  
 (C) + Zn (dust)  $\xrightarrow{\text{Warm}}$  gas (B) ; (A)  $\xrightarrow{\Delta}$  gas (D) + liquid (E)  
both triatomic

Gas (B) gives white fumes with HCl. Identify (A) to (E) and write the chemical reactions involved.

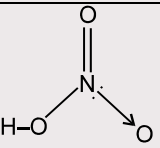
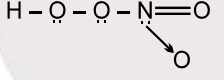
**Sol.**  $\text{NH}_4\text{NO}_3 + \text{NaOH} \xrightarrow{\Delta} \text{NH}_3 + \text{NaNO}_3 + \text{H}_2\text{O}$ ;  $\text{NH}_3 + \text{HCl} \longrightarrow \text{NH}_4\text{Cl}$  (white fumes)  
 $\text{NaNO}_3 + 7\text{NaOH} + 4\text{Zn} \longrightarrow 4\text{Na}_2\text{ZnO}_2 + \text{NH}_3\uparrow + 2\text{H}_2\text{O}$   
 $\text{NH}_4\text{NO}_3 \xrightarrow{\Delta} \text{N}_2\text{O} + 2\text{H}_2\text{O}$   
 So, (A) =  $\text{NH}_4\text{NO}_3$ , (B) =  $\text{NH}_3$ , (C) =  $\text{NaNO}_3$ , (D) =  $\text{N}_2\text{O}$  and (E) =  $\text{H}_2\text{O}$ .

**Ex-10.**  $\text{NO}_2$  can not be dried by an alkali, why ?

**Sol.**  $\text{NO}_2$  being acidic in nature is absorbed by alkali.

## 8.1 OXY ACIDS OF NITROGEN :

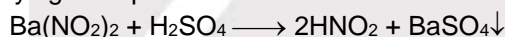
(N atom  $\text{sp}^2$  hybridised)

1.	$\text{HNO}_3$	Nitric acid (Colourless)	
2.	$\text{HNO}_2$	Nitrous acid (Pale blue)	$\text{H}-\ddot{\text{O}}-\ddot{\text{N}}=\text{O}$
3.	$\text{H}_2\text{N}_2\text{O}_2$	Hyponitrous acid	$\text{H}-\text{O}-\ddot{\text{N}}=\ddot{\text{N}}-\text{O}-\text{H}$
4.	$\text{HNO}_4$ or $\text{HNO}_2(\text{O}_2)$	Pernitric acid or Peroxy nitric acid	$\text{H}-\ddot{\text{O}}-\ddot{\text{O}}-\ddot{\text{N}}=\text{O}$ 
5.	$\text{HNO}(\text{O}_2)$	Peroxy nitrous acid	$\text{H}-\text{O}-\text{O}-\ddot{\text{N}}=\text{O}$

### 8.1.1 NITROUS ACID ( $\text{HNO}_2$ ) :

#### PREPARATION :

By acidifying an aqueous solution of a nitrite



#### PROPERTIES:

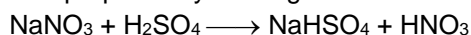
- It is an unstable, weak acid which is known only in aqueous solution.
- On trying to concentrate, the acid decomposes as given below.  
 $3\text{HNO}_2 \longrightarrow \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}$
- Nitrous acid and nitrites are good oxidizing agents and convert iodides to iodine, ferrous salts to ferric, stannous to stannic and sulphites to sulphates eg.  
 $2\text{KI} + 2\text{HNO}_2 + 2\text{HCl} \longrightarrow 2\text{H}_2\text{O} + 2\text{NO} + 2\text{KCl} + \text{I}_2$
- With strong oxidizing agents like  $\text{KMnO}_4$  nitrous acid and nitrites function as reducing agents and get oxidized to  $\text{NO}_3^-$  ions:  $2\text{KMnO}_4 + 5\text{KNO}_2 + 6\text{HCl} \longrightarrow 2\text{MnCl}_2 + 5\text{KNO}_3 + 3\text{H}_2\text{O} + 2\text{KCl}$

### 8.1.2 NITRIC ACID ( $\text{HNO}_3$ ) :

#### PREPARATION :

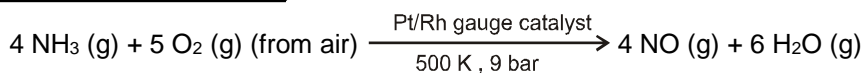
##### (i) In the laboratory :

Nitric acid is prepared by heating  $\text{KNO}_3$  or  $\text{NaNO}_3$  and concentrated  $\text{H}_2\text{SO}_4$  in a glass retort.

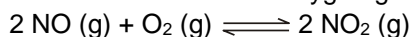


##### (ii) On a large scale it is prepared mainly by Ostwald's process.

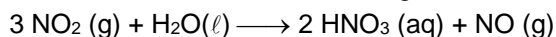
This method is based upon catalytic oxidation of  $\text{NH}_3$  by atmospheric oxygen.



Nitric oxide thus formed combines with oxygen giving  $\text{NO}_2$ .



Nitrogen dioxide so formed, dissolves in water to give  $\text{HNO}_3$ .



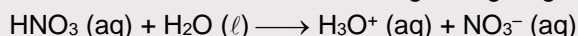
$\text{NO}$  thus formed is recycled and the aqueous  $\text{HNO}_3$  can be concentrated by distillation upto ~ 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated  $\text{H}_2\text{SO}_4$ .

### Physical properties :

It is a colourless liquid. Freezing point is 231.4 K and boiling point is 355.6 K. Laboratory grade nitric acid contains ~ 68% of the  $\text{HNO}_3$  by mass and has a specific gravity of 1.504.

In the gaseous state,  $\text{HNO}_3$  exists as a planar molecule.

In aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.



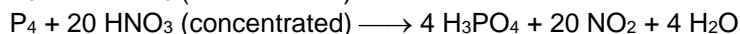
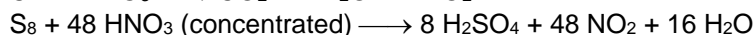
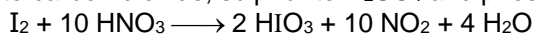
### Chemical properties :

- (i) Concentrated nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum. The products of oxidation depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation. Some metals (e.g. Cr, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

**Table-4 : Reactions of Elements (Metals/Metalloids with  $\text{HNO}_3$ )**

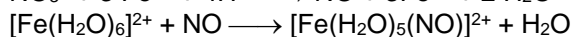
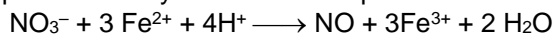
Element	Nature of $\text{HNO}_3$	Changes to	Reactions
<b>(A) Metals placed above H in electrochemical series (ECS)</b>			
1. Mg, Mn	cold and dilute	$\text{M}(\text{NO}_3)_2$	$\text{M} + 2\text{HNO}_3 \rightarrow \text{M}(\text{NO}_3)_2 + \text{H}_2$
2. Zn, Fe	(a) very dilute	$\text{NH}_4\text{NO}_3$	$4\text{Zn} + 10\text{HNO}_3 \rightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$
	(b) dilute	$\text{N}_2\text{O}$	$4\text{Zn} + 10\text{HNO}_3 \rightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{N}_2\text{O} + 5\text{H}_2\text{O}$
	(c) concentrated	$\text{NO}_2$	$\text{Zn} + 4\text{HNO}_3 \rightarrow \text{Zn}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
3. Sn	(a) dilute	$\text{NH}_4\text{NO}_3$	$4\text{Sn} + 10\text{HNO}_3 \rightarrow 4\text{Sn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$
	(b) concentrated	$\text{NO}_2$	$\text{Sn} + 4\text{HNO}_3 \rightarrow \text{H}_2\text{SnO}_3 + 4\text{NO}_2 + \text{H}_2\text{O}$ meta stannic acid
4. Pb	(a) dilute	$\text{NO}$	$3\text{Pb} + 8\text{HNO}_3 \rightarrow 3\text{Pb}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$
	(b) concentrated	$\text{NO}_2$	$\text{Pb} + 4\text{HNO}_3 \rightarrow \text{Pb}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
<b>(B) Metals below H in ECS</b>			
5. Cu, Ag, Hg	(a) dilute	$\text{NO}$	$3\text{Cu} + 8\text{HNO}_3 \rightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$ . Hg forms $\text{Hg}_2(\text{NO}_3)_2$
	(b) concentrated	$\text{NO}_2$	$\text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
<b>(C) Metalloids</b>			
Sb, As	concentrated	$\text{NO}_2$	$\text{Sb} + 5\text{HNO}_3 \rightarrow \text{H}_3\text{SbO}_4 + 5\text{NO}_2 + \text{H}_2\text{O}$ antimonic acid

- (ii) Concentrated nitric acid also oxidises non-metals and their compounds. Iodine is oxidised to iodic acid, carbon to carbon dioxide, sulphur to  $\text{H}_2\text{SO}_4$  and phosphorus to phosphoric acid.



### (iii) Brown Ring Test :

The familiar brown ring test for nitrates depends on the ability of  $\text{Fe}^{2+}$  to reduce nitrates to nitric oxide, which reacts with  $\text{Fe}^{2+}$  to form a brown coloured complex. The test is usually carried out by adding dilute ferrous sulphate solution to an aqueous solution containing nitrate ion, and then carefully adding concentrated sulphuric acid along the sides of the test tube. A brown ring at the interface between the solution and sulphuric acid layers indicate the presence of nitrate ion in solution.



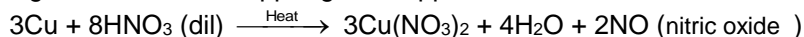
**USES OF HNO<sub>3</sub> :**

- (i) The major use of nitric acid is in the manufacture of ammonium nitrate for fertilizers and other nitrates for use in explosives and pyrotechnics.
- (ii) It is also used for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds.
- (iii) Other major uses are in the pickling of stainless steel, etching of metals and as an oxidiser in rocket fuels.

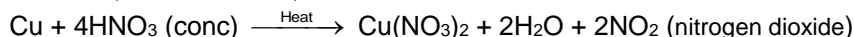
## Solved Examples

**Ex-11.** Illustrate how copper metal can give different products on reaction with HNO<sub>3</sub>.

**Sol.** On heating with dil. HNO<sub>3</sub>, copper gives copper nitrate and nitric oxide.



With conc. HNO<sub>3</sub>, instead of NO, NO<sub>2</sub> is evolved.



## Section (D) : Compounds of Phosphorous (Hydride, Halides, Oxides & Oxyacids)

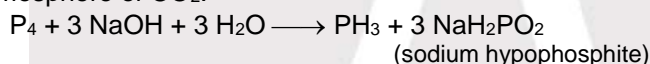
### 9. HYDRIDE

#### 9.1. PHOSPHINE (PH<sub>3</sub>) :

##### 9.1.1 PREPARATION :

- (i) Phosphine is prepared by the reaction of calcium phosphide with water.  

$$\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} \longrightarrow 3\text{Ca}(\text{OH})_2 + 2\text{PH}_3$$
- (ii) In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO<sub>2</sub>.



##### 9.1.2. PROPERTIES :

- (i) It is a colourless gas with a slightly garlic or rotten fish smell.
- (ii) It is highly poisonous.
- (iii) It explodes in contact with traces of oxidising agents like HNO<sub>3</sub>, Cl<sub>2</sub> and Br<sub>2</sub> vapours.
- (iv) It is slightly soluble in water but soluble in CS<sub>2</sub> and other organic solvents.
- (v) The solution of PH<sub>3</sub> in water decomposes in presence of light giving red phosphorus and H<sub>2</sub>.
- (vi) When absorbed in copper sulphate or mercuric chloride, the corresponding phosphides are obtained.  

$$3\text{CuSO}_4 + 2\text{PH}_3 \longrightarrow \text{Cu}_3\text{P}_2 \downarrow + 3\text{H}_2\text{SO}_4$$

$$3\text{HgCl}_2 + 2\text{PH}_3 \longrightarrow \text{Hg}_3\text{P}_2 \downarrow (\text{brownish black}) + 6\text{HCl}$$
- (vii) On reaction with silver nitrate, decomposes to black Ag.  

$$6\text{AgNO}_3 + \text{PH}_3 + 3\text{H}_2\text{O} \longrightarrow 6\text{Ag} + 6\text{HNO}_3 + \text{H}_3\text{PO}_4$$
- (viii) Phosphine is weakly basic and like ammonia. Phosphonium compounds are obtained when anhydrous phosphine reacts with anhydrous halogen acids.  

$$\text{PH}_3 + \text{HBr} \longrightarrow \text{PH}_4\text{Br}$$

##### 9.1.3. USES OF PH<sub>3</sub> :

- (i) The spontaneous combustion of phosphine is technically used in Holme's signals.
- (ii) Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.
- (iii) It is also used in the production of smoke screens. Calcium phosphide reacts with water producing phosphine which burns in air to give clouds of phosphorus pentoxide and that acts as smoke screens.

## Solved Examples

**Ex-12.** What happens ?

- (a) When phosphine is heated at 150°C.
- (b) When phosphine is dissolved in water in presence of light.

**Sol.** (a) Phosphine on heating at 150°C burns forming H<sub>3</sub>PO<sub>4</sub> 
$$\text{PH}_3 + 2\text{O}_2 \longrightarrow \text{H}_3\text{PO}_4$$
  
 (b) The solution of PH<sub>3</sub> in water decomposes in presence of light giving red phosphorus and H<sub>2</sub>.



## 9.2. OXIDES OF PHOSPHORUS :

Table : Oxides of phosphorus

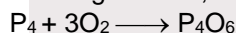
$P_4O_6$		P–O bond length shows that the bridging bonds on the edges are 1.65 Å and are normal single bonds. There is no P–P bonds.
$P_4O_{10}$		The P–O bond lengths shows that the bridging bonds on the edges are 1.60 Å but the P=O bonds on the corners are 1.43 Å and this P=O is formed by $p\pi-d\pi$ back bonding. A full p-orbital on the oxygen atom overlaps sideways with an empty d-orbital on the phosphorus atom. The bond angle POP is $127^\circ$ and there is no P–P bonds. Total L.P. = 20 Total no. of $p\pi-d\pi$ bonds = 4

### 9.2.1. PHOSPHORUS TRIOXIDE ( $P_2O_3$ ) :

It is dimeric and has formula  $P_4O_6$

#### PREPARATION :

It is prepared by burning phosphorus in a limited supply of oxygen when gaseous  $P_4O_{10}$  and  $P_4O_6$  are formed. On lowering the temperature using a condenser,  $P_4O_6$  remains in gaseous form whereas  $P_4O_{10}$  condenses as a solid which is stopped by glass wool. On passing the remaining gaseous mixture through freezing mixture, it converts into colourless crystals of  $P_4O_6$ .



#### PROPERTIES :

- It is colourless crystalline solid having melting point  $23.8^\circ\text{C}$  and boiling point  $178^\circ\text{C}$ .
- It dissolves in cold water to form phosphorus acid. It is thus the anhydride of phosphorus acid.  

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$$
- It dissolves in hot water liberating  $PH_3$   

$$P_4O_6 + 6H_2O \longrightarrow 3H_3PO_4 + PH_3$$
- It slowly gets oxidized in air to form  $P_4O_{10}$   

$$P_4O_6 + 2O_2 \longrightarrow P_4O_{10}$$
- It reacts with chlorine and bromine by forming oxyhalides  

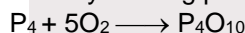
$$P_4O_6 + 5Cl_2 \longrightarrow 2POCl_3 + 2PO_2Cl$$

### 9.2.2 PHOSPHORUS PENTAOXIDE ( $P_4O_{10}$ ) :

It is dimeric and has the formula  $P_4O_{10}$ .

#### PREPARATION :

It is obtained by burning phosphorus in excess air.



#### PROPERTIES:

- It is a white powder, acidic in nature and is the anhydride of orthophosphoric acid.
- It sublimes on heating at  $250^\circ\text{C}$ .
- It dissolves in water with hissing sound forming metaphosphoric acid and finally orthophosphoric acid.  

$$P_4O_{10} + 2H_2O \longrightarrow 4HPO_3; \quad 4HPO_3 + 2H_2O \longrightarrow 2H_4P_2O_7; \quad 2H_4P_2O_7 + 2H_2O \longrightarrow 4H_3PO_4$$
- It dehydrates concentrated  $H_2SO_4$  and concentrated  $HNO_3$  to  $SO_3$  and  $N_2O_5$  respectively.  

$$4HNO_3 + P_4O_{10} \xrightarrow{\text{distillation}} 4HPO_3 + 2N_2O_5; \quad 2H_2SO_4 + P_4O_{10} \xrightarrow{\text{distillation}} 4HPO_3 + 2SO_3$$
- It can not be used to dry the basic substances such as  $CaO$  and  $NH_3$  because they form salts with  $P_4O_{10}$ .  

$$P_4O_{10} + 6CaO \longrightarrow 2Ca_3(PO_4)_2$$

#### USES OF $P_4O_{10}$ :

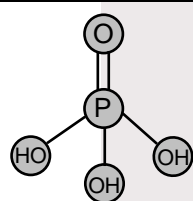
- For drying acidic gases.
- As a dehydrating agent
- For the preparation of  $SO_3$  and  $N_2O_5$ .
- For the preparation of phosphoric acid.



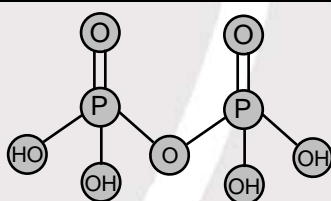


### 9.3. Oxy acids of phosphorous:

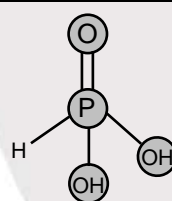
Name	Formula	Oxidation	Characteristic	Preparation
Hypophosphorous (Phosphinic)	$\text{H}_3\text{PO}_2$	+1	One P–OH Two P–H One P=O	White $\text{P}_4$ + alkali
Orthophosphorous (Phosphinic)	$\text{H}_3\text{PO}_3$	+3	Two P–OH One P–H One P=O	$\text{P}_2\text{O}_3 + \text{H}_2\text{O}$
Pyrophosphorous	$\text{H}_4\text{P}_2\text{O}_5$	+3	Two P–OH Two P–H Two P = O	$\text{PCl}_3 + \text{H}_3\text{PO}_3$
Hypophosphoric	$\text{H}_4\text{P}_2\text{O}_6$	+4	Four P–OH Two P = O One P–P	Red $\text{P}_4$ + alkali
Orthophosphoric	$\text{H}_3\text{PO}_4$	+5	Three P–OH One P = O	$\text{P}_4\text{O}_{10} + \text{H}_2\text{O}$
Pyrophosphoric	$\text{H}_4\text{P}_2\text{O}_7$	+5	Four P – OH Two P = O One P–O–P	Heating phosphoric acid
Metaphosphoric	$(\text{HPO}_3)_n$	+5	Three P–OH Three P = O Three P–O–P	Phosphorus acid + $\text{Br}_2$ , heat in a sealed tube



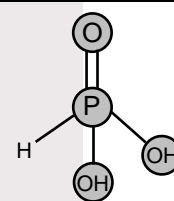
$\text{H}_3\text{PO}_4$   
Orthophosphoric acid



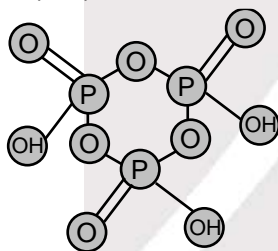
$\text{H}_4\text{P}_2\text{O}_7$   
Pyrophosphoric acid



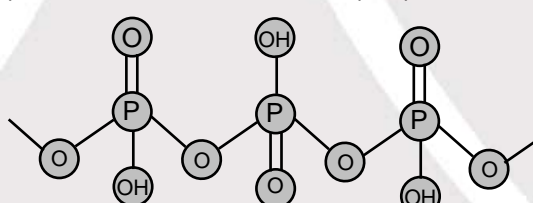
$\text{H}_3\text{PO}_3$   
Orthophosphorous acid



$\text{H}_3\text{PO}_2$   
Hypophosphorous acid

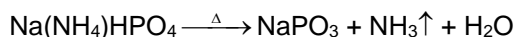
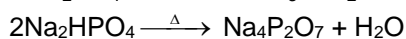
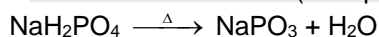
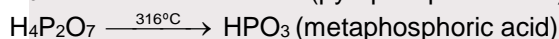
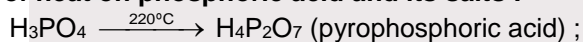


Cyclotrimetaphosphoric acid,  $(\text{HPO}_3)_3$



Polymetaphosphoric acid  $(\text{HPO}_3)_n$

#### Action of heat on phosphoric acid and its salts :



### Solved Examples

**Ex-13.**  $\text{P}_4 + \text{NaOH} \xrightarrow{\text{warm}}$  Products.

Explain the reducing character of one of the products obtained by taking the example of copper sulphate.

**Sol.**  $\text{P}_4 + 3 \text{NaOH} + 3 \text{H}_2\text{O} \longrightarrow \text{PH}_3 + 3 \text{NaH}_2\text{PO}_2$  ;  $4\text{Cu}^{2+} + \text{PH}_3 + 4\text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_4 + 4\text{Cu} \downarrow + 8\text{H}^+$   
(sodium hypophosphite)

Sodium hypophosphite also acts as a strong reducing agent and reduces copper sulphate to  $\text{Cu}_2\text{H}_2$ .



- Ex-14.** (i) Sodium salt of an acid (A) is formed on boiling white phosphorus with NaOH solution.  
(ii) On passing chlorine through phosphorus kept fused under water, another acid (B) is formed.  
(iii) Phosphorus on treatment with concentrated  $\text{HNO}_3$  gives an acid (C) which is also formed by the action of dilute  $\text{H}_2\text{SO}_4$  on powdered phosphorite rock.  
(iv) (A) on treatment with a solution of  $\text{HgCl}_2$  first gives a white precipitate of compound (D) and then a grey precipitate of (E). Identify (A) to (E) and write balanced chemical equations for the reactions at steps (i) to (iv).

**Ans.** (A)  $\text{NaH}_2\text{PO}_2$ ; (B)  $\text{H}_3\text{PO}_3$ ; (C)  $\text{H}_3\text{PO}_4$ ; (D)  $\text{Hg}_2\text{Cl}_2$ ; (E)  $\text{Hg}$

**Sol.** The given changes are :

- (i)  $\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow 3\text{NaH}_2\text{PO}_2$  (sodium hypophosphite) +  $\text{PH}_3$   
Thus acid (A) is  $\text{H}_3\text{PO}_2$ , i.e., hypophosphorus acid.
- (ii)  $2\text{P} + 3\text{Cl}_2 + 6\text{H}_2\text{O} \longrightarrow 2\text{H}_3\text{PO}_3$  (phosphorus acid) +  $6\text{HCl}$   
Thus, acid (B) is  $\text{H}_3\text{PO}_3$
- (iii)  $\text{P}_4 + 20\text{HNO}_3 \longrightarrow 4\text{H}_3\text{PO}_4$  (C) +  $20\text{NO}_2$  +  $4\text{H}_2\text{O}$   
 $\text{P}_4 + 10\text{H}_2\text{SO}_4 \longrightarrow 4\text{H}_3\text{PO}_4$  (C) (phosphoric acid) +  $10\text{SO}_2$  +  $4\text{H}_2\text{O}$   
Thus, acid (C) is  $\text{H}_3\text{PO}_4$
- (iv)  $\text{H}_3\text{PO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_4 + 4\text{H}$   
 $\text{HgCl}_2 + 2\text{H} \longrightarrow \text{Hg}_2\text{Cl}_2$  (D) (white) +  $2\text{HCl}$ ;  $\text{Hg}_2\text{Cl}_2 + 2\text{H} \longrightarrow 2\text{Hg}$  (E) (grey) +  $2\text{HCl}$

## 10. HALIDES AND OXYHALIDES

Phosphorus forms two types of halides,  $\text{PX}_3$  [ $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ] and  $\text{PX}_5$  [ $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ]

### 10.1. Phosphorus Trichloride :

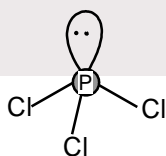
#### 10.1.1 Preparation :

- (i) It is obtained by passing dry chlorine over heated white phosphorus.  
 $\text{P}_4 + 6\text{Cl}_2 \longrightarrow 4\text{PCl}_3$
- (ii) It is also obtained by the action of thionyl chloride with white phosphorus.  
 $\text{P}_4 + 8\text{SOCl}_2 \longrightarrow 4\text{PCl}_3 + 4\text{SO}_2 + 2\text{S}_2\text{Cl}_2$

#### 10.1.2. Properties :

- (i) It is a colourless oily liquid and hydrolyses in the presence of moisture.  
 $\text{PCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_3 + 3\text{HCl}$
- (ii) It reacts with organic compounds containing  $-\text{OH}$  group such as  $\text{CH}_3\text{COOH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ .  
 $3\text{CH}_3\text{COOH} + \text{PCl}_3 \longrightarrow 3\text{CH}_3\text{COCl} + \text{H}_3\text{PO}_3$   
 $3\text{C}_2\text{H}_5\text{OH} + \text{PCl}_3 \longrightarrow 3\text{C}_2\text{H}_5\text{Cl} + \text{H}_3\text{PO}_3$
- (iii) It also act as a reducing agent when treated with  $\text{SO}_3$ , conc.  $\text{H}_2\text{SO}_4$  and Sulphur chloride  
 $\text{PCl}_3 + \text{SO}_3 \longrightarrow \text{POCl}_3 + \text{SO}_2$   
 $\text{PCl}_3 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{SO}_3\text{HCl} + \text{SO}_2 + 2\text{HCl} + \text{HPO}_3$   
 $3\text{PCl}_3 + \text{S}_2\text{Cl}_2 \longrightarrow \text{PCl}_5 + 2\text{PSCl}_3$

Structure :

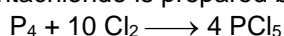


Pyramidal structure of  $\text{PCl}_3$

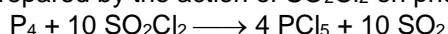
### 10.2. Phosphorus pentachloride :

#### 10.2.1 Preparation :

Phosphorus pentachloride is prepared by the reaction of white phosphorus with excess of dry chlorine.

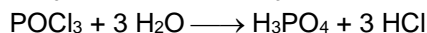
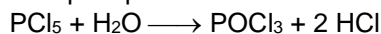


It can also be prepared by the action of  $\text{SO}_2\text{Cl}_2$  on phosphorus.

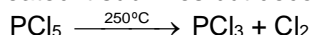


**10.2.2 Properties :**

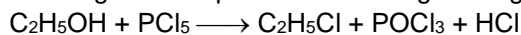
- (i)  $\text{PCl}_5$  is a yellowish white powder and in moist air, it hydrolyses to  $\text{POCl}_3$  and finally gets converted to phosphoric acid.



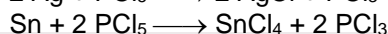
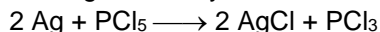
- (ii) When heated it sublimes but decomposes on stronger heating.



- (iii) It reacts with organic compounds containing  $-\text{OH}$  group converting them to chloro derivatives.



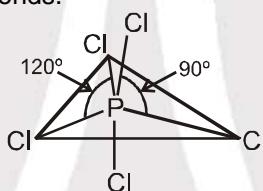
- (iv)  $\text{PCl}_5$  on heating with finely divided metals give corresponding chlorides.



It is used in the synthesis of some organic compounds, e.g.,  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{CH}_3\text{COCl}$ .

**Structure :**

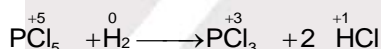
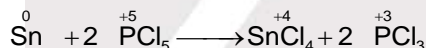
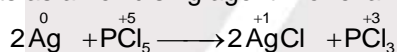
It is covalent in the gaseous state but in solid state exists as ionic solid consisting of  $[\text{PCl}_4]^+$  (tetrahedral) and  $[\text{PCl}_6]^-$  (octahedral). All  $\text{P}-\text{Cl}$  bonds are not of equal lengths. Here axial bonds are longer and weaker than equatorial bonds.



## Solved Examples

**Ex-15.** Can  $\text{PCl}_5$  act as an oxidising as well as a reducing agent? Justify.

**Sol.** The oxidation state of P in  $\text{PCl}_5$  is +5. Since P has five electrons in its valence shell, therefore, it cannot increase its oxidation state beyond +5 by donating electrons, therefore,  $\text{PCl}_5$  cannot act as a reducing agent. However, it can decrease its oxidation number from +5 to +3 or some lower value, therefore,  $\text{PCl}_5$  acts as an oxidising agent. For example, it oxidises Ag to  $\text{AgCl}$ , Sn to  $\text{SnCl}_4$  and  $\text{H}_2$  to  $\text{HCl}$ .



**Ex-16.** What happens when

- (a)  $\text{PCl}_5$  is heated, (b)  $\text{PCl}_5$  is reacted with heavy water, (c)  $\text{H}_3\text{PO}_3$  is heated.

**Ans :** (a)  $\text{PCl}_5 \xrightarrow{\Delta} \text{PCl}_3 + \text{Cl}_2$  ;

(b)  $\text{PCl}_5 + \text{D}_2\text{O} \xrightarrow{\Delta} \text{POCl}_3 + 2 \text{DCl}$  ;

(c)  $4 \text{H}_3\text{PO}_3 \xrightarrow{\Delta} 3 \text{H}_3\text{PO}_4 + \text{PH}_3$

## Section (E) : General facts, Based on trend, Chemical Bonding, Preparation & Properties of group 16 elements

**11. Occurrence :**

Element	Occurrence
Oxygen	Most abundant of all elements. Exists in free form as $\text{O}_2$ and makes up 20.9% by volume and 23% by weight of atmosphere. Most of this has been produced by photosynthesis. $6\text{CO}_2 + 6\text{H}_2\text{O} + \text{energy from sun} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$ Also occurs as many metal oxide ore and
Sulphur	Constitutes 0.034% by weight of earth's crust and occurs mainly in combined form as numerous sulphide ores and as sulphates (particularly gypsum).





## 12. ATOMIC & PHYSICAL PROPERTIES

Element		O	S	Se	Te
Atomic Number		8	16	34	52
Atomic Mass		16	32.06	78.96	127.6
Electronic configuration		[He] 2s <sup>2</sup> 2p <sup>4</sup>	[Ne] 3s <sup>2</sup> 3p <sup>4</sup>	[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>4</sup>	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>4</sup>
Covalent Radius / pm		74	103	119	142
Ionic Radius X <sup>-2</sup> / pm		140	184	198	221
Ionization enthalpy / (kJ mol <sup>-1</sup> )	I	1314	1000	941	869
	II	3388	2251	2045	1790
Electronegativity		3.5	2.44	2.48	2.01
Density/[g cm <sup>-3</sup> (293 K)]		1.32	2.06	4.19	6.25
Melting point / K		54	393	490	725
Boiling point / K		90	718	958	1260

Oxygen, sulphur, selenium, tellurium and polonium constitute group 16 of the periodic table. This is sometimes known as group of chalcogens the ore forming elements because a large number of metals ores are oxides or sulphides.

Oxygen } Non metals      Selenium }  
 Sulphur }                      Tellurium } Metalloids      Polonium {Radio activeMetal}

- (i) **Electronic Configuration** : The elements of group 16 have six electrons in the outermost shell and have ns<sup>2</sup> np<sup>4</sup> general valence shell electronic configuration.
- (ii) **Atomic and Ionic Radii** : Due to increase in the number of shells, atomic and ionic radii increase from top to bottom in the group. The size of oxygen atoms is however, exceptionally small.
- (iii) **Ionisation Enthalpy** : Ionisation enthalpy decreases down the group. It is due to increase in size. However, the element of this group have lower ionisation enthalpy values compared to those of group 15 in the corresponding periods. This is due to the fact that group 15 elements have extra stable half-filled p orbitals electronic configurations.
- (iv) **Electron Gain Enthalpy** : Because of the compact nature of oxygen atom, it has less negative electron gain enthalpy than sulphur. However from sulphur onwards the value again becomes less negative upto polonium.
- (v) **Electronegativity** : Next to fluorine, oxygen has the highest electronegativity value amongst the elements. Within the group, electronegativity decrease with an increase in atomic number. This indicates that the metallic character increases from oxygen to polonium.
- (vi) **Physical Properties** :
  - Oxygen and sulphur are non-metal, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life 13.8 days).
  - The melting and boiling points increase with an increase in atomic number down the group.
  - The larger difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity; oxygen exist as diatomic molecules (O<sub>2</sub>) whereas sulphur exists as polyatomic molecule (S<sub>8</sub>).
- (vii) **Catenation** : Tendency for catenation decreases down the group. This property is prominently displayed by sulphur (S<sub>8</sub>). The S—S bond is important in biological system and is found in some proteins and enzymes such as cysteine.
- Selenium has unique property of photo conductivity and is used in photocopying machines and also a decolouriser of glass.

## 13. Allotropes

**13.1 Oxygen** : Exists in 2 allotropic forms :

- (a) O<sub>2</sub>                      (b) O<sub>3</sub> (unstable and decomposes to O<sub>2</sub>)

**13.2 Sulphur** : It has more allotropic forms than any other element. This difference arise partly from the extent to which sulphur has polymerized and partly from the crystal structure adopted. Two common forms are α or rhombic sulphur and β or monoclinic sulphur which is stable above 95.5°C (transition temperature). These two forms change reversibly with slow heating or slow cooling. A third form known





as  $\gamma$ -monoclinic sulphur is also present. All three forms contains puckered  $S_8$  rings with a crown conformation.

(a) **Rhombic sulphur ( $\alpha$ -sulphur) :**

(i) This allotrope is yellow in colour, melting point 385.8 K and specific gravity 2.06.

(ii) Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in  $CS_2$ . It is insoluble in water but dissolved to some extent in benzene, alcohol and ether. It is readily soluble in  $CS_2$ .

(b) **Monoclinic sulphur ( $\beta$ -sulphur) :**

(i) Its melting point is 393 K and specific gravity 1.98. It is soluble in  $CS_2$ .

(ii) This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling till crust is formed.

(iii) Two holes are made in the crust and the remaining liquid poured out. On removing the crust, colourless needle shaped crystals of  $\beta$  - sulphur are formed.

(iv) Both rhombic and monoclinic sulphur have  $S_8$  molecules these  $S_8$  molecules are packed to give different crystal structures. The  $S_8$  ring in both the forms is puckered and has a crown shape. The molecular dimensions are given in figure.

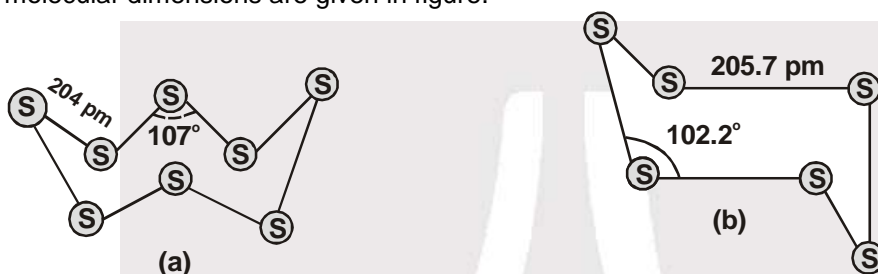


Fig. : The structures of (a)  $S_8$  ring in rhombic sulphur and (b)  $S_6$  form

(v) Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesised in the last two decades. In cyclo-  $S_6$ , the ring adopts the chair form and the molecular dimension are as shown in fig. (b).

(c) **Plastic Sulphur :**

(i) It is formed when molten sulphur is poured into cold water. It consists of chain like molecule and has rubber like properties when formed.

(ii) On standing it becomes brittle and finally converts to rhombic sulphur.

**Heating effect on sulphur :**

$S_8$  (melt)  $\xrightleftharpoons[160^\circ C]{160^\circ C}$  some  $S_8$  rings break. Diradical so formed polymerises to forms long chain polymer.

Viscosity starts to increase  $\xrightarrow{\text{At } 200^\circ C}$  Viscosity further increases  $\xrightarrow[\text{boiling point}]{\text{At } 444^\circ C}$  viscosity decreases,

shorter chains and rings are formed  $\xrightarrow{\text{At } 600^\circ C}$  in vapour state exist as  $S_2$  molecules (paramagnetic like  $O_2$ ).

## Solved Examples

**Ex-17.** Write the allotropic forms of oxygen

**Ans.** Ordinary oxygen and ozone.

**Ex-18.** Which allotropic form of sulphur is stable at room temperature?

**Ans.** Rhombic sulphur

**Ex-19.** Out of following forms of sulphur which one is paramagnetic in nature and why?  $S_8$ ,  $S_6$  and  $S_2$

**Ans.** Sulphur exist as  $S_2$  in vapour state which has two unpaired electrons in the anti-bonding  $\pi^*$  orbitals like  $O_2$ .

**Ex-20.** Describe the changes which occur on heating sulphur.

**Ans.**  $S_8$  (melt)  $\xrightleftharpoons[160^\circ C]{160^\circ C}$   $S_8$  ring break and diradical so formed polymerises to forms long chain polymer and viscosity starts to increase  $\xrightarrow{\text{at } 200^\circ C}$  Viscosity further  $\uparrow$   $\xrightarrow[\text{boiling point}]{\text{at } 444^\circ C}$  viscosity  $\downarrow$  shorter chains and rings are formed  $\xrightarrow{\text{at } 600^\circ C}$  in vapour state exist as  $S_2$  molecules (paramagnetic like  $O_2$ ).



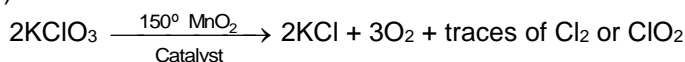


## 14. Preparation & Properties of elements

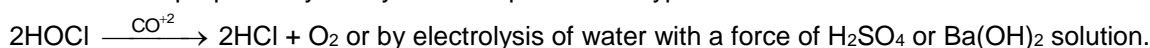
### 14.1 Preparation of Elements :

#### 14.1.1 Oxygen :

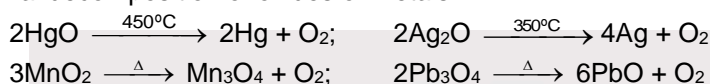
- (a) Dioxygen is produced industrially by fractional distillation of liquid air.  
 (b) It is prepared on a small scale in a laboratory by thermal decomposition of  $\text{KClO}_3$  (with  $\text{MnO}_2$  as catalyst)



- (c) It can also be prepared by catalytic decomposition of hypochlorites.



- (d) By thermal decomposition of oxides of metals.

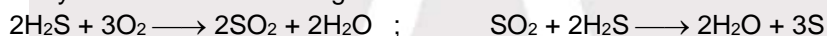


- (e) Thermal decomposition of  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{KMnO}_4$



#### 14.1.2 Sulphur :

- (a) Large amounts of sulphur are obtained from natural gas plants, oil refineries. It is obtained from gas and petroleum. After cracking long chain hydrocarbon,  $\text{H}_2\text{S}$  and other sulphur derivatives are removed because of their objectionable smell. About a third of  $\text{H}_2\text{S}$  is oxidized in air to give  $\text{SO}_2$  which is subsequently reacted with remaining  $\text{H}_2\text{S}$ .



- (b) Deposits of sulphur were formed by anaerobic bacteria which metabolize  $\text{CaSO}_4$  to form  $\text{H}_2\text{S}$  and S. This was mined by Frash process, now obsolete.

### 14.2 Physical Properties of Oxygen & Sulphur

Element	Physical Properties
Oxygen	<ul style="list-style-type: none"> <li>Pale blue in colour and the colour arises from electronic transitions which excites the ground state. This transition is 'forbidden' in gaseous dioxygen.</li> <li>Three isotopes are <math>^{16}_8\text{O}</math>, <math>^{17}_8\text{O}</math> and <math>^{18}_8\text{O}</math>.</li> <li>Does not burn but is a strong supporter of combustion.</li> </ul>
Sulphur	<ul style="list-style-type: none"> <li>Melts to form a mobile liquid.</li> <li>Dissolves in oleum giving brightly coloured solutions which may be yellow, deep blue or bright red.</li> </ul>

### Section (F) : General trends & Chemical Properties of group 16 elements

#### 15. Oxidation states and trends in chemical reactivity:

- The elements of group 16 exhibit a number of oxidation states. The stability of  $-2$  oxidation state decreases down the group. Polonium hardly shows  $-2$  oxidation states.
- Electronegativity of oxygen is very high, therefore it shows only negative oxidation states as  $-2$  except in the case of  $\text{OF}_2$  where its oxidation states is  $+2$ .
- Other elements of the group exhibit  $+2$ ,  $+4$ ,  $+6$  oxidation states but  $+4$  and  $+6$  are more common. Sulphur, selenium and tellurium usually show  $+4$  oxidation in their compounds with oxygen and  $+6$  oxidation state with fluorine.
- The stability of  $+6$  oxidation state decreases down the group and stability of  $+4$  oxidation state increases (inert pair effect). Bonding in  $+4$  and  $+6$  oxidation states are primarily covalent.

- $\text{HNO}_3$  oxidises sulphur to  $\text{H}_2\text{SO}_4$  (S + VI) but only oxidises selenium to  $\text{H}_2\text{SeO}_3$  (Se + IV) as the atoms are smaller and there is poor shielding of 3d electrons as a result the electrons are held more tightly with nucleus.

(ii) **Reactivity with hydrogen** : All the elements of group 16 form hydrides of the type  $\text{H}_2\text{E}$  (E = S, Se, Te, Po). Some properties of hydrides are given in Table.





**Table : Properties of Hydrides of Group 16 Elements**

Property	H <sub>2</sub> O	H <sub>2</sub> S	H <sub>2</sub> Se	H <sub>2</sub> Te
m.p./K	273	188	208	222
b.p./K	373	213	232	269
H-E distance/pm	96	134	146	169
HEH angle (°)	104	92	91	90
$\Delta_f H / \text{kJ mol}^{-1}$	-286	-20	73	100
$\Delta_{\text{diss}} H (\text{H-E}) / \text{kJ mol}^{-1}$	463	347	276	238
Dissociation constant <sup>a</sup>	$1.8 \times 10^{-16}$	$1.3 \times 10^{-7}$	$1.3 \times 10^{-4}$	$2.3 \times 10^{-3}$

The order of volatility is : **H<sub>2</sub>S > H<sub>2</sub>Se > H<sub>2</sub>Te > H<sub>2</sub>O**

The order of stability : **H<sub>2</sub>O > H<sub>2</sub>S > H<sub>2</sub>Se > H<sub>2</sub>Te**

The order of boiling points : **H<sub>2</sub>O > H<sub>2</sub>Te > H<sub>2</sub>Se > H<sub>2</sub>S**

The order of  $K_a$  values : **H<sub>2</sub>Te > H<sub>2</sub>Se > H<sub>2</sub>S > H<sub>2</sub>O**

**(iii) Reactivity towards oxygen :**

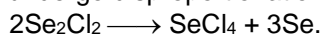
- All these elements form oxides of the EO<sub>2</sub> and EO<sub>3</sub> types where E = S, Se, Te or Po.
- Ozone (O<sub>3</sub>) and sulphur dioxide (SO<sub>2</sub>) are gases while selenium dioxide (SeO<sub>2</sub>) is solid.
- Reducing property of dioxide decreases from SO<sub>2</sub> to TeO<sub>2</sub>; while oxidation property increases from SO<sub>2</sub> to TeO<sub>2</sub>.
- Both dioxides and trioxides are acidic in nature.
- Trioxides act only as oxidising agents. Oxidation power of trioxides should increase from SO<sub>3</sub> to SeO<sub>3</sub> but SO<sub>3</sub> act as strong oxidising agent in acid medium due to protonation S-O bond becomes weak.

**Table : Oxides of Group 16 Elements**

Element	Dioxide	Trioxide	Other oxide
Sulphur	SO <sub>2</sub>	SO <sub>3</sub>	S <sub>2</sub> O, S <sub>6</sub> O, S <sub>8</sub> O
Selenium	SeO <sub>2</sub>	SeO <sub>3</sub>	—
Tellurium	TeO <sub>2</sub>	TeO <sub>3</sub>	TeO
Polonium	PoO <sub>2</sub>	—	PoO

**(iv) Reactivity toward the Halogens :**

- Elements of group 16 form a larger number of halides of the type EX<sub>6</sub>, EX<sub>4</sub> and EX<sub>2</sub> where E is an element of the group –16 and X is an halogen.
- The order of stability of halides of sulphur with different halogens is : F<sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup>
- Amongst hexahalides, hexafluorides are the only stable halides.
- All hexafluorides are gaseous in nature. They have octahedral structure. Sulphur hexafluoride SF<sub>6</sub> is exceptionally stable for steric reasons.
- Amongst tetrafluorides, SF<sub>4</sub> is a gas, SeF<sub>4</sub> liquid and TeF<sub>4</sub> a solid.
- The tetrafluorides have sp<sup>3</sup>d hybridisation and thus, have trigonal bipyramidal structure in which one of the equatorial position is occupied by a lone pair of electrons. This geometry is also regarded as see - saw geometry.
- All elements except selenium form dichlorides and dibromides. These dihalides are formed by sp<sup>3</sup> hybridisation and thus have tetrahedral structure.
- The well known monohalides are dimeric in nature, Examples are S<sub>2</sub>F<sub>2</sub>, S<sub>2</sub>Cl<sub>2</sub>, S<sub>2</sub>Br<sub>2</sub>, Se<sub>2</sub>Cl<sub>2</sub> and Se<sub>2</sub>Br<sub>2</sub>. These are having open book structure.
- These dimeric halides undergo disproportionation as given below :

**Table : Halides of Group 16 Elements**

Element	M <sub>2</sub> X <sub>2</sub> type	Mx <sub>2</sub> type	Mx <sub>4</sub> type	Mx <sub>6</sub> type	Other types of halides
Sulphur	S <sub>2</sub> F <sub>2</sub> S <sub>2</sub> Cl <sub>2</sub> S <sub>2</sub> Br <sub>2</sub>	SF <sub>2</sub> SCl <sub>2</sub>	SF <sub>4</sub> SCl <sub>4</sub>	SF <sub>6</sub>	S <sub>2</sub> F <sub>4</sub> S <sub>2</sub> F <sub>10</sub>
Selenium	Se <sub>2</sub> Cl <sub>2</sub> Se <sub>2</sub> Br <sub>2</sub>	—	SeF <sub>4</sub> SeCl <sub>4</sub> SeBr <sub>4</sub>	SeF <sub>6</sub>	Se <sub>2</sub> F <sub>4</sub>



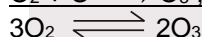
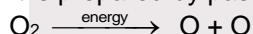
Tellurium	–	TeCl <sub>2</sub> TeBr <sub>2</sub> Tel <sub>2</sub>	TeF <sub>4</sub> TeCl <sub>4</sub> TeBr <sub>4</sub> Tel <sub>4</sub>	TeF <sub>6</sub>	–
Polonium	–	PoCl <sub>2</sub> PoBr <sub>2</sub>	PoCl <sub>4</sub> PoBr <sub>4</sub> Pol <sub>4</sub>	–	–

**(v) Anomalous behaviour of oxygen :**

- The anomalous behaviour of oxygen, like other member of p-block present in second period is due to its:
  - (a) Small size and
  - (b) high electronegativity.
- Because of this strong hydrogen bonding is present in H<sub>2</sub>O which is not found in H<sub>2</sub>S.
- The absence of d orbitals in oxygen restricts its covalency to four and in practice, rarely increases beyond two.
- In case of other elements of the same group, the valence shell can be expanded and covalence exceeds four.

**Section (G) : Ozone and Hydrogen peroxide****16. OZONE (O<sub>3</sub>)****16.1.1. PREPARATION :**

It is prepared by passing silent electric discharge through pure and dry oxygen.



Mixture obtained contains 5-10% ozone by volume and this mixture is called ozonised oxygen.

- Higher concentration or pure O<sub>3</sub> can be obtained by fractional liquefaction of the mixture.
- Low concentration of O<sub>3</sub> can be made by UV irradiation of O<sub>2</sub>.
- $\text{O}_2 \xrightarrow[\text{(ii) quenching}]{\text{(i) 2500}^\circ\text{C}} \text{O}_3$

**16.1.2. PROPERTIES :****(a) PHYSICAL PROPERTIES :**

- Dark blue gas which forms a blue liquid on cooling and on solidification forms violet black crystals. The colour is due to intense absorption of red light.
- It also absorbs strongly in the UV region. Thus it protects the people on the earth from the harmful UV radiation from the sun.
- It has sharp smell often associated with sparking electrical equipment. It is toxic and is slightly soluble in water but more in turpentine oil, glacial acetic acid or CCl<sub>4</sub>. O<sub>3</sub> molecule is diamagnetic but O<sub>3</sub><sup>–</sup> is paramagnetic.

**(b) CHEMICAL PROPERTIES:**

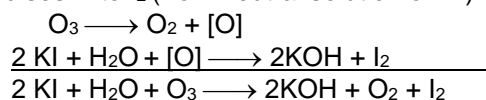
- Oxidising agent :**

$$\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{O}_2 + \text{H}_2\text{O} ; \text{SRP} = + 2.07 \text{ V (in acidic medium)}$$

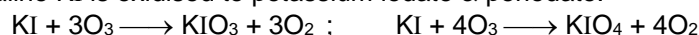
$$\text{O}_3 + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{O}_2 + 2\text{OH}^- ; \text{SRP} = + 1.24 \text{ V (in alkaline medium)}$$

Therefore, ozone is a strong oxidising agent in acidic medium.

- It oxidises I<sup>–</sup> to I<sub>2</sub> (from neutral solution of KI)



- Alkaline KI is oxidised to potassium iodate & periodate.



**Note:** Similarly S<sup>2–</sup> to SO<sub>4</sub><sup>2–</sup> (but not H<sub>2</sub>S), NO<sub>2</sub><sup>–</sup> to NO<sub>3</sub><sup>–</sup>, SO<sub>3</sub><sup>2–</sup> to SO<sub>4</sub><sup>2–</sup>, AsO<sub>3</sub><sup>3–</sup> to AsO<sub>4</sub><sup>3–</sup>, Sn<sup>2+</sup> to Sn<sup>4+</sup> (acidic medium).

- $$\text{O}_3 \longrightarrow \text{O}_2 + [\text{O}]$$

$$2\text{K}_2\text{MnO}_4 + [\text{O}] + \text{H}_2\text{O} \longrightarrow 2\text{KMnO}_4 + 2\text{KOH}$$

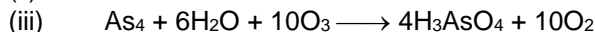
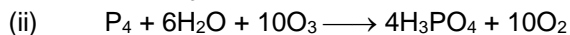
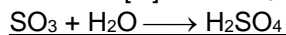
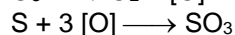
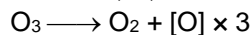
$$2\text{K}_2\text{MnO}_4 + \text{O}_3 + \text{H}_2\text{O} \longrightarrow 2\text{KMnO}_4 + 2\text{KOH} + \text{O}_2$$

- Similarly [Fe(CN)<sub>6</sub>]<sup>4–</sup> oxidises to [Fe(CN)<sub>6</sub>]<sup>3–</sup> (basic medium).

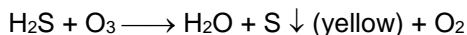
- $2\text{NO}_2 + \text{O}_3 \longrightarrow \text{N}_2\text{O}_5 + \text{O}_2$



- (b) (i) It oxidises moist S, P, As into their oxy acids.



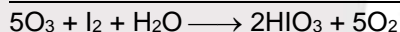
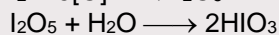
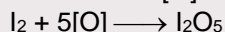
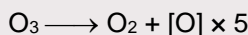
- (c) It oxidises  $H_2S$  to S.



- (d) **Reaction with dry  $I_2$**  :  $2 I_2 + 9[O_3] \longrightarrow I_4O_9 + 9O_2$

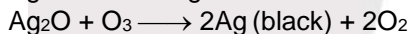
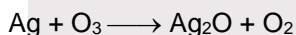
- $I_4O_9$  yellow solid has the composition  $I^{+3} (IO_3^-)_3$ . Formation of this compound is a direct evidence in favour of basic nature of  $I_2$  (i.e. its tendency to form cations).

- (e) **Reaction with moist iodine :**

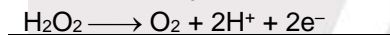
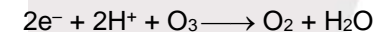


- (f) **Reaction with Silver :**

Silver articles become black in contact with ozone.



- (g) **Reaction with  $H_2O_2$  :**

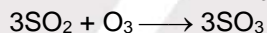


Oxidising agent      Reducing agent

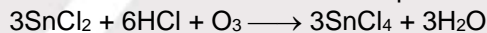
It is supported by the fact that SRP of ozone is higher (+2.07) than SRP of hydrogen peroxide (+1.77). Therefore, ozone is stronger oxidising agent than hydrogen peroxide.

- (h) **Reactions with  $SO_2$  &  $SnCl_2$**

- (i)  $SO_2$  is oxidised to  $SO_3$

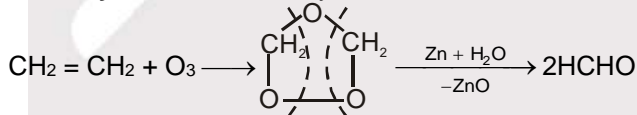


- (ii)  $SnCl_2$  is oxidised to  $SnCl_4$  in the presence of HCl.



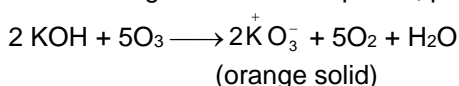
- (i) **Bleaching Action** :  $O_3$  also bleaches coloured substances through oxidation.

- (j) **Ozonolysis** : Alkenes, alkynes react with ozone forming ozonides.



- (k) **Reaction with KOH :**

Forms orange coloured compound, potassium ozonide.



### 16.1.3. TESTS FOR OZONE

- (i) A filter paper soaked in an alcoholic benzidine  $[H_2N-C_6H_4-C_6H_4-NH_2]$  becomes brown when brought in contact with  $O_3$  (this is not shown by  $H_2O_2$ ).
- (ii) **Tailing of mercury**  
Pure mercury is a mobile liquid but when brought in contact with  $O_3$  its mobility decreases and it starts sticking to glass surface forming a type of tail due to the dissolution of  $Hg_2O$  (mercury sub-oxide) in Hg.
- $$2 Hg + O_3 \longrightarrow Hg_2O + O_2$$



**USES OF OZONE :**

1. As a germicide and disinfectant for sterilising water and improving the atmosphere of crowded places.
2. For detecting the position of double bond in the unsaturated organic compounds.
3. In mfg. of artificial silk, synthetic camphor,  $\text{KMnO}_4$  etc.
4. It is also used for bleaching oil, ivory, flour starch etc.

## Solved Examples

**Ex-21.**  $\text{O}_3$  is a powerful oxidising agent. Write equation to represent oxidation of

- (a)  $\text{I}^-$  to  $\text{I}_2$  in acidic solutions,  
 (b) sulphur to sulphuric acid in the presence of moisture,

**Sol.** (a)  $\text{O}_3 + 2\text{I}^- + 2\text{H}^+ \longrightarrow \text{O}_2 + \text{I}_2 + \text{H}_2\text{O}$  ; (b)  $3\text{O}_3 + \text{S} + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + 3\text{O}_2$  .

**Ex-22.** Give the important applications of  $\text{O}_3$ .

**Sol.** (A) As a germicide and disinfectant for sterilising water and improving the atmosphere of crowded places.  
 (B) For detecting the position of double bond in the unsaturated organic compounds.  
 (C) In mfg. of artificial silk, synthetic camphor,  $\text{KMnO}_4$  etc. It is also used for bleaching oil, ivory, flour starch etc.

**Ex-23.** Ozone layer is being depleted. This is due to :

- (A) NO emission from supersonic jets (B) chlorofluorocarbon used as aerosols  
 (C\*) both (A) and (B) (D) none of the above

**Sol.** (A)  $\text{O}_3 + \text{NO} \longrightarrow \text{NO}_2 + \text{O}_2$



**Ex-24.**  $\text{O}_3$  is a powerful oxidising agent. Write equation to represent oxidation of

- (a)  $\text{I}^-$  to  $\text{I}_2$  in acidic solutions,  
 (b) sulphur to sulphuric acid in the presence of moisture,

**Ans.** (a)  $\text{O}_3 + 2\text{I}^- + 2\text{H}^+ \longrightarrow \text{O}_2 + \text{I}_2 + \text{H}_2\text{O}$  (b)  $3\text{O}_3 + \text{S} + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + 3\text{O}_2$ .

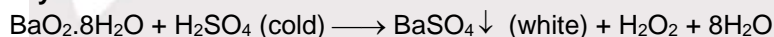
**Ex-25.** Give the important applications of  $\text{O}_3$ .

**Sol.** (A) As a germicide and disinfectant for sterilising water and improving the atmosphere of crowded places.  
 (B) For detecting the position of double bond in the unsaturated organic compounds.  
 (C) In mfg. of artificial silk, synthetic camphor,  $\text{KMnO}_4$  etc. It is also used for bleaching oil, ivory, flour starch etc.

## 16.2. HYDROGEN PEROXIDE ( $\text{H}_2\text{O}_2$ ) :

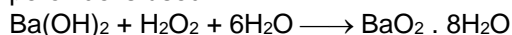
### 16.2.1 PREPARATION :

#### (i) Laboratory Method :

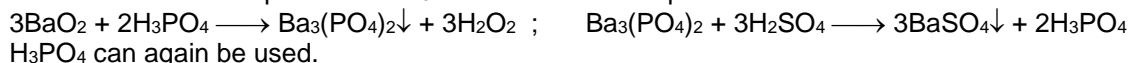


$\text{BaSO}_4$  is filtered to get aqueous hydrogen peroxide.

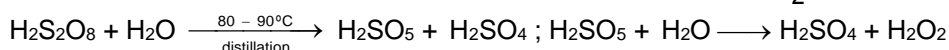
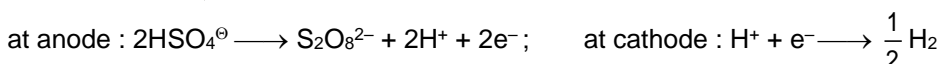
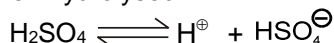
- The reaction between anhydrous  $\text{BaO}_2$  and  $\text{H}_2\text{SO}_4$  is slow and practically ceases after sometimes due to the formation of a protective layer of  $\text{BaSO}_4$  on  $\text{BaO}_2$ . So hydrated barium peroxide is used.

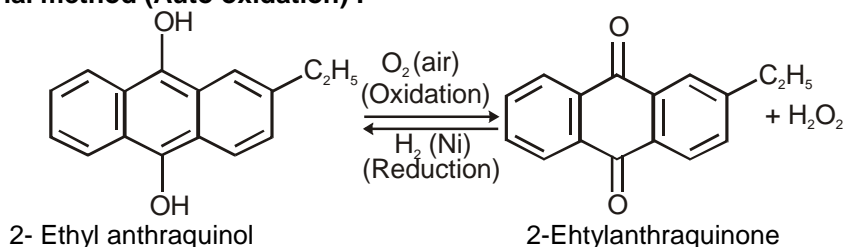


- Since  $\text{H}_2\text{SO}_4$  can decompose  $\text{H}_2\text{O}_2$  at a higher temperature, therefore, the reaction should be carried out at low temperature or  $\text{H}_3\text{PO}_4$  can be used in place of  $\text{H}_2\text{SO}_4$



- (ii) By electrolysis of concentrated  $\text{H}_2\text{SO}_4$  or  $(\text{NH}_4)_2\text{SO}_4$  at a high current density to form peroxosulphates, which then hydrolysed.

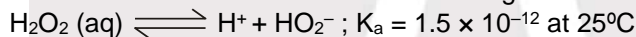


(iii) **Industrial method (Auto oxidation) :****16.2.2 PROPERTIES :****(a) PHYSICAL PROPERTIES :**

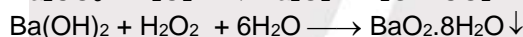
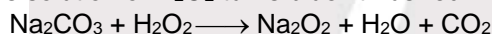
- (i) Colourless viscous liquid which appears blue in the larger quantity and is soluble in water (due to H-bonding) in all proportions and form a hydrate H<sub>2</sub>O<sub>2</sub>·H<sub>2</sub>O (melting point 221 K).
- (ii) Its boiling point 423 K is more than water but freezing point (−4°C) is less than water. Density and dielectric constant are also higher than H<sub>2</sub>O
- (iii) Its aqueous solution is more stable than the anhydrous liquid where it decomposes into water and O<sub>2</sub> slowly on exposure to light.  $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$

**Note :** H<sub>2</sub>O<sub>2</sub> is not kept in glass containers because traces of alkali metal ions from the glass can catalyse the explosive decomposition of H<sub>2</sub>O<sub>2</sub>. Therefore, aqueous solution is stored in plastic or wax-lined glass containers and some urea or phosphoric acid or glycerol is added to that solution because these compounds have been found to behave as negative catalyst for the decomposition of H<sub>2</sub>O<sub>2</sub>.

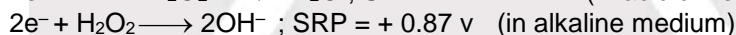
- (iv) **Acidic nature :** Behaves as a weak acid according to the following equation



Aqueous solution of H<sub>2</sub>O<sub>2</sub> turns blue litmus red which is then bleached by the oxidising property of H<sub>2</sub>O<sub>2</sub>



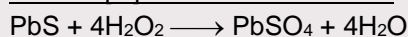
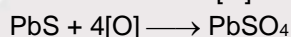
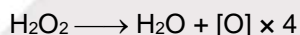
- A 30% H<sub>2</sub>O<sub>2</sub> solution has pH = 4.0

**(b) CHEMICAL PROPERTIES :****(i) Oxidising Agent :**

- On the basis of the above potentials, we can say that H<sub>2</sub>O<sub>2</sub> is strong oxidising agent in acidic medium but kinetically it is found that reactions are faster in basic medium.

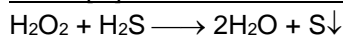
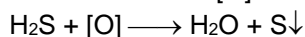
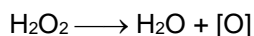
**(A) In acidic medium :**

- (a) It oxidises PbS to PbSO<sub>4</sub>.

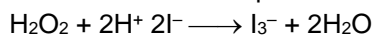


This property is utilised in restoring the white colour in old paintings which turns black due to the formation of PbS by the action of atmospheric H<sub>2</sub>S.

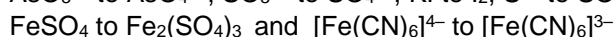
- (b) H<sub>2</sub>O<sub>2</sub> oxidises H<sub>2</sub>S to sulphur.

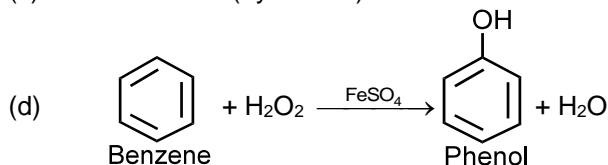


- Potassium iodide and starch produces deeper blue colour with acidified H<sub>2</sub>O<sub>2</sub>.

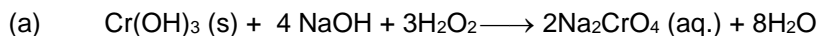


- H<sub>2</sub>O<sub>2</sub> in acidic medium also oxidises

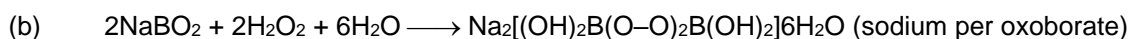
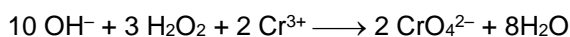




**(B) In alkaline medium :**

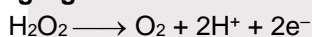


or

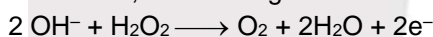


○ Used as a brightener in washing powder.

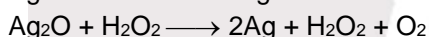
**(ii) Reducing Agent :** It acts as a reducing agent towards powerful oxidising agent.



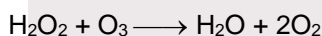
○ In alkaline solution, its reducing character is more than in acidic medium.



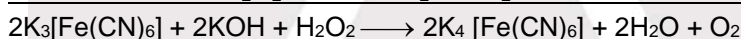
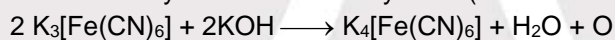
(a)  $\text{Ag}_2\text{O}$  is reduced to  $\text{Ag}$ .



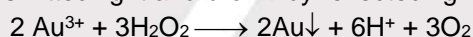
(b) It reduces  $\text{O}_3$  to  $\text{O}_2$ .



(c) It reduces ferric cyanide to ferrous cyanide (basic medium).



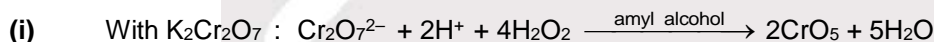
(d) It reduces gold chloride solution to finely divided metallic gold which appears greenish-blue by transmitted light and brown by reflected light.



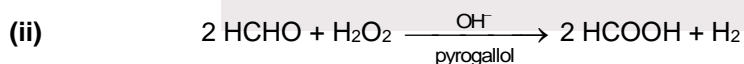
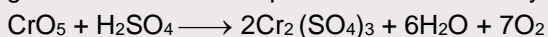
○ It also reduces  $\text{MnO}_4^-$  to  $\text{Mn}^{2+}$  (acidic medium),  $\text{MnO}_4^-$  to  $\text{MnO}_2$  (basic medium),

$\text{OCl}^-$  to  $\text{Cl}^-$ ,  $\text{IO}_4^-$  to  $\text{IO}_3^-$  and  $\text{Cl}_2$  to  $\text{Cl}^-$

**16.2.3 TESTS FOR  $\text{H}_2\text{O}_2$  :**

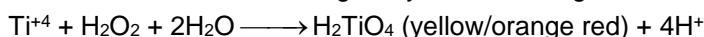


○  $\text{CrO}_5$  bright blue coloured compound soluble in diethyl ether, amyl alcohol and amyl acetate.



When this reaction is carried out in dark, it is accompanied by emission of light (yellow coloured). It is an example of chemiluminescence.

(iii) An acidified solution of titanium salt gives yellow or orange colour with  $\text{H}_2\text{O}_2$ .



○ Orange red coloured in slightly acid solution and yellow colour with very dilute solution.

**16.2.4 USES OF  $\text{H}_2\text{O}_2$  :**

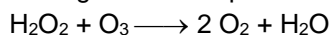
1. In bleaching of delicate materials such as silk, wool, cotton, ivory etc.
2. As a valuable antiseptic and germicide for washing wounds, teeth and ears under the name perhydrol.
3. As 'antichlor' to remove traces of chlorine and hypochlorite.
4. As oxidising agent in rocket fuels.



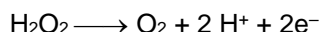
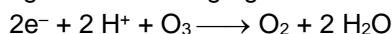


## Solved Examples

**Ex.26** In the following reaction explain which one is oxidising agent and which one is reducing agent ?



**Sol.** Ozone is behaving as an oxidising agent and  $\text{H}_2\text{O}_2$  is behaving as reducing agent.



The above interpretations is further supported on the following grounds.

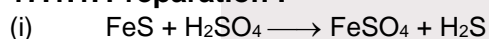
SRP of  $\text{H}_2\text{O}_2$  is + 1.77 V while SRP of  $\text{O}_3$  is + 2.07 V. Therefore,  $\text{O}_3$  is stronger oxidising agent than  $\text{H}_2\text{O}_2$ .

## Section (H) : Compounds of Sulphur (Hydrides, Oxides, Oxyacids and $\text{Na}_2\text{S}_2\text{O}_3$ )

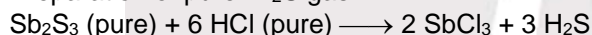
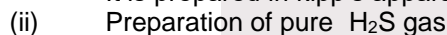
### 17. HYDRIDE

#### 17.1 HYDROGEN SULPHIDE ( $\text{H}_2\text{S}$ ) :

##### 17.1.1. Preparation :



It is prepared in kipp's apparatus



##### 17.1.2 Physical Properties :

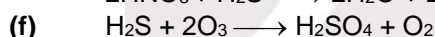
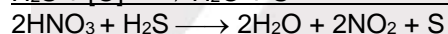
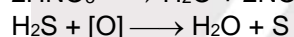
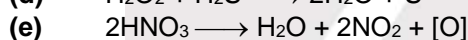
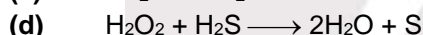
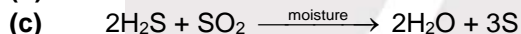
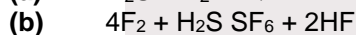
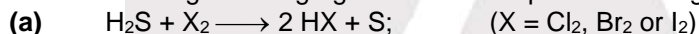
(i) Colourless gas with rotten egg smell .

(ii) Moderately soluble in water but solubility decreases with increasing temperature.

##### 17.1.3. Chemical Properties :

##### (i) Reducing Agent :

Acts as a strong reducing agent as it decomposes evolving hydrogen.

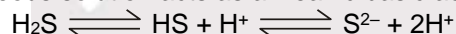


(g) It also reduces  $\text{MnO}_4^-$  to  $\text{Mn}^{2+}$ ,  $\text{H}_2\text{SO}_4$  to  $\text{SO}_2$  &  $\text{K}_2\text{Cr}_2\text{O}_7$  to  $\text{Cr}^{3+}$  (acidic medium)

(h)  $\text{MnO}_4^-$  to  $\text{MnO}_2$  (alkaline medium)

##### (ii) Acidic Nature :

Its aqueous solution acts as a weak dibasic acid according to following reaction.

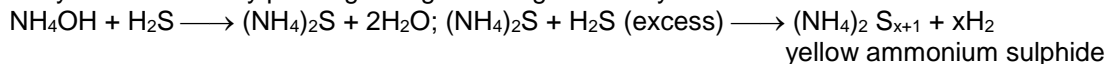


Therefore, It forms two series of salts as given below



##### (iii) Formation of Polysulphides :

They are obtained by passing  $\text{H}_2\text{S}$  gas through metal hydroxides.



#### 17.1.4. TESTS FOR $\text{H}_2\text{S}$ :

(i) Turns acidified lead acetate paper black.

(ii) Gives violet or purple colouration with alkaline sodium nitroprusside solution (containing  $\text{NaOH}$ ).

#### 17.1.5. USES OF $\text{H}_2\text{S}$ :

1. As a laboratory reagent for the detection of basic radicals in qualitative analysis.

2. As reducing agent.

Other hydrides not in syllabus



## 18. OXIDES OF SULPHUR :

SO <sub>2</sub>		Both bonds are equivalent
SO <sub>3</sub>		All three S–O bonds are equivalent. Out of 3π bonds. One is pπ-pπ other two are pπ-dπ.

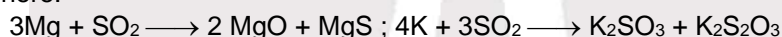
### 18.1 SULPHUR DIOXIDE :

#### 18.1.1 PREPARATION :

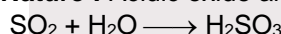
- (i)  $S + O_2 \text{ or air} \xrightarrow{\text{Burn}} SO_2$
- (ii)  $CaSO_4 \text{ (gypsum)} + C \xrightarrow[1000^\circ C]{\Delta} 2 CaO + SO_2 + CO_2$
- By this method SO<sub>2</sub> is obtained in large scale

#### 18.1.2 PROPERTIES :

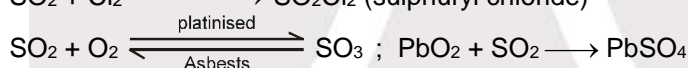
- (i) Colourless gas with burning sulphur smell.
- (ii) It is heavier than air and is highly soluble in water. SO<sub>2</sub> in solution is almost completely present as SO<sub>2</sub>·6H<sub>2</sub>O and only traces of H<sub>2</sub>SO<sub>3</sub>.
- (iii) Neither burns nor helps in burning but burning magnesium and potassium continue to burn in its atmosphere.



- (iv) **Acidic Nature :** Acidic oxide and thus dissolve in water forming sulphurous acid.



- (v) **Addition Reaction :**



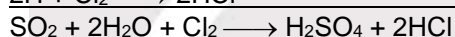
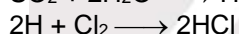
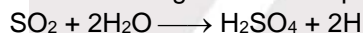
- (vi) **Reducing Nature :**

It is a more powerful reducing agent in alkaline medium than in acidic medium.

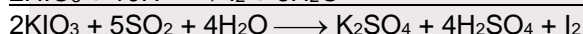
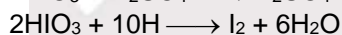
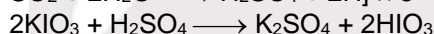
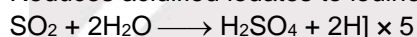


- Reducing character is due to the liberation of nascent hydrogen.

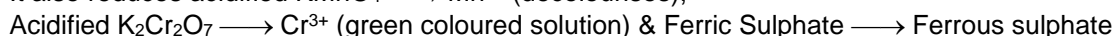
- (a) Reduces halogens to corresponding halides.



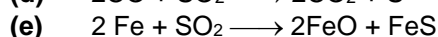
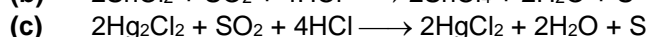
- (b) Reduces acidified iodates to iodine



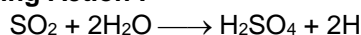
- It also reduces acidified KMnO<sub>4</sub> → Mn<sup>2+</sup> (decolourises),



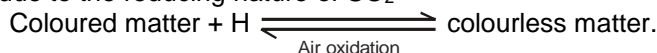
- (vii) **Oxidising nature :** Acts as oxidising agent with strong reducing agent



- (viii) **Bleaching Action :**



This is due to the reducing nature of SO<sub>2</sub>



Therefore, bleaching is temporary.



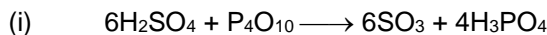


### 18.1.3 USES OF SO<sub>2</sub> :

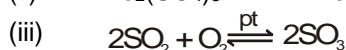
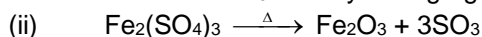
1. Used in manufacture of H<sub>2</sub>SO<sub>4</sub> & paper from wood pulp.
2. As a bleaching agent for delicate articles like wool, silk and straw.
3. Used in refining of petroleum and sugar.

## 18.2 SULPHUR TRIOXIDE (SO<sub>3</sub>) :

### 18.2.1 PREPARATION :



○ P<sub>4</sub>O<sub>10</sub> is dehydrating agent

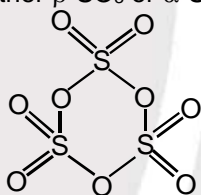


### 18.2.2 PROPERTIES :

**SO<sub>3</sub> exists in three allotropic forms :**

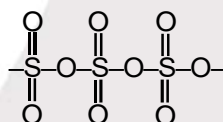
At room temperature SO<sub>3</sub> is solid and exists in three distinct forms.

(a) **γ-SO<sub>3</sub>** : It is ice-like and is a cyclic trimer (SO<sub>3</sub>)<sub>3</sub>, m.p. 16.8°C. If SO<sub>3</sub> is kept for a long time, or if a trace of water is present, either β-SO<sub>3</sub> or α-SO<sub>3</sub> is formed.



**Cyclic trimer of γ-SO<sub>3</sub>**

(b) **α-SO<sub>3</sub>/β-SO<sub>3</sub>** : β-SO<sub>3</sub> (m.p. 32.5°C) is made up of infinite helical chains of tetrahedral [SO<sub>4</sub>] unit each sharing two corners. This structure is similar to that of chain phosphates. α-SO<sub>3</sub> (m.P. 62.2°C) is the most stable form, and is made of chains cross-linked into sheets. Both look like asbestos, and comprise bundles of white silky needles.

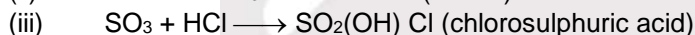
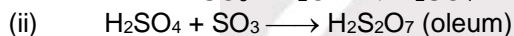
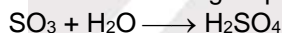


**Structure of SO<sub>3</sub> chains (α-SO<sub>3</sub> or β-SO<sub>3</sub>).**

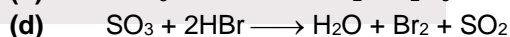
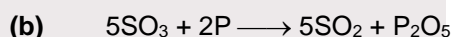
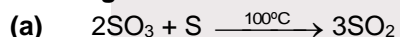
**SO<sub>3</sub> is a powerful oxidizing agent, especially when hot. It oxidizes HBr to Br<sub>2</sub> and P to P<sub>4</sub>O<sub>10</sub>.**

(i) **Acidic Nature :**

Dissolves in water forming sulphuric acid



(iv) **Oxidising Nature :**



### 18.2.3 USES OF SO<sub>3</sub> :

1. Used in manufacture of H<sub>2</sub>SO<sub>4</sub> and oleum.
2. Used as a drying agent for gases.
3. Used for the sulphonation of long chain alkyl benzene compounds (like dodecyl benzene). The sodium salt of these alkyl benzene sulphonic acid are anionic surface active agents and are the active ingredient of detergent.

## 19. OXY ACIDS OF SULPHUR

Sulphur forms a number of oxoacid such as H<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, H<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, H<sub>2</sub>S<sub>2</sub>O<sub>6</sub> (x = 2 to 5,) H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>, H<sub>2</sub>SO<sub>8</sub>. Some of these acids are unstable and cannot be isolated. They are known in aqueous solution or in the forms of their salts. Structures of some important oxoacids are shown in figure.





Oxyacid	Formula of acid	Oxidation state of S	Structure	Other information
<b>(a) Sulphurous acid series</b>				
Sulphurous acid	$\text{H}_2\text{SO}_3$	+4	$\begin{array}{c} \text{HO}-\ddot{\text{S}}-\text{OH} \\    \\ \text{O} \end{array}$	Tautomeric structures are possible
Thiosulphurous acid	$\text{H}_2\text{S}_2\text{O}_2$	-2, +4	$\begin{array}{c} \text{HO}-\ddot{\text{S}}-\text{OH} \\    \\ \text{S} \end{array}$	$p\pi-d\pi$ bond between sulphur atoms
Dithionous acid	$\text{H}_2\text{S}_2\text{O}_4$	+3, +3	$\begin{array}{c} \text{HO}-\ddot{\text{S}}-\ddot{\text{S}}-\text{OH} \\    \quad    \\ \text{O} \quad \text{O} \end{array}$	Unstable and is known as hyposulphurous form
Pyrosulphurous acid	$\text{H}_2\text{S}_2\text{O}_5$	+5, +3	$\begin{array}{c} \text{O} \\    \\ \text{HO}-\text{S}-\ddot{\text{S}}-\text{OH} \\    \quad    \\ \text{O} \quad \text{O} \end{array}$	Average oxidation state of sulphur is +4
<b>(b) Sulphuric acid series</b>				
Sulphuric acid	$\text{H}_2\text{SO}_4$	+6	$\begin{array}{c} \text{O} \\    \\ \text{HO}-\text{S}-\text{OH} \\    \\ \text{O} \end{array}$	Has 2 $p\pi-d\pi$ bond
Thiosulphuric acid	$\text{H}_2\text{S}_2\text{O}_3$	-2, +6	$\begin{array}{c} \text{S} \\    \\ \text{HO}-\text{S}-\text{OH} \\    \\ \text{O} \end{array}$	Hydrated thiosulphates are familiar as hypo ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ).
Pyrosulphuric acid	$\text{H}_2\text{S}_2\text{O}_7$	+6, +6	$\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ \text{HO}-\text{S}-\text{O}-\text{S}-\text{OH} \\    \quad    \\ \text{O} \quad \text{O} \end{array}$	It is called oleum and also as fuming sulphuric acid
<b>(c) Thionic acid series</b>				
Dithionic acid	$\text{H}_2\text{S}_2\text{O}_6$	+5, +5	$\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ \text{HO}-\text{S}-\text{S}-\text{OH} \\    \quad    \\ \text{O} \quad \text{O} \end{array}$	Has 2 $p\pi-d\pi$ bonds each sulphur atom
Polythionic acid ( $x = n + 2$ ) ( $n = 1-12$ )	$\text{H}_2\text{S}_x\text{O}_6$	+5, 0, +5	$\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ \text{HO}-\text{S}-\text{S}_n-\text{S}-\text{OH} \\    \quad    \\ \text{O} \quad \text{O} \end{array}$	Middle sulphur atom have zero oxidation state
<b>(d) Peroxy acid series</b>				
Peroxy mono-sulphuric acid	$\text{H}_2\text{SO}_5$	+6	$\begin{array}{c} \text{O} \\    \\ \text{HO}-\text{S}-\text{O}-\text{OH} \\    \\ \text{O} \end{array}$	Called Caro's acid. Fairly stable



Peroxydi-sulphuric acid	$\text{H}_2\text{S}_2\text{O}_8$	+6, +6	$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \parallel \\ \text{HO}-\text{S}-\text{O}-\text{O}-\text{S}-\text{OH} \\ \parallel \quad \parallel \\ \text{O} \quad \quad \text{O} \end{array}$	Called Marshall's acid. Persulphates are well known
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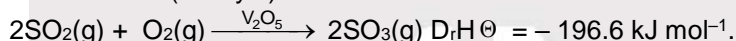
## 19.1 SULPHURIC ACID ( $\text{H}_2\text{SO}_4$ ) :

### 19.1.1 Preparation :

Sulphuric acid is one of the most important industrial chemicals world wide.

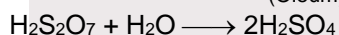
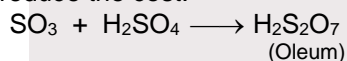
#### (a) Contact process :

- (i) Burning of sulphur or sulphide ores in air to generate  $\text{SO}_2$
- (ii) Conversion of  $\text{SO}_2$  to  $\text{SO}_3$  by the reaction with oxygen in the presence of a catalyst ( $\text{V}_2\text{O}_5$ ), and
- (iii) Absorption of  $\text{SO}_2$  in  $\text{H}_2\text{SO}_4$  to give Oleum ( $\text{H}_2\text{S}_2\text{O}_7$ )
- (iv) The  $\text{SO}_2$  produced is profiled by removing dust and other impurities such as arsenic compounds.
- (v) The key step in the manufacture of  $\text{H}_2\text{SO}_4$  is the catalytic oxidation of  $\text{SO}_2$  with  $\text{O}_2$  to give  $\text{SO}_3$  in the presence of  $\text{V}_2\text{O}_5$  (catalyst).



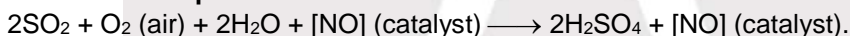
(vi) The  $\text{SO}_3$  gas from the catalytic converter is absorbed in concentrated  $\text{H}_2\text{SO}_4$  to produce oleum. Dilution of oleum with water gives  $\text{H}_2\text{SO}_4$  of the desired concentration.

(vii) In the industry two steps are carried out simultaneously to make the process a continuous one and also to reduce the cost.



**Note :** The sulphuric acid obtained by Contact process is 96-98% pure.

#### (b) Lead chamber process :



Acid obtained is 80% pure and is known as brown oil of vitriol.

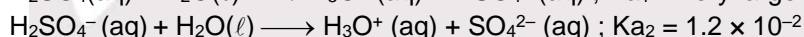
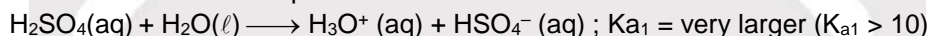
**Note :** It is outdated process, need not remember.

### 19.1.2 (a) Physical Properties :

- (i) Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K.
- (ii) The acid freezes at 283 K and boils at 611 K. It dissolves in water with the evolution of a larger quantity of heat.
- (iii) The chemical reaction of sulphuric acid are as a result of the following characteristics:
  - (a) low volatility
  - (b) strong acidic character
  - (c) strong affinity for water and
  - (d) ability to act as an oxidising agent in aqueous solution.

#### (b) Chemical Properties :

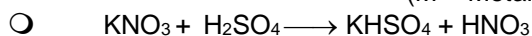
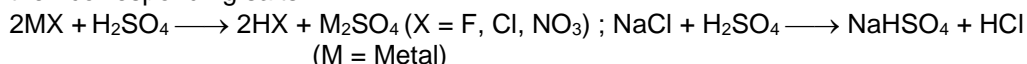
##### (i) Sulphuric acid ionises in two steps.



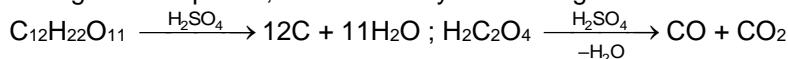
The larger value of  $K_{a1}$  ( $K_{a1} > 10$ ) means that  $\text{H}_2\text{SO}_4$  is largely dissociated into  $\text{H}^+$  and  $\text{HSO}_4^-$ . Greater the value of dissociation constant ( $K_a$ ) the stronger is the acid.

- (a) The acid forms two series of salts : normal sulphates (such as sodium sulphate and copper sulphate and acid sulphate (e.g., sodium hydrogen sulphate)
- (b) Decomposes carbonates and bicarbonates into  $\text{CO}_2$ .  

$$\text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2 ; \text{NaHCO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{H}_2\text{O} + \text{CO}_2$$
- (c) Sulphuric acid, because of its low volatility can be used to manufacture more volatile acid from their corresponding salts.

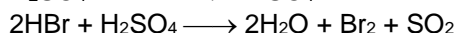
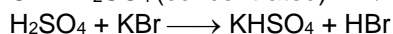
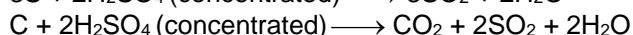
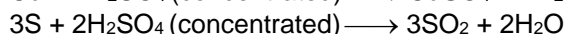


- (ii) Concentrated sulphuric acid is a strong dehydrating agent. Many wet gases can be dried by passing them through sulphuric acid, provided the gases do not react with the acid. Sulphuric acid removes water from organic compound; it is evident by its charring action on carbohydrates.

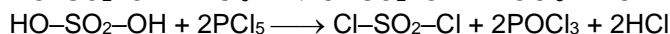




- (iii) Hot concentrated sulphuric acid is moderately strong oxidising agent. In this respect it is intermediate between phosphoric and nitric acids. Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to  $\text{SO}_2$ .



- (iv) With  $\text{PCl}_5$  forms mono and di-acid chlorides.



- (v)  $\text{K}_4 [\text{Fe}(\text{CN})_6] (\text{s}) + 6\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O} \xrightarrow{\Delta} 2\text{K}_2\text{SO}_4 + \text{FeSO}_4 + 3(\text{NH}_4) \text{SO}_4 + 6\text{CO}$

- (vi)  $3\text{KClO}_3 + 3\text{H}_2\text{SO}_4 \longrightarrow 2\text{KHSO}_4 + \text{HClO}_4 + 2\text{ClO}_2 + \text{H}_2\text{O}$

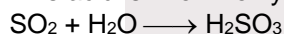
### 19.1.3 USES OF $\text{H}_2\text{SO}_4$ :

(i) Sulphuric acid is a very important industrial chemical.

(ii) The bulk of sulphuric acid produced is used in the manufacture of fertilisers (e.g., ammonium sulphate, superphosphate). Other uses are in : (a) petroleum refining (b) manufacture of pigment, paints and dyestuff intermediates (c) detergent industry (d) metallurgical applications (e.g., cleansing metal before enameling, electroplating and galvanising) (e) storage batteries (f) in the manufacture of nitrocellulose products and (g) as a laboratory reagent.

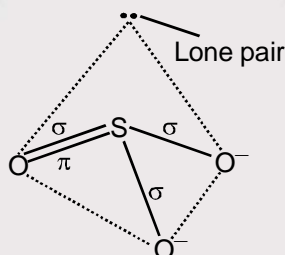
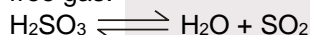
### 19.2.1 SULPHUROUS ACID ( $\text{H}_2\text{SO}_3$ ) :

This acid is known only in solution. The solution is obtained by dissolving  $\text{SO}_2$  in water.



Though  $\text{SO}_2$  is very soluble in water, most is present as hydrated  $\text{SO}_2(\text{SO}_2 \cdot \text{H}_2\text{O})$ . Sulphurous acid.  $\text{H}_2\text{SO}_3$  may exist in the solution in minute amounts, or not at all, though the solution is acidic. Its salts, the sulphites  $\text{SO}_3^{2-}$  form stable crystalline solids.

On heating it gives a smell of  $\text{SO}_2$ . It is, thus, believed that the acid is present in equilibrium with the free gas.



### 19.2.2 Properties :

(i) It is a strong dibasic acid. It ionises in two stages.

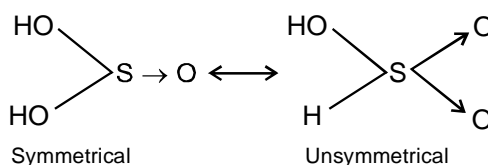


(ii) It thus forms two series of salts. The salts are known as bisulphites (e.g.  $\text{NaHSO}_3$ ) and sulphites (e.g.,  $\text{Na}_2\text{SO}_3$ ). The salts are fairly stable.

(iii) Like  $\text{SO}_2$ , it acts as a reducing agent and shows bleaching properties. These properties have been described under sulphur dioxide.

(iv) The acid also acts as an oxidising agent particularly when treated with strong reducing agents.

**Structure :** Sulphurous acid is believed to exist in two forms which are always in equilibrium with each other.







## Solved Examples

**Ex-27.**  $\text{SO}_2$  and  $\text{Cl}_2$  both are used as bleaching agent. What factors cause bleaching ?

**Sol.**  $\text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + 2\text{H}$ .

$\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow 2\text{HCl} + \text{O}$ .

Bleaching action of  $\text{SO}_2$  is due to H (that causes reduction) and that of  $\text{Cl}_2$  is due to O (that causes oxidation).

**Ex-28.** Acid salt (A)  $\xrightarrow{\text{heat}}$  (B)  $\xrightarrow{\text{HCl}}$  (C) gas  $\xrightarrow{\text{Cr}_2\text{O}_7^{2-}/\text{H}^+}$  (G) green  
Molar mass 84

(B)  $\xrightarrow{\text{BaCl}_2}$  White ppt (D) soluble in HCl  
(C) gas  $\xrightarrow{\text{Ca(OH)}_2}$  Milkyness appears

(D)  $\xrightarrow{\text{Br}_2 \text{ water}}$  White ppt (H)  
(C) gas  $\xrightarrow{\text{Ca(OH)}_2}$  Milkyness disappears (F)

**Sol.**  $\text{NaHSO}_3 \xrightarrow{\text{heat}} \text{Na}_2\text{SO}_3 \xrightarrow{\text{HCl}} \text{SO}_2 \xrightarrow{\text{Cr}_2\text{O}_7^{2-}/\text{H}^+} \text{Cr}^{3+} \text{ (green solution)}$   
 $\text{Na}_2\text{SO}_3 \xrightarrow{\text{BaCl}_2(\text{aq})} \text{BaSO}_3 \xrightarrow{\text{Br}_2 \text{ water}} \text{BaSO}_4$   
 $\text{SO}_2 \xrightarrow{\text{Ca(OH)}_2(\text{aq})} \text{CaSO}_3(\text{aq}) \xrightarrow{\text{SO}_2} \text{CaHSO}_3$

**Ex-29.** Why  $\text{NH}_3$  gas cannot be dried by passing over  $\text{P}_2\text{O}_5$ ,  $\text{CaCl}_2$  and  $\text{H}_2\text{SO}_4$  ?

**Sol.**  $\text{CaCl}_2 + 8\text{NH}_3 \longrightarrow \text{CaCl}_2 \cdot 8\text{NH}_3$  ;

$\text{P}_2\text{O}_5 + 6\text{NH}_3 + 3\text{H}_2\text{O} \longrightarrow 2(\text{NH}_4)_3\text{PO}_4$

$\text{H}_2\text{SO}_4 + 2\text{NH}_3 \longrightarrow (\text{NH}_4)_2\text{SO}_4$

So it is dried by passing over quick lime ( $\text{CaO}$ ).

$\text{CaO} + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2$

**Ex-30.** Black (A) +  $\text{H}_2\text{SO}_4 \longrightarrow$  (B) gas + (C)

(B) +  $(\text{CH}_3\text{COO})_2\text{Pb} \longrightarrow$  (D) black ppt.

(C) +  $\text{K}_3[\text{Fe(CN)}_6] \longrightarrow$  (E) blue.

(C) also decolourises acidified  $\text{KMnO}_4$ . Identify (A) to (E).

**Sol.**  $\text{FeS} + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{S} + \text{FeSO}_4$  ;  $\text{H}_2\text{S} + (\text{CH}_3\text{COO})_2\text{Pb} \longrightarrow \text{PbS} \text{ (black ppt.)} + 2\text{CH}_3\text{COOH}$ .

$\text{Fe}^{2+} + \text{K}_3[\text{Fe(CN)}_6]^{3-} \longrightarrow \text{KFe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$  Turnbull's blue.

**Ex-31.** Why concentrated  $\text{H}_2\text{SO}_4$  can not be used for drying  $\text{H}_2$  ?

**Ans.** As hydrogen catches fire due to heat liberated when water is absorbed by acid.

## 20. SODIUM THIOSULPHATE ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) :

### 20.1.1 PREPARATION :

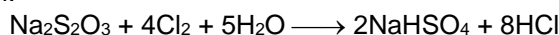
(i)  $\text{Na}_2\text{SO}_3 + \text{S} \xrightarrow{\text{Boiled in absence of air}} \text{Na}_2\text{S}_2\text{O}_3$

(ii)  $6\text{NaOH} + 4\text{S} \xrightarrow{\Delta} \text{Na}_2\text{S}_2\text{O}_3 + 2\text{Na}_2\text{S} + \text{H}_2\text{O}$



### 20.1.2 PROPERTIES:

- (i) It is a colourless crystalline substance soluble in water which loses water of crystallisation on strong heating
- (ii) **As antichlor** : It removes the chlorine from the surface of fibres (while dyeing) according to following reaction.



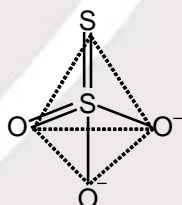
Therefore, it is known as antichlor.

- (iii) **Reaction with HCl** :  $\text{S}_2\text{O}_3^{2-} + \text{H}^+ \longrightarrow \text{S} \downarrow (\text{white}) + \text{SO}_2 + \text{H}_2\text{O}$  (disproportionation reaction)  
This test is used for distinction between  $\text{S}_2\text{O}_3^{2-}$  and  $\text{SO}_3^{2-}$  ions as  $\text{SO}_3^{2-}$  ions give only  $\text{SO}_2$  with HCl.
- (iv) **Complex formation reactions:**

Reactants	Main Products	Special Points
Reaction with silver salts ( $\text{AgNO}_3$ , $\text{AgCl}$ , $\text{AgBr}$ or $\text{AgI}$ )	$\text{Ag}_2\text{S}_2\text{O}_3 \downarrow$ (white)	This hydrolytic decomposition can be accelerated by warming. If hypo is in excess, then soluble complex is formed. $2\text{S}_2\text{O}_3^{2-} + \text{Ag}^+ \rightarrow [\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ (soluble complex) or $[\text{Ag}(\text{S}_2\text{O}_3)_3]^{5-}$ This reaction is utilized in photography where hypo is used as fixer.
Reaction with $\text{FeCl}_3$	$[\text{Fe}(\text{S}_2\text{O}_3)_2]^-$ (Pink or violet) Unstable complex	The colour fades off in a few seconds.
Reaction with $\text{AuCl}_3$	$\text{Na}_3[\text{Au}(\text{S}_2\text{O}_3)_2]$ (soluble and unstable complex)	
Reaction with $\text{CuCl}_2$	$\text{Na}_4[\text{Cu}_6(\text{S}_2\text{O}_3)_5]$ (soluble complex)	

- (v) **As reducing agent :**  
(a)  $\text{MnO}_4^- \longrightarrow \text{Mn}_2\text{O}_3$  ; (b)  $\text{I}_3^- \longrightarrow 3\text{I}^-$   
Reaction (b) finds application in the iodometric and iodimetric methods of titrimetric analysis.
- (vi) **Heating effects** :  $4\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} \xrightarrow[215^\circ\text{C}]{- \text{H}_2\text{O (All)}} 4\text{Na}_2\text{S}_2\text{O}_3 \xrightarrow{220^\circ\text{C}} 3\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_5$
- (vii) **Reaction with soluble salt of lead :**  
 $\text{S}_2\text{O}_3^{2-} + \text{Pb}^{2+} \longrightarrow \text{PbS}_2\text{O}_3 \downarrow (\text{white})$   
 $\text{PbS}_2\text{O}_3 \downarrow + \text{H}_2\text{O} \longrightarrow \text{PbS} \downarrow (\text{black}) + 2\text{H}^+ + \text{SO}_4^{2-}$   
○  $\text{Ba}^{2+}$  gives white precipitate of  $\text{BaS}_2\text{O}_3$  but calcium thiosulphate is soluble.

**Structure :**



Thio sulphate ion is regarded as derived from the sulphate ion by replacement of one oxygen atom by sulphur

### 20.1.3 USES OF HYPO :

- As an 'antichlor' to remove excess of chlorine from bleached fabrics.
- In photography as fixer.
- As a reagent in iodometric and idiometric titrations.

### Solved Examples

**Ex-32.** Colourless salt (A) decolourises  $\text{I}_2$  solution and gives white precipitate (changing to black) with  $\text{AgNO}_3$  solution. (A) also produces pink colour with  $\text{FeCl}_3$  solution. Identify (A) and explain reactions.

**Sol.**  $2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \longrightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$   
 $\text{S}_2\text{O}_3^{2-} + 2\text{Ag}^+ \longrightarrow \text{Ag}_2\text{S}_2\text{O}_3 \downarrow (\text{white})$   
 $\text{Ag}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \longrightarrow \text{Ag}_2\text{S} \downarrow (\text{Black}) + \text{H}_2\text{SO}_4$   
 $\text{Fe}^{3+} + 2\text{S}_2\text{O}_3^{2-} \longrightarrow [\text{Fe}(\text{S}_2\text{O}_3)_2]^- (\text{Pink or violet})$