

# p-Block : Nitrogen and Oxygen Family (Group 15<sup>th</sup> and 16<sup>th</sup>)

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# Syllabus

## Nitrogen and Oxygen Family (Group 15<sup>th</sup> and 16<sup>th</sup>)

**Isolation/preparation and properties of the following non-metals :** Nitrogen, phosphorus, oxygen, sulphur, phosphorus and sulphur.

#### Preparation and properties of the following compounds :

Nitrogen: oxides, oxyacids and ammonia; Phosphorus: oxides, oxyacids (phosphorus acid, phosphoric acid) and phosphine; Oxygen: ozone and hydrogen peroxide; Sulphur: hydrogen sulphide, oxides, sulphurous acid, sulphuric acid and sodium thiosulphate;

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#### **GROUP 15 ELEMENTS : THE NITROGEN FAMILY**

Commonly Called as Pnicogens and their Compounds are Pniciticles :

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 metalloidic character. Nitrogen and phosphorus are non-metal, arsenic and antimony metalloid and bismuth is a typical metal.

The valence shell electronic configuration of these element is ns<sup>2</sup> np<sup>3</sup>. The s orbital in these element is completely filled and p orbitals are half- filled, making their electronic configuration extra stable.

#### 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.

#### **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  $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$ 

#### **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.

#### Catenation :

Only N, P and As exhibit the property of catenation.

#### **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. Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids and bismuth is a metal. This is due to decrease in ionisation enthalpy and increase in atomic size. 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.

Element		N	Р	As	Sb	Bi
Atomic Number		7	15	33	51	83
Atomic Mass		14.01	30.97	74.92	121.76	208.98
Electronic configuration		[He] 2s <sup>2</sup> 2p <sup>3</sup>	[Ne] 3s <sup>2</sup> 3p <sup>3</sup>	[Ar] $3d^{10} 4s^2 4p^3$	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>3</sup>	[Xe] $4f^{14} 5d^{10} 6s^2 6p^3$
Covalent Radius / pm		70	110	120	140	150
lonic Radius / pm a = M³⁻, b = M⁺³		171 <sup>a</sup>	212 <sup>a</sup>	222 <sup>a</sup>	76 <sup>b</sup>	103 <sup>b</sup>
lenization onthe law	Ι	1402	1012	947	834	703
$/(k_1 \text{ mol}^{-1})$	II	2856	1903	1798	1595	1610
/ ( / / / / / / / / / / / / / / / /	III	4577	2910	2736	2443	2466
Electronegativity		3.0	2.1	2.0	1.9	1.9

#### ATOMIC AND PHYSICAL PROPERTIES

#### **CHEMICAL PROPERTIES :**

#### 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, bismuth hardly forms any compound in -3 oxidation state. The stability of +5 oxidation state decreases down the group. The only well characterised Bi (V) compound is BiF<sub>5</sub>. The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group.

$$Bi^{3+} > Sb^{3+} > As^{3+}$$
;  $Bi^{5+} < Sb^{5+} < As^{5+}$ 

Nitrogen exhibits +1, +2, +4 oxidation states also when it reacts with oxygen. 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. 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  $PF_{e}^{-}$ .

#### ANOMALOUS PROPERTIES OF NITROGEN :

Nitrogen differs from the rest of the members of this group due to its smaller size , high electronegativity, high ionisation enthalpy and non–availability of d orbitals. Nitrogen has unique ability to 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. Consequently , its bond enthalpy (941.1 kJ mol<sup>-1</sup>) is very high. On the contrary, phosphorus, arsenic and antimony form metallic bonds in elemental state. 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 as the heavier elements can e.g., R<sub>3</sub>P=O or R<sub>3</sub>P=CH<sub>2</sub> (R = alkyl group). Phosphorus and arsenic can form  $d\pi$ – $p\pi$  bond also with transition metals when their compounds like P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> act as ligands.

#### Hydrides :

All the elements of Group 15 form hydrides of the type EH<sub>3</sub> where E=N, P, As, Sb or Bi. Some of the properties of these hydrides are shown in Table. The hydrides show regular gradation in their properties. The stability of hydrides decreases from NH<sub>3</sub> to BiH<sub>3</sub> which can be observed from their bond dissociation enthalpy. Consequently, the reducing character of the hydrides increases. Ammonia is only a mild reducing agent while BiH<sub>3</sub> is the strongest reducing agent amongst all the hydrides. Basicity also decreases in the order NH<sub>3</sub> > PH<sub>3</sub> > AsH<sub>3</sub> > SbH<sub>3</sub> ≥ BiH<sub>3</sub>.

Property	$NH_3$	PH <sub>3</sub>	AsH₃	SbH <sub>3</sub>	BiH <sub>3</sub>
Melting point / K	195.2	139.5	156.7	185	-
Boiling point / K	238.5	185.5	210.6	254.6	290
(E – H) Distance / pm	101.7	141.9	151.9	170.7	-
HEH angle ( <sup>0</sup> )	107.8	93.6	91.8	91.3	-
$\Delta_{\rm f} {\rm H}^-$ / kJ mol <sup>-1</sup>	- 46.1	13.4	66.4	145.1	278
$\Delta_{diss}H^{-}(E - H) / kJ mol^{-1}$	389	322	297	255	_

**PROPERTIES OF HYDRIDES OF GROUP 15 ELEMENTS** 

#### Oxides :

All these elements form two types of oxides :  $E_2O_3$  and  $E_2O_5$ . 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  $E_2O_3$  of nitrogen and phosphorus are purely acidic , that of arsenic and antimony amphoteric and those of bismuth is predominantly basic.

**OXIDES OF 15TH GROUP ELEMENTS** 

Element Types of Oxides	N	Р	As	Sb	Bi
X <sub>2</sub> O <sub>3</sub>	N <sub>2</sub> O <sub>3</sub>	$P_2O_3$	$As_2O_3$	$Sb_2O_3$	Bi <sub>2</sub> O <sub>3</sub>
X <sub>2</sub> O <sub>4</sub>	$N_2O_4$	$P_2O_4$	$As_2O_4$	Sb <sub>2</sub> O <sub>4</sub>	$\operatorname{Bi}_2\operatorname{O}_4$
X <sub>2</sub> O <sub>5</sub>	N <sub>2</sub> O <sub>5</sub>	$P_2O_5$	$As_2O_5$	$Sb_2O_5$	



#### Halides :

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<sub>3</sub> is known to be stable. Trihalides except BiF<sub>3</sub> are predominantly covalent in nature. Halides are hydrolysed in water forming oxyacids or oxychlorides.

$$\begin{array}{l} \mathsf{PCI}_3 + \mathsf{H}_2\mathsf{O} & \longrightarrow & \mathsf{H}_3\mathsf{PO}_3 + \mathsf{HCI} \\ \mathsf{SbCI}_3 + \mathsf{H}_2\mathsf{O} & \longrightarrow & \mathsf{SbOCI} \downarrow (\mathsf{orange}) + 2\mathsf{HCI} \\ \mathsf{BiCI}_3 + \mathsf{H}_2\mathsf{O} & \longrightarrow & \mathsf{BiOCI} \downarrow (\mathsf{white}) + 2\mathsf{HCI} \end{array}$$

### NITROGEN (N) :

Dinitrogen comprises 78% of the earth atmosphere but it is not a very abundant element in the earth's crust. Nitrates are all very soluble in water so they are not wide spread in the earth's crust. NaNO<sub>3</sub> is found together with small amounts of KNO<sub>3</sub>, CaSO<sub>4</sub> and NaIO<sub>3</sub> along the coast of southern Chile under a thin layer of sand or soil. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Nitrogen is an important and essential constituent of proteins and amino acids. Nitrates and other nitrogen compounds are extensively used in fertilizers and explosive.

#### Preparation :

(i) Laboratory method of preparation :  $NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + H_2O(\ell) + NaCl_{(aq)} N_2$  is collected by the downward displacement of water. This reaction takes place in two steps as given below :

$$NH_4CI + NaNO_2 \xrightarrow{\Lambda} NH_4NO_2 + NaCI;$$
  $NH_4NO_2 \xrightarrow{\Lambda} N_2^{\uparrow} + 2H_2O.$ 

- (ii) By heating ammonium dichromate :  $(NH_4)_2Cr_2O_7 \xrightarrow{\Lambda} N_2 \uparrow + 4H_2O + Cr_2O_3$
- (iii) By oxidation of ammonia :

### (A) At lower temperature

- (a)
- $8NH_3(\ell) + 3CI_2(g) \longrightarrow 6NH_4CI + N_2^{\uparrow}$
- If excess of  $Cl_2$  is used in this reaction, nitrogen trichloride is formed as per the following reaction,  $NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$ Nitrogen trichloride is an explosive substance.
- (b) By reaction of ammonia with calcium hypochlorite or  $Br_2$  $4NH_3 + 3Ca(OCI)_2 \longrightarrow 3CaCI_2 + N_2 + H_2O$

#### (B) At higher temperature

- By passing ammonia over heated cupric oxide or PbO :  $2NH_3 + 3CuO \longrightarrow N_2^{\uparrow} + 3Cu + 3H_2O$
- (iv) Very pure nitrogen ;  $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$ Sodium azide also gives  $N_2$  on heating.

## INDUSTRIAL METHODS OF PREPARATION :

- (i) From liquified air by fractional distillation : The boiling point of  $N_2$  is -196°C and that of oxygen is -183°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<sub>2</sub> which is absorbed in alkalies &  $N_2$  remains which is collected in gas cylinders.

#### **Properties :**

- (i) N<sub>2</sub> is a colourless, odourless gas insoluble in water. It is neither combustible nor a supporter of combustion.
- (ii) It is absorbed by heated Mg and Al. The nitrides formed thus react with water to form NH<sub>a</sub>.

$$3Mg + N_2 \longrightarrow Mg_3N_2 \quad ; \qquad Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_3 + 2NH_3^{\uparrow}$$
  
$$2AI + N_2 \longrightarrow 2AIN \quad ; \qquad 2AIN + 6H_2O \longrightarrow 2AI(OH)_3 + 2NH_3^{\uparrow}$$

(iii) Reaction with  $H_2$ : At 200 atm and 500°C, and in the presence of iron catalyst and molybdenum promoter,  $N_2$  combines with  $H_2$  reversibly to form ammonia. The process is called Haber's Process and is the industrial method of manufacturing ammonia. The reaction is exothermic.

 $N_2 + 3H_2 \longrightarrow 2NH_3$ 



(iv) Reaction with oxygen: When air free from CO, and moisture is passed over an electric arc at about 2000 K, nitric oxide is formed. This reaction is endothermic.

 $N_2 + O_2 \longrightarrow 2NO$ 

Reaction with CaC, and BaC,: At 1100°C, these carbides react with N, forming CaCN, and Ba(CN), respectively. (v)

> $CaC_2 + N_2 \xrightarrow{\Delta} CaCN_2 + C$  (nitrolim, a fertilizer);  $BaC_2 + N_2 \xrightarrow{\Delta} Ba(CN)_2$

CaCN, reacts with H<sub>2</sub>O in the soil to produce NH<sub>3</sub> gas. NH<sub>3</sub> gas is converted into nitrates by the nitrating bacteria present in soil. (The nitrates are readily absorbed by the plants and meet their requirement of the element nitrogen.)

### **COMPOUNDS OF NITROGEN:** AMMONIA: **Preparation** :

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

> $NH_4NO_3 + NaOH \longrightarrow NH_3^{\uparrow} + NaNO_3 + H_2O; (NH_4)_2SO_4 + CaO \longrightarrow 2NH_3^{\uparrow} + CaSO_4 + H_2O$ This is a general method and is used as a test for ammonium salts.

By the hydrolysis of metal nitrides like AIN or Mg<sub>3</sub>N<sub>2</sub>. (ii)

 $AIN + NaOH + H_2O \longrightarrow NaAIO_2 + NH_3$ 

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

$$\begin{split} \text{NaNO}_3 + 7\text{NaOH} + 4\text{Zn} & \longrightarrow 4\text{Na}_2\text{ZnO}_2 + \text{NH}_3^\uparrow + 2\text{H}_2\text{O} \\ \text{NaNO}_2 + 3\text{Zn} + 5\text{NaOH} & \longrightarrow 3\text{Na}_2\text{ZnO}_2 + \text{H}_2\text{O} + \text{NH}_3^\uparrow \end{split}$$

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

 $\triangleright$ 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<sub>2</sub>, P<sub>2</sub>O<sub>5</sub> or concentrated H<sub>2</sub>SO<sub>4</sub> because NH<sub>3</sub> reacts with all of these.

$$\begin{array}{ll} \mathsf{CaCl}_2 + \mathsf{8NH}_3 \longrightarrow \mathsf{CaCl}_2 \cdot \mathsf{8NH}_3 \ ; & \mathsf{P}_2\mathsf{O}_5 + \mathsf{6NH}_3 + \mathsf{3H}_2 \\ \mathsf{H}_2\mathsf{SO}_4 + \mathsf{2NH}_3 \longrightarrow (\mathsf{NH}_4)_2\mathsf{SO}_4 \ ; & \mathsf{CaO} + \mathsf{H}_2\mathsf{O} \end{array}$$

$$P_2O_5 + 6NH_3 + 3H_2O \longrightarrow 2(NH_4)_3PO_2$$
  
CaO + H\_2O  $\longrightarrow$  Ca(OH)\_2

#### **INDUSTRIAL METHODS OF PREPARATION :**

- Haber's process :  $N_2 + 3H_2 \xrightarrow{500^{\circ}C, 200 \text{ atm.}}_{\text{Iron oxide}+K_2O\& AI_2O_3} 2NH_3$ (i)
  - Principle: Haber process is the most important industrial method of preparing ammonia. This method was discovered by a German chemist Fritz Haber. The method involves the direct combination of nitrogen and hydrogen according to the following reaction.

 $N_2 + 3H_2 = 2NH_3 + 24.0$  kcal

The reaction is reversible, exothermic and formation of NH<sub>3</sub> is followed by a decreased in volume. According to Le Chatelier's principle, the optimum conditions for the greater yield of ammonia are :

- (a) High pressure : Usually a pressure of 200 atmospheres is applied.
- (b) Low temperature : The working temperature of 450-550°C is maintained.
- (c) Catalyst : At low temperature, although the yield of ammonia is more yet the reaction is very slow. In order to speed up the reaction, a catalyst is used. The following catalysts have been proposed for this purpose.
- (i) Finely divided iron with some molybdenum as a promotor.
- (ii) Finely divided nickel and sodalime deposited over pumice stone.

#### (ii) **Cyanamide process :**

 $CaO + 2C + N_2 \xrightarrow{2000\,^{\circ}C} CaCN_2 + CO^{\uparrow}; CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3^{\uparrow}$ 

#### **Physical properties :**

Ammonia is a colourless gas with a pungent odour. Its freezing point and boiling point are 198.4 and 239.7 K respectively. 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.

Ammonia gas is highly soluble in water. Its aqueous solution is weakly basic due to the formation of OH-ions.  $NH_{a}(g) + H_{2}O(\ell) \longrightarrow NH_{4}^{+}(aq) + OH^{-}(aq)$ 



#### **Chemical properties :**

(i) It forms ammonium salts with acids, e.g.,  $NH_4CI$ ,  $(NH_4)_2SO_4$  etc. As a weak base, it precipitates the hydroxides of many metals from their salt solutions. For example,

$$2 \operatorname{FeCl}_{3}(\operatorname{aq}) + 3 \operatorname{NH}_{4}OH(\operatorname{aq}) \longrightarrow \operatorname{Fe}_{2}O_{3} \cdot \operatorname{xH}_{2}O(\operatorname{s}) + 3 \operatorname{NH}_{4}CI(\operatorname{aq})$$

$$\operatorname{ZnSO}_{4}(\operatorname{aq}) + 2 \operatorname{NH}_{4}OH(\operatorname{aq}) \longrightarrow \operatorname{Zn}(OH)_{2}(\operatorname{s}) + (\operatorname{NH}_{4})_{2} \operatorname{SO}_{4}(\operatorname{aq})$$

$$(\text{white ppt})$$

(ii) 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 Cu<sup>2+</sup>, Ag<sup>+</sup>; Cd<sup>2+</sup>:

$$Cu^{2+} (aq) + 4 NH_3 (aq) = [Cu(NH_3)_4]^{2+} (aq)$$
(blue)
(deep blue)
(deep blue)

$$Ag^+$$
 (aq) + Cl<sup>-</sup> (aq)  $\implies$  AgCl (s)  
colourless) (white ppt)

 $\begin{array}{lll} \mbox{AgCI (s) + 2 NH}_3 (aq) & \longrightarrow & [\mbox{Ag (NH}_3)_2]\mbox{CI (aq)} \\ (\mbox{white ppt)} & (\mbox{colourless}) \end{array}$ 

$$\begin{array}{c} Cd^{2+}\left(aq\right) + 4NH_{_{3}}\!\left(aq\right) \longrightarrow [Cd(NH_{_{3}})_{_{4}}]^{2+}\left(aq\right) \\ \scriptstyle (\text{colourless}) \end{array}$$

(iii) 
$$4NH_3 + 5O_2 \xrightarrow{Pt, 550^{\circ}C} 4NO + 6H_2O$$
 (Ostwald's process-Mgf. HNO<sub>3</sub>)

(iv)  $NH_3$  burns in dioxygen with a pale yellow flame  $4NH_3 + 3O_2 \longrightarrow 2N_2 + 3H_2O$ 

(v) 
$$2NH_3 + CO_2 + H_2O \longrightarrow (NH_4)_2CO_3; \quad 2NH_3 + CO_2 \xrightarrow{high pressure}{\Delta} NH_2CONH_2 (urea) + H_2O$$

Ammonium salts decompose quite readily on heating. If the anion is not particularly oxidising (e.g.  $Cl^{-} CO_{3}^{2-}$  or  $SO_{4}^{2-}$ ) then ammonia is evolved.

$$NH_4CI \xrightarrow{\Delta} NH_3 + HCI;$$
  $(NH_4)_2SO_4 \xrightarrow{\Delta} 2NH_3 + H_2SO_4$ 

If the anion is more oxidising (e.g.  $NO_2^-$ ,  $NO_3^-$ ,  $CIO_4^-$ ,  $Cr_2O_7^{2-}$ ) then  $NH_4^+$  is oxidised to  $N_2$  or  $N_2O$ .

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$
;  $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$ 

- $> 2NH_3 + 2KMnO_4 \xrightarrow{\text{Neutral}} 2KOH + 2MnO_2 + N_2 + 2H_2O$
- Ammonia is oxidised by sodium hypochlorite in dilute aqueous solution :

 $NH_3 + NaOCI \longrightarrow NH_2CI + NaOH$  (fast)

$$NH_3 + NH_2CI \longrightarrow NH_2NH_2 + NH_4CI$$
(slow)

(Rasching process for manufacture of hydrazine)

A small quantity or all the product may be destroyed by the side reaction given below.

$$N_2H_4 + 2NH_2CI \longrightarrow N_2 + 2NH_4CI$$
  
Chloramine

This reaction is catalysed by heavy metal ions present in solution. For this distilled water is used (rather than tap water) and glue or gelatin is added to mask (i.e. complex with) the remaining metal ions. The use of excess of ammonia reduces the incidence of chloramine reacting with hydrazine. The use of a dilute solution of the reactant is necessary to minimize another side reaction.

 $3NH_2CI + 2NH_3 \longrightarrow N_2 + 3NH_4CI$ 

#### **OXIDES OF NITROGEN :**

Nitrogen forms a number of oxides, N<sub>2</sub>O, NO, N<sub>2</sub>O<sub>3</sub>, NO<sub>2</sub> or N<sub>2</sub>O<sub>4</sub> and N<sub>2</sub>O<sub>5</sub>, and also very unstable NO<sub>3</sub> and N<sub>2</sub>O<sub>6</sub>. All these oxides of nitrogen exhibit  $p\pi$ - $p\pi$  multiple bonding between nitrogen and oxygen.



#### **Properties of Oxides of Nitrogen**

Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide ]	N₂O	+ 1	$NH_4NO_3 \xrightarrow{Heat} N_2O + 2 H_2O$	colourless gas , neutral
Nitrogen monoxide [Nitrogen(II) oxide]	NO	+ 2	$NO_{3}^{-} + 3Fe^{2*} + 4H^{*} \longrightarrow NO + 3Fe^{3*} + 2H_{2}O$ $2HNO_{2} + 2I^{-} + 2H^{*} \longrightarrow 2NO + I_{2} + 2H_{2}O$ $KNO_{2}(\ell) + KNO_{3}(\ell) + Cr_{2}O_{3}(s) \longrightarrow$ $2K_{2}CrO_{4}(s,\ell) + 4NO$	colourless gas , neutral
Dinitrogen trioxide [Nitrogen(III) oxide]	N <sub>2</sub> O <sub>3</sub>	+ 3	$2 \text{ NO} + \text{N}_2\text{O}_4 \xrightarrow{250 \text{ K}} 2 \text{ N}_2\text{O}_3$	blue solid/liquid , acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO <sub>2</sub>	+ 4	$2 \operatorname{Pb}(\operatorname{NO}_3)_2 \xrightarrow{673 \text{ K}} 4 \operatorname{NO}_2 + 2 \operatorname{PbO} + \operatorname{O}_2$ Cu +4HNO <sub>3</sub> $\longrightarrow$ Cu(NO <sub>3</sub> ) <sub>2</sub> + 2NO <sub>2</sub> + 2H <sub>2</sub> O (conc.)	brown gas, acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N <sub>2</sub> O <sub>4</sub>	+ 4	$2 \text{ NO}_2 \xrightarrow{\text{cool}} \text{N}_2\text{O}_4$	colourless solid / liquid , acidic
Dinitrogen pentoxide [Nitrogen(IV) oxide]	N <sub>2</sub> O <sub>5</sub>	+ 5	$4 \text{ HNO}_3 + P_4O_{10} \longrightarrow 4 \text{ HPO}_3 + 2 \text{ N}_2O_5$ $2 \text{ NO}_2 + O_3 \longrightarrow \text{ N}_2O_5 + O_2$	colourless solid, acidic

#### **Properties :**

N<sub>2</sub>O: It is poisonous and when inhaled in small quantities if causes hysterical laughing.

Supporter of combustion : Mg + N<sub>2</sub>O 
$$\longrightarrow$$
 MgO + N<sub>2</sub>  
P<sub>4</sub> + 10N<sub>2</sub>O  $\longrightarrow$  P<sub>4</sub>O<sub>10</sub>

 $\begin{array}{l} 5\mathrm{H_2} + 2\mathrm{NO} \xrightarrow{\mathrm{Pt-black}} 2\mathrm{NH_3} + 2\mathrm{H_2O} \\ \mathrm{SO_2} + \mathrm{H_2O} + 2\mathrm{NO} \longrightarrow \mathrm{H_2SO_4} + \mathrm{N_2O} \end{array}$ 

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

(b) Reducing properties (oxidation of NO) :

$$2NO + X_2 \longrightarrow 2NOX (X = Cl or Br)$$

 $6KMnO_4 + 9H_2SO_4 + 10NO \longrightarrow 3K_2SO_4 + 6MnSO_4 + 4H_2O + 10HNO_3$ 

- (c) On lowering the temperature paramagnetic nature of NO decreases and in the liquid state it becomes diamagnetic in nature.
- $N_2O_3$ : (a) It is anhydride of  $HNO_2$ :

$$2HNO_2 \longrightarrow N_2O_3 + H_2O_3$$

(b) 
$$N_2O_3 + KOH \longrightarrow 2KNO_2 + H_2O$$

 $NO_2$ : (a)  $N_2O_4$  is mixed anhydride of  $HNO_3$  and  $HNO_2$ 

(b)  $NO_2 - N_2O_4$  system is a strong oxidising agent.

$$2NO_2 + CI_2 \longrightarrow 2NO_2CI$$

$$2NO_2 + 4HCI \longrightarrow 2NOCI + CI_2 + H_2O$$

(c) As reducing agent :  $SO_2 + H_2O + NO_2 \longrightarrow H_2SO_4 + NO$ 



 $N_2O_5$ : (a) It is anhydride of HNO<sub>3</sub>

- (b)  $2N_2O_5 \xrightarrow{\Delta} 2N_2O_4 + O_2$
- (c)  $N_2O_5 + 2NaOH \longrightarrow 2NaNO_3 + H_2O$

(d)  $N_2O_5 + I_2 \longrightarrow 10 NO_2 + I_2O_5$ 

- (e)  $N_2O_5 + NaCI \longrightarrow NaNO_3 + NO_2CI$
- (f)  $N_2O_5 + 3H_2SO_4 \longrightarrow H_3O^+ + 2NO_2^+ + 3HSO_4^-$

### **OXY ACIDS OF NITROGEN :**

(1)	Nitrous Acid : HNO <sub>2</sub>	(2) Nitric Acid : HNO <sub>3</sub>	(3)	Per Nitrous Acid : HOONC
-----	---------------------------------	------------------------------------	-----	--------------------------

(4) Per Nitric Acid :  $HNO_4$  (5) Hypo Nitrous Acid :  $H_2N_2O_2$ .

## NITROUS ACID (HNO,):

#### **Preparation :**

- (i) By acidifying an aqueous solution of a nitrite Ba(NO<sub>2</sub>)<sub>2</sub> + H<sub>2</sub>SO<sub>4</sub>  $\longrightarrow$  2HNO<sub>2</sub> + BaSO<sub>4</sub> $\downarrow$
- (ii) By passing an equimolar mixture of NO and NO<sub>2</sub> into water: NO + NO<sub>2</sub> + H<sub>2</sub>O  $\longrightarrow$  2HNO<sub>2</sub>

### **Properties:**

- (i) It is an unstable, weak acid which is known only in aqueous solution.
- (ii) On trying to concentrate, the acid decomposes as given below.

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

(iii) 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.

 $2\mathsf{KI} + 2\mathsf{HNO}_2 + 2\mathsf{HCI} \longrightarrow 2\mathsf{H}_2\mathsf{O} + 2\mathsf{NO} + 2\mathsf{KCI} + \mathsf{I}_2$ 

(iv) With strong oxidizing agents like KMnO<sub>4</sub> nitrous acid and nitrites function as reducing agents and get oxidized to NO<sub>3</sub><sup>-</sup> ions:

 $2KMnO_4 + 5KNO_2 + 6HCI \longrightarrow 2MnCl_2 + 5KNO_3 + 3H_2O + 2KCI$ 

#### NITRIC ACID (HNO<sub>3</sub>):

Commonly called as *Aqua Fortis*. This indicates that strong water, when it falls on skin it causes mild burning.

#### **Preparation :**

(ii)

#### **Ostwald Process :**

(i) In the laboratory, nitric acid is prepared by heating  $KNO_3$  or  $NaNO_3$  and concentrated  $H_2SO_4$  in a glass retort.

 $NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$ 

On a large scale it is prepared mainly by Ostwald's process. This method is based upon catalytic oxidation of NH, by atmospheric oxygen.

$$4 \text{ NH}_{3}(g) + 5 \text{ O}_{2}(g) \text{ (from air)} \xrightarrow{\text{Pt/Rh gauge catalyst}} 500 \text{ K}, 9 \text{ bar} \rightarrow 4 \text{ NO}(g) + 6 \text{ H}_{2}\text{O}(g)$$

Nitric oxide thus formed combines with oxygen giving NO2.

$$2 \text{ NO}(g) + O_2(g) \Longrightarrow 2 \text{ NO}_2(g)$$

Nitrogen dioxide so formed, dissolves in water to give  $HNO_3$ .

$$3 \operatorname{NO}_2(g) + \operatorname{H}_2O(\ell) \longrightarrow 2 \operatorname{HNO}_3(\operatorname{aq}) + \operatorname{NO}(g)$$

NO thus formed is recycled and the aqueous  $HNO_3$  can be concentrated by distillation upto ~ 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated  $H_2SO_4$ .

## Properties :

#### 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  $HNO_3$  by mass and has a specific gravity of 1.504.

In the gaseous state,  $HNO_3$  exists as a planar molecule.

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

$$HNO_3$$
 (aq) +  $H_2O(\ell) \longrightarrow H_3O^+$  (aq) +  $NO_3^-$  (aq)



(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, AI) do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

#### Reactions of Elements (Metals/Metalloids with HNO<sub>3</sub>) Nature of HNO Changes to Reactions

#### (A) Metals placed above H in electrochemical series (ECS) 1 Ma Ma cold and dilute

Element

1. Mg, Mn 2. Zn, Fe	cold and dilute (a) very dilute (b) dilute (c) concentrated	M(NO <sub>3</sub> ) <sub>2</sub> NH <sub>4</sub> NO <sub>3</sub> N <sub>2</sub> O NO <sub>2</sub>	$M + 2HNO_3 \rightarrow M(NO_3)_2 + H_2$ $4Zn+10HNO_3 \rightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$ $4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$ $Zn + 4HNO_3 \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$
			Fe becomes passive with 80% $HNO_3$
<b>3.</b> Sn	(a) dilute (b) concentrated	NH <sub>4</sub> NO <sub>3</sub> NO <sub>2</sub>	$\begin{array}{rl} 4\text{Sn}+10\text{HNO}_3 \rightarrow 4\text{Sn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O} \\ \text{Sn} + 4\text{HNO}_3 \rightarrow \text{H}_2\text{SnO}_3 & + & 4\text{NO}_2 + \text{H}_2\text{O} \\ & \text{meta stannic acid} \end{array}$
<b>4.</b> Pb	(a) dilute (b) concentrated	NO NO <sub>2</sub>	$\begin{array}{l} 3Pb+8HNO_3\rightarrow 3Pb(NO_3)_2+2NO+4H_2O\\ Pb+4HNO_3\rightarrow Pb(NO_3)_2+2NO_2+2H_2O \end{array}$
(B) Metals below H in ECS			
<b>5.</b> Cu, Ag,Hg	(a) dilute	NO	$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O.$ Hg forms Hg <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub>
	(b) concentrated	NO <sub>2</sub>	$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$
(C) Metalloids			
Sb, As	concentrated	NO <sub>2</sub>	Sb + 5HNO <sub>3</sub> $\rightarrow$ H <sub>3</sub> SbO <sub>4</sub> + 5NO <sub>2</sub> + H <sub>2</sub> O antimonic acid

(ii) Concentrated nitric acid also oxidises non-metals and their compounds. lodine is oxidised to iodic acid, carbon to carbon dioxide, sulphur to H<sub>2</sub>SO<sub>4</sub> and phosphorus to phosphoric acid.

 $I_{2} + 10 \text{ HNO}_{3} \longrightarrow 2 \text{ HIO}_{3} + 10 \text{ NO}_{2} + 4 \text{ H}_{2}\text{O}$  $C + 4 \text{ HNO}_{3} \longrightarrow CO_{2} + 2 \text{ H}_{2}\text{O} + 4 \text{ NO}_{2}$  $S_8 + 48 HNO_3$  (concentrated)  $\longrightarrow 8 H_2SO_4 + 48 NO_2 + 16 H_2O$  $P_4 + 20 HNO_3$  (concentrated)  $\longrightarrow 4 H_3PO_4 + 20 NO_2 + 4 H_2O$ 

#### **PHOSPHORUS:**

It occurs in nature in the form of stable phosphates. (Animal bones also contain calcium phosphate (58%)). The important minerals are:

(i) Phosphorite, $Ca_3(PO_4)_2$	(ii) Chloraptite, $Ca_3(PO_4)_2CaCl_2$	
(iii) Fluoraptite, $Ca_3(PO_4)_2CaF_2$	(iv) Vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$	(v) Redonda phosphate, $AIPO_4$

ALLOTROPIC FORMS OF PHOSPHORUS :

White or yellow phosphorus (P<sub>1</sub>) : (i)

#### **Preparation :**

 $2Ca_3(PO_4)_2$  (from bone-ash) + 10C + 6SiO<sub>2</sub>  $\longrightarrow$  6CaSiO<sub>3</sub> + 10CO + P<sub>4</sub>(s) (electric furnace method)

#### **Properties :**

It is white-to-transparent and soft waxy solid. It is soluble in CS, but insoluble in water. It glows in dark due to slow oxidation producing yellowish-green light. This phenomenon is called phosphorescence

 $P_4 + 5O_2 \rightarrow P_4O_{10}$ 

White phosphorus is poisonous. It undergoes oxidation in the presence of air which slowly raises its temperature and due to its low ignition temperature (~ 30°C) after a few moments it catches fire spontaneously. Due to this reason, it is stored under water.



It exist as tetrahedral  $P_{4}$  molecule and tetrahedral structure remains in the liquid and gaseous states.



#### (ii) Red phosphorus:

#### **Preparation :**

When white phosphorus is heated in the atmosphere of  $CO_2$  or coal gas at 573 K red phosphorus is produced. This red phosphorus may still contain some white phosphorus which is removed by boiling the mixture with NaOH where white phosphorus is converted into PH<sub>3</sub> gas but red phosphorus remains inert.

$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3(g) + 3NaH_2PO_2$$

It is also prepared by heating white phosphorus with a few crystals of iodine catalyst at 250°C for a few hours in a closed iron vessel fitted with a safety valve.

#### **Properties :**

It is a reddish-violet crystalline solid. It is stable in air and does not ignite unless it is heated to 400°C. It is less reactive than white phosphorus and does not dissolve in liquid  $CS_2$ . This is a polymeric substance forming linear chains like this.



(iii) Black phosphorus has two forms  $\alpha$ -black phosphorus and  $\beta$ -black phosphorous,  $\alpha$ -black phosphorus is formed when red phosphorus is heated in a sealed tube at 803 K. It can be sublimed in air and has opaque monoclinic or rhombohedral crystal. It does not oxidise in air,  $\beta$ -black phosphorus is prepared by heating white phosphorus at 473 K under high pressure. It does not burn in air upto 673 K.

 $\beta$ -black phosphorus is a good conductor of electricity whereas  $\alpha$ -black phosphorous is non-conductor.  $\beta$ -black phosphorus has layered structure like graphite. The distance between the two layers is found to be 3.68 Å.



**Density :** White phosphorus= 1.83; Red phosphorus = 2.20; Black phosphorus = 2.70 gm/cc; As polymerisation increases compactness increases and therefore, density increases.

#### Chemical properties of phosphorus :

Reactivity of the various allotropic forms of phosphorus towards other substances decreases in the order: white > red > black, the last one being almost inert i.e. most stable. Apart from their reactivity difference, all the forms are chemically similar.

(i) White phosphorus burns in air to form phosphorus trioxide and pentoxide.

$$P_4 + 3O_2 \longrightarrow P_4O_6$$
 (limited supply of air) ;  $P_4 + 5O_2 \longrightarrow P_4O_{10}$  (excess of air)

Red and other forms of phosphorus also burn in air or oxygen but on heating.

- (ii) When white phosphorus is heated with CaO and water phosphine gas is evolved.  $3CaO + 8P + 9H_2O \longrightarrow 3Ca(H_2PO_2)_2 + 2PH_3$
- (iii) When heated with concentrated H<sub>2</sub>SO<sub>4</sub>, phosphorus is oxidized to H<sub>3</sub>PO<sub>4</sub>. 2P + 5H<sub>2</sub>SO<sub>4</sub>  $\xrightarrow{\Lambda}$  2H<sub>3</sub>PO<sub>4</sub> + 5SO<sub>2</sub>↑ + 2H<sub>2</sub>O



## COMPOUNDS OF PHOSPHORUS : PHOSPHINE :

#### **Preparation :**

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

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

(ii) In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO<sub>2</sub>.

 $P_4 + 3 NaOH + 3 H_2O \longrightarrow PH_3 + 3 NaH_2PO_2$ (sodium hypophosphite)

When pure, it is non inflammable but becomes inflammable owing to the presence of  $P_2H_4$  or  $P_4$  vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH<sub>4</sub>I) which on treating with KOH gives off phosphine.

$$PH_4I + KOH \longrightarrow KI + H_2O + PH_3$$

(iii) It is prepared by hydrolysis of metal phosphides with acids.

$$2Na_{3}P + 3H_{2}SO_{4} \longrightarrow 3Na_{2}SO_{4} + 2PH_{3}\uparrow; \qquad Ca_{3}P_{2} + 6HCI \longrightarrow 3CaCl_{2} + 2PH_{3}\uparrow;$$

#### **Properties:**

- (i) It is a colourless gas with a slightly garlic or rotten fish smell and is highly poisonous. It explodes in contact with traces of oxidising agents like  $HNO_3$ ,  $CI_2$  and  $Br_2$  vapours.
- (ii) It is slightly soluble in water but soluble in  $CS_2$  and other organic solvents. The solution of  $PH_3$  in water decomposes in presence of light giving red phosphorus and  $H_2$ .
- (iii) When absorbed in copper sulphate or mercuric chloride, the corresponding phosphides are obtained.

$$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 \downarrow + 3H_2SO_4$$

$$3HgCl_2 + 2 PH_3 \longrightarrow Hg_3P_2 \downarrow$$
 (brownish black) + 6 HCl

(iv) Phosphine on heating at 150°C burns forming  $H_3PO_4$ 

$$PH_3 + 2O_2 \longrightarrow H_3PO_4$$

#### Uses :

The spontaneous combustion of phosphine is technically used in Holme's signals. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.

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 pentaoxide and that acts as smoke screens.

#### **OXIDES OF PHOSPHORUS :**

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

It is dimeric and has formula P<sub>4</sub>O<sub>6</sub>

#### **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  $P_4O_6$ .

$$P_4 + 3O_2 \longrightarrow P_4O_6$$

#### **Properties :**

- (i) It is colourless crystalline solid having melting point 23.8°C and boiling point 178°C.
- (ii) It dissolves in cold water to form phosphorus acid. It is thus the anhydride of phosphorus acid.

 $P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$ 

(iii) It dissolves in hot water liberating PH<sub>3</sub>

$$P_4O_6 + 6H_2O \longrightarrow 3H_3PO_4 + PH_3$$

(iv) It slowly gets oxidized in air to form  $P_4O_{10}$ 

$$P_4O_6 + 2O_2 \longrightarrow P_4O_{10}$$



(v)

## It burns in Cl<sub>2</sub> gas forming phosphorus oxytrichloride (POCl<sub>3</sub>) and phosphoryl chloride (PO<sub>2</sub>Cl) P<sub>4</sub>O<sub>6</sub> + 4Cl<sub>2</sub> $\longrightarrow$ 2POCl<sub>3</sub> + 2PO<sub>2</sub>Cl

## PHOSPHORUS PENTAOXIDE ( $P_4 O_{10}$ ):

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

### **Preparation :**

It is obtained by burning phosphorus in excess air.

 $P_4 + 5O_2 \longrightarrow P_4O_{10}$ 

## **Properties:**

- (i) It is a white powder ,acidic in nature and is the anhydride of orthophosphoric acid.
- (ii) It sublimes on heating at 250°C.
- (iii) It dissolves in water with hissing sound forming metaphosphoric acid and finally orthophosphoric acid.

$$\mathsf{P}_4\mathsf{O}_{10} + 2\mathsf{H}_2\mathsf{O} \longrightarrow 4\mathsf{HPO}_3; \quad 4\mathsf{HPO}_3 + 2\mathsf{H}_2\mathsf{O} \longrightarrow 2\mathsf{H}_4\mathsf{P}_2\mathsf{O}_7; \quad 2\mathsf{H}_4\mathsf{P}_2\mathsf{O}_7 + 2\mathsf{H}_2\mathsf{O} \longrightarrow 4\mathsf{H}_3\mathsf{PO}_4$$

(iv) It dehydrates concentrated  $H_2SO_4$  and concentrated  $HNO_3$  to  $SO_3$  and  $N_2O_5$  respectively.

$$4\text{HNO}_3 + \text{P}_4\text{O}_{10} \xrightarrow{\text{distillation}} 4\text{HPO}_3 + 2\text{N}_2\text{O}_5 \ ; \ 2\text{H}_2\text{SO}_4 + \text{P}_4\text{O}_{10} \xrightarrow{\text{distillation}} 4\text{HPO}_3 + 2\text{SO}_3$$

 $\succ \qquad 2CH_{3}CONH_{2} + P_{4}O_{10} \longrightarrow 4HPO_{3} + 2CH_{3}CN; 4CH_{3}COOH + P_{4}O_{10} \longrightarrow 4HPO_{3} + 2(CH_{3}CO)_{2}O$ 

# OXY ACIDS OF PHOSPHORUS : PHOSPHORUS ACID $(H_3PO_3)$ :

## **Preparation** :

- (i) By dissolving  $P_4O_6$  in water :  $P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$
- (ii) By hydrolysis of  $PCI_3$  with water :  $PCI_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCI$

The solution containing  $H_3PO_3$  and HCl is heated to 180°C and HCl gas is driven out. The resulting solution on crystallization gives white crystals of  $H_3PO_3$ .

## **Properties :**

- (i) It is a white crystalline solid, soluble in water and having melting point of 74°C.
- (ii) When neutralized with bases or alkalies, it forms neutral salts called phosphites which are unstable.

$$H_3PO_3 + NaOH \longrightarrow NaH_2PO_3 + H_2O$$
  
 $NaH_2PO_3 + NaOH \longrightarrow Na_2HPO_3 + H_2O$ 

- (iii)  $4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$  (disproportionation)
- (iv) It is a strong reducing agent :
  - (a) Reduces  $AgNO_3$  to Ag.

 $HPO_{3}^{2-} + 2Ag^{+} \longrightarrow 2Ag^{\downarrow} (black) + H_{3}PO_{4}$ 

(b) Mercury (II) chloride on warming with excess of the phosphite solution gives grey metallic mercury.  $HPO_3^{2-} + 2HgCI_2 + H_2O \longrightarrow Hg_2CI_2 \downarrow$  (white)  $+ 2CI^- + H_3PO_4$  $Hg_2CI_2 \downarrow$  (white)  $+ HPO_3^{2-} + H_2O \longrightarrow 2Hg \downarrow$  (grey)  $+ 2CI^- + H_3PO_4$ 

## ORTHOPHOSPHORIC ACID (H<sub>3</sub>PO<sub>4</sub>):

## Preparation :

(i) By heating calcium phosphate with concentrated  $H_2SO_4$ 

 $Ca_{3}(PO_{4})_{2} + 3H_{2}SO_{4} \longrightarrow 2CaSO_{4} + 2H_{3}PO_{4}$ 

 $CaSO_4$  is insoluble. Solution of  $H_3PO_4$  is separated from  $CaSO_4$ . It is then concentrated by evaporating it at 180°C and dehydrated by concentrated  $H_2SO_4$  placed in a vacuum desiccator cooled by freezing mixture. White crystals of  $H_3PO_4$  are thus formed.



- (ii) By hydrolysis of  $PCI_{5}$ :  $PCI_{5} + 4H_{2}O \longrightarrow H_{3}PO_{4} + 5HCI$
- (iii) By heating white phosphorus with concentrated HNO<sub>3</sub> : P + 5HNO<sub>3</sub>  $\longrightarrow$  H<sub>3</sub>PO<sub>4</sub> + 5NO<sub>2</sub> + H<sub>2</sub>O

#### **Properties :**

(i) Pure orthophosphoric acid is a white crystalline solid highly soluble in water having melting point of 42°C. It is a weak acid. It forms two acid salts and one normal salt.

#### (ii) Reaction with silver nitrate :

 $\begin{array}{l} \mathsf{HPO}_4^{2-} + 3\mathsf{Ag}^{+} \longrightarrow \mathsf{Ag}_3\mathsf{PO}_4 \downarrow (\mathsf{yellow}) + \mathsf{H}^{+} \\ \mathsf{Ag}_3\mathsf{PO}_4 \downarrow (\mathsf{yellow}) + 6\mathsf{NH}_3 \longrightarrow 3 \left[\mathsf{Ag}(\mathsf{NH}_3)_{2}\right]^{+1} + \mathsf{PO}_4^{2-} \end{array}$ 

#### (iii) Neutralization with alkalies or bases :

 $H_3PO_4 \xrightarrow{NaOH} NaH_2PO_4$  (pri. phosphate)  $\xrightarrow{NaOH} Na_2HPO_4$  (sec. phosphate)  $\xrightarrow{NaOH} Na_3PO_4$  (tert. phosphate)

#### (iv) Action of heat :

 $\triangleright$ 

 $H_{3}PO_{4} \xrightarrow{220^{\circ}C} H_{4}P_{2}O_{7}$  (pyrophosphoric acid);  $H_{4}P_{2}O_{7} \xrightarrow{316^{\circ}C} HPO_{3}$  (metaphosphoric acid) Na $H_{2}PO_{4} \xrightarrow{\Delta} NaPO_{3} + H_{2}O$ 

 $2Na_2HPO_4 \xrightarrow{\Lambda} Na_4P_2O_7 + H_2O_7$ 

 $Na(NH_4)HPO_4 \xrightarrow{\Delta} NaPO_3 + NH_3^{\uparrow} + H_2O$ 

### **Oxoacids of Phosphorus**

Name	Formula	Oxidation state of Phosphorus	Characteristic bonds and their number	Preparation
Hypohosphorous (Phosphinic)	H <sub>3</sub> PO <sub>2</sub>	+1	One P – OH Two P – H One P = O	white $P_4$ + alkali
Orthophosphorous (Phosphonic)	H <sub>3</sub> PO <sub>3</sub>	+3	Two P – OH One P – H One P = O	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+3	Two P – OH Two P – H Two P = O	PCI <sub>3</sub> +H <sub>3</sub> PO <sub>3</sub>
Hypohosphoric	$H_4P_2O_6$	+4	Four P – OH Two P = O One P – P	red P₄+ alkali
Orthophosphoric	$H_{3}PO_{4}$	+5	Three P – OH One P = O	$P_4O_{10}+H_2O$
Pyrophosphoric	$H_4P_2O_7$	+5	Four P – OH Two P = O One P – O – P	heat phosphoric acid
Metaphosphoric*	(HPO₃),	+5	Three P – OH Three P = O Three P – O – P	Phosphorus acid + Br <sub>2</sub> , heat in a sealed tube

Exists in polymeric forms only. Characteristic bonds of (HPO<sub>3</sub>)<sub>3</sub> have been given in the Table.



The chemical compositions of the various oxoacids are interrelated in terms of loss or gain of  $H_2O$  molecule or O-atom. The structures of some important oxoacids are given below:

HO

ОН





 $H_4P_2O_7$ Pyrophosphoric acid

0



H<sub>3</sub>PO<sub>3</sub>

Orthophosphorous acid



H<sub>3</sub>PO<sub>2</sub> Hypophosphorous acid





Cyclotrimetaphosphoric acid,  $(HPO_3)_3$  Polymetaphosphoric acid,  $(HPO_3)_n$ 

#### **PHOSPHORUS HALIDES :**

Phosphorus can form two types of halides,  $PX_3$  (X = F, CI, Br, I) and  $PX_5$  (X = F, CI, Br). **PHOSPHORUS TRICHLORIDE :** 

#### **Preparation** :

- (i) It is obtained by passing dry chlorine over heated white phosphorus.
  - $P_4 + 6Cl_2 \rightarrow 4PCl_2$
- (ii) It is also obtained by the action of thionyl chloride with white phosphorus.

 $P_4 + 8SOCI_2 \rightarrow 4PCI_3 + 4SO_2 + 2S_2CI_2$ 

#### Properties :

(i) It is a colourless oily liquid and hydrolyses in the presence of moisture.

 $PCI_3 + 3H_2O \rightarrow H_3PO_3 + 3HCI$ 

(ii) It reacts with organic compounds containing -OH group such as

CH<sub>3</sub>COOH, C<sub>2</sub>H<sub>5</sub>OH.

 $3CH_3COOH + PCI_3 \rightarrow 3CH_3COCI + H_3PO_3$  $3C_2H_5OH + PCI_3 \rightarrow 3C_2H_5CI + H_3PO_3$ 

#### PHOSPHORUS PENTACHLORIDE :

#### **Preparation :**

(i) Phosphorus pentachloride is prepared by the reaction of white phosphorus with excess of dry chlorine.  $P_4 + 10Cl_2 \rightarrow 4PCl_5$ 

(ii) It can also be prepared by the action of SO2Cl2 on phosphorus.

 $P_4 + 10SO_2 CI_2 \rightarrow 4PCI_5 + 10SO_2$ 

### **Properties :**

(i)  $PCI_5$  is a yellowish white powder and in moist air, it hydrolyses to  $POCI_3$  and finally gets converted to phosphoric acid.

 $PCI_5 + H_2O \rightarrow POCI_3 + 2HCI_3$ 

 $POCI_3 + 3H_2O \rightarrow H_3PO_4 + 3HCI$ 

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

 $PCI_5 \longrightarrow PCI_3 + CI_2$ 

(iii) It reacts with organic compounds containing –OH group converting them to chloro derivatives.

 $C_2H_5OH + PCI_5 \rightarrow C_2H_5CI + POCI_3 + HCI$ 

 $CH_3COOH + PCI_5 \rightarrow CH_3COCI + POCI_3 + HCI$ 

(iv)Finely divided metals on heating with  $PCI_5$  give corresponding chlorides.

$$2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$$

$$Sn + 2PCl_5 \rightarrow SnCl_4 + 2PCl_3$$

(v) It is used in the synthesis of some organic compounds, e.g.,  $C_2H_5CI$ ,  $CH_3COCI$ .



#### FERTILIZER : PHOSPHATE FERTILIZERS :

- (a) These are phosphorus containing direct fertilizers.
- (b) Important function of Phosphourus :
  - (1) It stimulates root formation.
  - (2) It stimulates rapid growth.
- (c) Types of phosphateFertilizers :

(i) 
$$[3(Ca_{3}(PO_{4})_{2}CaF_{2}) + 7H_{2}SO_{4} \longrightarrow \frac{3Ca(H_{2}PO_{4})_{2} + 7CaSO_{4}}{Super phosphate} + 2HF$$

(ii)  $[3(Ca_{3}(PO_{4})_{2}CaF_{2}) + 14H_{3}PO_{4} \longrightarrow \underbrace{\frac{10 Ca(H_{2}PO_{4})_{2}}{\text{triple super phosphate}} + 2HF$ 

 $H_3PO_4$  is used to avoid the formation of the insoluble CaSO<sub>4</sub> (waste product).

### **GROUP 16 ELEMENTS : THE OXYGEN FAMILY :**

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.

### State and Nature :

- (a) Only  $O_2$  in gaseous state and rest all are solid.
- $\therefore$  Only form  $p\pi p\pi$  bond.
- (b) O and S both non metal
- (c) Se and Te are metalloids.
- (d) Po is metallic.

### Occurrence:

Oxygen is the most abundant of all the elements on the earth. Oxygen forms about 46.6% by mass of earth's crust . Dry air contains 20.946% oxygen by volume.

However, the abundance of sulphur in the earth's crust is only 0.03-0.1%. Combined sulphur exists primarily as sulphates such as gypsum  $CaSO_4.2H_2O$ , epsom salt  $MgSO_4.7H_2O$ , baryta  $BaSO_4$  and sulphides such as galena PbS, zinc blende ZnS, copper pyrites  $CuFeS_2$ . Traces of sulphur occur as hydrogen sulphide in volcanoes.

Selenium and tellurium are also found as metal selenides and tellurides in sulphide ores. Polonium occurs in nature as a decay product of thorium and uranium minerals.

## **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.

#### 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.

#### 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.

#### **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.



### 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.

#### Melting Point and Boiling Point :

From oxygen to tellurium melting and boiling points go on increasing. The M.P. of polonium is less than tellurium.

### Allotropy and Allotropic Forms :

Oxygen has two allotropes  $O_2$  and  $O_3$ . The type of allotropy is called as monotropy. Sulphur has number of allotropic forms. The most common are Rhombic sulphur, monolinic sulphur, plastic sulphur, colloidal sulphur etc.

### **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 ( $O_2$ ) whereas sulphur exists as polyatomic molecule ( $S_8$ ).

#### Catenation :

Tendency for catenation decreases down the group. This property is prominently displayed by sulphur ( $S_8$ ). 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.

Element		0	S	Se	Те
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
lonization enthalpy / (kJ mol <sup>-1</sup> )	Ι	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

## ATOMIC AND PHYSICAL PROPERTIES

## **Chemical Properties :**

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. Since electronegativity of oxygen is very high, it shows only negative oxidation states as -2 except in the case of  $OF_2$  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 oxidations 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.



- HNO<sub>3</sub> oxidises sulphur to  $H_2SO_4$  (S + VI) but only oxidises selenium to  $H_2SeO_3$  (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.
- Polonium shows metallic properties since it dissolves in  $H_2SO_4$ , HF, HCI and HNO<sub>3</sub> forming pink solution of Po<sup>II</sup>. However Po<sup>II</sup> is strongly radio active and the  $\alpha$ -emission decomposes the water and the Po<sup>II</sup> is quickly oxidised to yellow solution of Po<sup>IV</sup>.

#### Anomalous behaviour of oxygen :

The anomalous behaviour of oxygen, like other member of p-block present in second period is due to its small size and high electronegativity. One typical example of effects of small size and high electronegativity is the presence of strong hydrogen bonding in  $H_2O$  which is not found in  $H_2S$ .

The absence of d orbitals in oxygen limits its covalency to four and in practice, rarely increases beyond two. On the other hand, in case of other elements of the group, the valence shell can be expanded and covalence exceeds four.

(i) **Reactivity with hydrogen :** All the elements of group 16 form hydrides of the type  $H_2E$  (E = S, Se, Te, Po). Some properties of hydrides are given in Table. Their acidic character increases from  $H_2O$  to  $H_2Te$ . The increase in acidic character can be understood in terms of decrease in bond (H-E) dissociation enthalpy down the group. Owing to the decrease in bond (H-E) dissociation enthalpy down the group , the thermal stability of hydrides also decreases from  $H_2O$  to  $H_2Po$ . All the hydrides except water possess reducing property and this property increases from  $H_2S$  to  $H_2Te$ .

Property	H <sub>2</sub> O	H₂S	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
∆ <sub>f</sub> H/kJ mol <sup>-1</sup>	-286	-20	73	100
∆ <sub>diss</sub> H (H-E)/kJ mol⁻¹	463	347	276	238
Dissociation constant <sup>a</sup>	1.8 × 10 <sup>-16</sup>	1.3 × 10 <sup>-7</sup>	1.3 × 10 <sup>-4</sup>	2.3 × 10 <sup>-3</sup>

**PROPERTIES OF HYDRIDES OF GROUP 16 ELEMENTS** 

- (ii) **Reactivity with 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>; SO<sub>2</sub> is reducing while TeO<sub>2</sub> is an oxidising agent. Besides EO<sub>2</sub> type sulphur, selenium and tellurium also form EO<sub>3</sub> type oxides (SO<sub>3</sub>, SeO<sub>3</sub>, TeO<sub>3</sub>). Both types of oxides are acidic in nature.
- (iii) Reactivity toward the halogens : Elements of group 16 form a larger number of halides of the type  $EX_6$ ,  $EX_4$  and  $EX_2$  where E is an element of the group -16 and X is an halogen. The stabilities of the halides decrease in the order F > CI > Br > I. 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,  $SF_4$  is a gas,  $SeF_4$  liquid and  $TeF_4$  a solid These fluorides have  $sp^3d$  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  $S_2F_2$ ,  $S_2Cl_2$ ,  $S_2Br_2$ ,  $Se_2Cl_2$  and  $Se_2Br_2$ . These dimeric halides undergo disproportionation as given below :

$$2Se_2Cl_2 \longrightarrow SeCl_4 + 3Se.$$



### DIOXYGEN (O<sub>2</sub>):

It differs from the remaining elements of the VI<sup>th</sup> group because of the following properties. (A) small size (B) high electronegativity and (C) non-availability of d-orbitals.

#### **Preparation :**

2

(i) By thermal decomposition of oxides of metals.

HgO 
$$\xrightarrow{450^{\circ}C}$$
 2 Hg + O<sub>2</sub>; 2 Ag<sub>2</sub>O  $\xrightarrow{350^{\circ}C}$  4 Ag + O<sub>2</sub>

(ii) By thermal decomposition of oxygen rich compounds.

$$(CIO_3 \longrightarrow 2 \text{ KCl} + 3O_2 \text{ (laboratory method)}; 4 \text{ K}_2\text{Cr}_2\text{O}_7 \longrightarrow 4 \text{ K}_2\text{CrO}_4 + 2 \text{ Cr}_2\text{O}_3 + 3O_2 \text{ (laboratory method)};$$

(iii) By the action of concentrated  $H_2SO_4$  on  $MnO_2$ .

$$2 \operatorname{MnO}_2 + 2\operatorname{H}_2\operatorname{SO}_4 \longrightarrow 2 \operatorname{MnSO}_4 + 2\operatorname{H}_2\operatorname{O} + \operatorname{O}_2$$

(iv) By the action of concentrated  $H_2SO_4$  on KMnO<sub>4</sub> or  $K_2Cr_2O_7$ .

$$4 \text{ KMnO}_4 + 6 \text{ H}_2\text{SO}_4 \longrightarrow 2 \text{ K}_2\text{SO}_4 + 4\text{MnSO}_4 + 6\text{H}_2\text{O} + 5\text{O}_2;$$

$$2 \operatorname{K}_{2}\operatorname{Cr}_{2}\operatorname{O}_{7} + 8\operatorname{H}_{2}\operatorname{SO}_{4} \longrightarrow 2 \operatorname{K}_{2}\operatorname{SO}_{4} + 2\operatorname{Cr}_{2}(\operatorname{SO}_{4})_{3} + 8\operatorname{H}_{2}\operatorname{O} + 3\operatorname{O}_{2}$$

#### (vi) By Catalytic decomposition of hypochlorites :

$$2 \text{ HOCI} \xrightarrow{\text{Co}^{2+}} 2 \text{HOCI} + \text{O}_2$$

#### (vii) By Brins process (mfg.) :

$$2 \text{ BaO} + \text{O}_2(\text{air}) \xrightarrow{500^{\circ}\text{C}} 2\text{BaO}_2$$
;  $2 \text{ BaO}_2 \xrightarrow{800^{\circ}\text{C}} 2 \text{ BaO} + \text{O}_2$ 

#### **Properties :**

Colourless, odourless and tasteless gas. It is paramagnetic and exhibits allotropy. Three isotopes of oxygen are  ${}^{16}_{8}$ O,  ${}^{17}_{8}$ O and  ${}^{18}_{8}$ O. Oxygen does not burn but is a strong supporter of combustion.

#### **OXIDES**:

#### (i) Acidic oxides :

The covalent oxides of non-metal are usually acidic; dissolves in water to produce solutions of acids e.g.,  $CO_2$ ,  $SO_2$ ,  $SO_3$ ,  $N_2O_5$ ,  $N_2O_3$ ,  $P_4O_6$ ,  $P_4O_{10}$ ,  $CI_2O_7$ ,  $CrO_3$ ,  $Mn_2O_7$  etc. They are termed as acid anhydride.  $CI_2O_7 + H_2O \longrightarrow 2 HCIO_4$ ;  $Mn_2O_7 + H_2O \longrightarrow 2 HMnO_4$ 

#### (ii) Basic oxides :

Metallic oxides are generally basic oxides. They either dissolve in water to form alkalies or combine with acids to form salts and water or combine with acidic oxides to form salts; e.g., Na<sub>2</sub>O, CaO. CuO, FeO, BaO etc.

$$Na_{2}O + H_{2}O \longrightarrow 2 NaOH$$
;  $CaO + H_{2}O \longrightarrow Ca(OH)_{2}$ ;  $CuO + H_{2}SO_{4} \longrightarrow CuSO_{4} + H_{2}O$ 

The metallic oxides with lowest oxidation sate is the most ionic and the most basic but with increasing oxidation sate the acidic character increases e.g., CrO is basic, Cr<sub>2</sub>O<sub>2</sub> amphoteric and CrO<sub>2</sub> acidic.

#### (iii) Neutral Oxides :

They neither combine with acids nor with the bases to form salts e.g., CO, N<sub>2</sub>O, NO etc.

#### (iv) Amphoteric Oxides :

Many metals yield oxides which combine with both strong acid as well as strong bases e.g., ZnO,  $Al_2O_3$ , BeO,  $Sb_2O_3$ ,  $Cr_2O_3$ , PbO, SnO, SnO<sub>2</sub>, GaO etc.

$$\begin{array}{l} \mathsf{PbO}+2\ \mathsf{NaOH} \longrightarrow \mathsf{Na}_2 \mathsf{PbO}_2 + \mathsf{H}_2\mathsf{O} \ ; \ \mathsf{PbO} + \mathsf{H}_2\mathsf{SO}_4 \longrightarrow \mathsf{PbSO}_4 + \mathsf{H}_2\mathsf{O} \\ \mathsf{Cr}_2\mathsf{O}_3 + 2\ \mathsf{NaOH} \longrightarrow \mathsf{Na}_2\mathsf{Cr}_2\mathsf{O}_4 + \mathsf{H}_2\mathsf{O} ; \ \mathsf{Cr}_2\mathsf{O}_3 + 3\ \mathsf{H}_2\mathsf{SO}_4 \longrightarrow \mathsf{Cr}_2(\mathsf{SO}_4)_3 + 3\ \mathsf{H}_2\mathsf{O} \end{array}$$

#### (v) Mixed Oxides :

They behave as mixture of two simple oxides.

e.g.,  $Pb_3O_4$  (2PbO + PbO<sub>2</sub>);  $Fe_3O_4$  (FeO +  $Fe_2O_3$ );  $Mn_3O_4$  (2 MnO + MnO<sub>2</sub>)



#### (vi) Peroxides :

They react with dilute acids and form H<sub>2</sub>O<sub>2</sub>, e.g., Na<sub>2</sub>O<sub>2</sub>, K<sub>2</sub>O<sub>2</sub>, BaO<sub>2</sub> etc. They contain O<sub>2</sub><sup>2-</sup> ions.

 $Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$ 

They also react with water forming  $O_2$ .

 $Na_2O_2 + H_2O \longrightarrow 2NaOH + 1/2O_2$ 

#### (vii) Super Oxides :

They contain  $O_2^-$  ion, e.g.,  $KO_2^-$ ,  $RbO_2^-$  and  $CsO_2^-$ . These oxides react with water forming  $H_2O_2^-$  and  $O_2^-$ 2 KO<sub>2</sub> + 2 H<sub>2</sub>O  $\longrightarrow$  2 KOH + H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub>.

#### $OZONE(O_3):$

#### **Preparation :**

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

 $\begin{array}{c} O_2 & \stackrel{\text{energy}}{\longrightarrow} O + O \\ \\ O_2 + O & \longrightarrow O_3 ; \Delta H = 2845 \text{ kJ mol}^{-1} \\ \hline \\ 3O_2 & \stackrel{\frown}{\longrightarrow} 2O_3 \end{array}$ 

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

#### **Properties:**

- (i) 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  $CCl_4$ .  $O_3$  molecule is diamagnetic but  $O_3^-$  is paramagnetic.
- (ii) **Oxidising agent :**  $O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O$ ; SRP = + 2.07 v (in acidic medium)  $O_3 + H_2O + 2e^- \longrightarrow O_2 + 2OH^-$ ; SRP = + 1.24 v (in alkaline medium)

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

(a) It oxidises I<sup>-</sup> to  $I_2$  (from neutral solution of KI)

$$O_{3} \longrightarrow O_{2} + [O]$$

$$2 \text{ KI} + H_{2}O + [O] \longrightarrow 2 \text{ KOH} + I_{2}$$

$$2 \text{ KI} + H_{2}O + O_{3} \longrightarrow 2 \text{ KOH} + O_{2} + I_{2}$$

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

$$O_{3} \longrightarrow O_{2} + [O] \times 3$$

$$S + 3 [O] \longrightarrow SO_{3}$$

$$SO_{3} + H_{2}O \longrightarrow H_{2}SO_{4}$$

$$\overline{S + 3O_{3} + H_{2}O \longrightarrow H_{2}SO_{4} + 3O_{2}}$$

- (c) It oxidises  $H_2S$  to S.  $H_2S + O_3 \longrightarrow H_2O + S \downarrow$  (yellow)
- (iii) Reaction with dry  $I_2$ : 2  $I_2$  + 9[O<sub>3</sub>]  $\longrightarrow$   $I_4O_9$  + 9O<sub>2</sub>
- $I_4O_9$  yellow solid has the composition I<sup>+3</sup> (IO<sub>3</sub><sup>-</sup>)<sub>3</sub>. Formation of this compound is a direct evidence in favour of basic nature of I<sub>2</sub> (i.e. its tendency to form cations).
- (iv) Reaction with moist iodine :

$$\begin{array}{c} \mathsf{O}_3 \longrightarrow \mathsf{O}_2 + [\mathsf{O}] \times \mathsf{5} \\ \mathsf{I}_2 + \mathsf{5}[\mathsf{O}] \longrightarrow \mathsf{I}_2 \mathsf{O}_5 \end{array}$$



$$I_2O_5 + H_2O \longrightarrow 2HIO_3$$
  
$$5O_3 + I_2 + H_2O \longrightarrow 2HIO_3 + 5O_2$$

#### (v) Bleaching Action :

O<sub>3</sub> also bleaches coloured substances through oxidation.

#### (vi) Ozonolysis :

Alkenes, alkynes react with ozone forming ozonides.

$$CH_{2} = CH_{2} + O_{3} \longrightarrow \bigcup_{\substack{i=1 \ i \in I \\ O \neq i \in$$

#### (vii) Reaction with KOH :

Forms orange coloured compound, potassium ozonide.

$$2 \text{ KOH} + 5\text{O}_3 \longrightarrow 2 \text{ KO}_3^- + 5\text{O}_2 + \text{H}_2\text{O}$$
  
(orange solid)

#### **TESTS FOR OZONE :**

(i) A filter paper soaked in a alcoholic benzidine  $[H_2N - O - NH_2]$  becomes brown when brought in contact with O<sub>3</sub> (this is not shown by H<sub>2</sub>O<sub>3</sub>)

#### (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<sub>2</sub>O (mercury sub-oxide) in Hg.

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

Uses :

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, KMnO, etc.

4. It is also used for bleaching oil, ivory, flour starch etc.

## HYDROGEN PEROXIDE $(H_2O_2)$ :

## Preparation :

(i) Laboratory method:

 $BaO_2 \cdot 8H_2O + H_2SO_4 \text{ (cold)} \longrightarrow BaSO_4 \downarrow \text{ (white)} + H_2O_2 + 8H_2O_2 \text{ (cold)}$ 

 $BaSO_4$  is filtered to get aqueous hydrogen peroxide.

Since  $H_2SO_4$  can decompose  $H_2O_2$  at a higher temperature, therefore, the reaction should be carried out at low temperature or  $H_3PO_4$  can be used in place of  $H_2SO_4$ 

 $3BaO_2 + 2H_3PO_4 \longrightarrow Ba_3(PO_4)_2 \downarrow + 3H_2O_2$ ;  $Ba_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3BaSO_4 \downarrow + 2H_3PO_4$ H<sub>2</sub>PO<sub>4</sub> can again be used.

(ii) By electrolysis of concentrated  $H_2SO_4$  or  $(NH_4)_2SO_4$  at a high current density to form peroxosulphates, which then hydrolysed.

$$H_2SO_4 \implies H^{\oplus} + HSO_4^{\Theta}$$

at anode :  $2HSO_4^{\Theta} \longrightarrow S_2O_8^{2^-} + 2H^+ + 2e^-$ ; at cathode :  $H^+ + e^- \longrightarrow \frac{1}{2}H_2$ 

$$H_{2}S_{2}O_{8} + H_{2}O \xrightarrow{80-90^{\circ}C} H_{2}SO_{5} + H_{2}SO_{4}; H_{2}SO_{5} + H_{2}O \longrightarrow H_{2}SO_{4} + H_{2}O_{2}$$

#### (iii) Industrial method (Auto oxidation) :

 $\begin{array}{c} OH \\ C_2H_5 \\ OXidation) \\ H_2 (Ni) \\ (Reduction) \end{array} \qquad O \\ C_2H_5 \\ H_2O_2 \\ C_2H_5 \\ H_2O_2 \\ OH \end{array}$ 

2- Ethyl anthraquinol





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#### **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  $H_2O_2$ . $H_2O$  (melting point 221 K).
- (ii) Its boiling point 423 K is more than water but freezing point ( $-4^{\circ}$ 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.

 $2H_2O_2 \longrightarrow 2H_2O + O_2$ 

 $H_2O_2$  is not kept in glass containers because traces of alkali metal ions from the glass can catalyse the explosive decomposition of  $H_2O_2$  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  $H_2O_2$ 

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

 $H_2O_2$  (aq)  $\longrightarrow$   $H^+ + HO_2^-$ ;  $K_a = 1.5 \times 10^{-12}$  at 25°C

Aqueous solution of  $H_2O_2$  turns blue litmus red which is then bleached by the oxidising property of  $H_2O_2$ Na<sub>2</sub>CO<sub>3</sub> +  $H_2O_2 \longrightarrow Na_2O_2 + H_2O + CO_2$ 

$$Ba(OH)_2 + H_2O_2 + 6H_2O \longrightarrow BaO_2 \cdot 8H_2O \downarrow$$

A 30%  $H_2O_2$  solution has pH = 4.0

### (v) Oxidising Agent :

 $\begin{array}{ll} 2e^- + 2H^+ + H_2O_2 \longrightarrow 2H_2O \ ; \ SRP = + \ 1.77 \ v & (in \ acidic \ medium) \\ 2e^- + H_2O_2 \longrightarrow 2OH^- \ ; \ SRP = + \ 0.87 \ v & (in \ alkaline \ medium) \end{array}$ 

> On the basis of the above potentials, we can say that  $H_2O_2$  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>.  $H_2O_2 \longrightarrow H_2O + [O] \times 4$ PbS + 4[O]  $\longrightarrow$  PbSO<sub>4</sub>

 $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$ 

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  $H_2S$ .

(b) 
$$\begin{array}{c} H_2O_2 \text{ oxidises } H_2S \text{ to sulphur.} \\ H_2O_2 \longrightarrow H_2O + [O] \\ H_2S + [O] \longrightarrow H_2O + S\downarrow \\ \hline \\ \hline \\ H_2O_2 + H_2S \longrightarrow 2H_2O + S\downarrow \end{array}$$

Potassium iodide and starch produces deeper blue colour with acidified  $H_2O_2$ .  $H_2O_2 + 2H^+ 2I^- \longrightarrow I_3^- + 2H_2O$ 

 $\begin{array}{lll} \blacktriangleright & \mathsf{H_2O_2} \text{ in acidic medium also oxidises} \\ & \mathsf{AsO_3^{3^-} to } \mathsf{AsO_4^{3^-}}, \mathsf{SO_3^{2^-} to } \mathsf{SO_4^{2^-}}, \mathsf{KI to I_2}, \mathsf{S^{2^-} to } \mathsf{SO_4^{2^-}}, \\ & \mathsf{FeSO_4} \text{ to } \mathsf{Fe_2}(\mathsf{SO_4})_3 \text{ and } [\mathsf{Fe}(\mathsf{CN})_6]^{4^-} \text{ to}[\mathsf{Fe}(\mathsf{CN})_6]^{3^-} \end{array}$ 

#### (B) In alkaline medium :

- (a)  $\operatorname{Cr}(\operatorname{OH})_{3}(s) + 4\operatorname{NaOH} + 3\operatorname{H}_{2}\operatorname{O}_{2} \longrightarrow 2\operatorname{Na}_{2}\operatorname{CrO}_{4}(\operatorname{aq.}) + 8\operatorname{H}_{2}\operatorname{O}_{0}$ or  $10 \operatorname{OH}^{-} + 3\operatorname{H}_{2}\operatorname{O}_{2} + 2\operatorname{Cr}^{3+} \longrightarrow 2\operatorname{CrO}_{4}^{2-} + 8\operatorname{H}_{2}\operatorname{O}_{2}$
- (b)  $2NaBO_2 + 2H_2O_2 + 6H_2O \longrightarrow Na_2[(OH)_2B(O-O)_2B(OH)_2] 6H_2O$  (sodium per oxoborate)
- Used as a brightener in washing powder.

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$$



In alkaline solution, its reducing character is more than in acidic medium.  $2 \text{ OH}^- + \text{H}_2\text{O}_2 \longrightarrow \text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^-$ 

- (a) Ag<sub>2</sub>O is reduced to Ag. Ag<sub>2</sub>O + H<sub>2</sub>O<sub>2</sub>  $\longrightarrow$  2Ag + H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub>
- (b) It reduces  $O_3$  to  $O_2$ ..  $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$
- (c) It reduces ferric cyanide to ferrous cyanide (basic medium).  $2 K_3 [Fe(CN)_6] + 2KOH \longrightarrow K_4 [Fe(CN)_6] + H_2O + O$  $H_2O_2 + O \longrightarrow H_2O + O_2$

$$2K_{3}[Fe(CN)_{6}] + 2KOH + H_{2}O_{2} \longrightarrow 2K_{4}[Fe(CN)_{6}] + 2H_{2}O + O_{2}$$

## Tests for $H_2O_2$ :

(i) With 
$$K_2 Cr_2 O_7 : Cr_2 O_7^{2-} + 2H^+ + 4H_2 O_2 \xrightarrow{\text{amyl alcohol}} 2CrO_5 + 5H_2 O_3$$

 $\begin{array}{ll} \succ & \operatorname{CrO}_5 \text{ bright blue coloured compound soluble in diethyl ether, amyl alcohol and amyl acetate.} \\ & \operatorname{CrO}_5 + \operatorname{H}_2 \operatorname{SO}_4 \longrightarrow 2\operatorname{Cr}_2(\operatorname{SO}_4)_3 + 6\operatorname{H}_2 \operatorname{O} + 7\operatorname{O}_2 \end{array}$ 

(

$$2 \text{ HCHO} + \text{H}_2\text{O}_2 \xrightarrow{\text{OH}^-} 2 \text{ HCOOH} + \text{H}_2$$

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  $H_2O_2$ .

$$Ti^{+4} + H_2O_2 + 2H_2O \longrightarrow H_2TiO_4$$
 (yellow/orange red) + 4H<sup>+</sup>

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

#### Uses :

- 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.

## SULPHUR (S) :

## ALLOTROPIC FORMS OF SULPHUR :

Sulphur forms numerous allotropes of which the **yellow rhombic** ( $\alpha$  - sulphur) and **monoclinic** ( $\beta$  - sulphur) forms are the most important. The stable forms at room temperature is rhombic sulphur, which transforms to monoclinic sulphur when heated above 369 K.

## RHOMBIC SULPHUR ( $\alpha$ -SULPHUR):

This allotrope is yellow in colour, melting point 385.8 K and specific gravity 2.06. 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  $CS_2$ .

## MONOCLINIC SULPHUR ( $\beta$ - SULPHUR) :

Its melting point is 393 K and specific gravity 1.98. It is soluble in  $CS_2$ . This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling till crust is formed. 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. It is stable above 369 K and transforms into  $\alpha$  - sulphur below it . Conversely,  $\alpha$  - sulphur is stable below 369 K and transforms into  $\beta$  - sulphur above this. At 369 K both the forms are stable. This temperature is called transition temperature.

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.





The structures of (a)  $S_{s}$  ring in rhombic sulphur and (b)  $S_{s}$  form

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).

**PLASTIC SULPHUR :** It is formed when molten sulphur ( $\mu$ ) is poured into cold water. It consists of chain like molecule and has rubber like properties when formed. On standing it becomes brittle and finally converts to rhombic sulphur.

- Sulphur melts to form a mobile liquid. As the temperature is raised the colour darkens. At 160°C C<sub>8</sub> rings break, and the diradicals so formed polymerize, forming long chains of up to a million atoms. The viscosity increases sharply, and continues to rise up to 200°C. At higher temperatures chains break, and shorter chains and rings are formed, which makes the viscosity decrease upto 444°C, the boiling point. The vapour at 200°C consists mostly of S<sub>8</sub> rings, but contains 1-2% of S<sub>2</sub> molecules. At elevated temperature (~1000 K), S<sub>2</sub> is the dominant species and is paramagnetic like O<sub>2</sub>, and presumably has similar bonding. S<sub>2</sub> gas is stable upto 2200°C.
- The sulphur is mined using a process called as Frasch process.
- From hydrocarbons contaminated with  $H_2S$  or a stream of gas containing  $H_2S$ . It involves two steps :

(i) 
$$H_2S + O_2 \xrightarrow{\text{Burn}} SO_2 + H_2S$$
(ii)  $H_2S + SO_2 \xrightarrow{\text{catalyst converter}} 3S(g + 2H_2O(g))$ 

## COMPOUNDS OF SULPHUR : HYDROGEN SULPHIDE $(H_2S)$ : Preparation :

 $FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$ 

It is prepared in kipp's apparatus

(ii) Preparation of pure  $H_2S$  gas  $Sb_2S_3$  (pure) + 6 HCl (pure)  $\longrightarrow 2 SbCl_3 + 3 H_2S$ 

## **Properties :**

(i)

- (i) Colourless gas with rotten egg smell .
- (ii) Moderately soluble in water but solubility decreases with increasing temperature.

## (iii) Reducing Agent :

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

- (a)  $H_2S + X_2 \longrightarrow 2 HX + S;$
- (b)  $H_2S + SO_2 \xrightarrow{\text{moisture}} H_2O + S;$

(c)  $2HNO_3 \longrightarrow H_2O + 2NO_2 + [O]$ 

$$\frac{H_2S + [O] \longrightarrow H_2O + S}{2HNO_3 + H_2S \longrightarrow 2H_2O + NO_2 + S}$$



#### SULPHUR DIOXIDE :

## **Preparation** :

(i)	$S + O_2 \text{ or air } \xrightarrow{Burn} SO_2$		
(ii)	By hea	ating Cu or Ag with concentrated $H_2SO_4$ Cu + $H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$	
(iii)	By rea	ction of metal sulphites with dilute HCI (Laboratory method)	
	Simila	$Na_2SO_3 + 2HCI \longrightarrow 2NaCI + SO_2 + H_2O$ rly bisulphites also give SO <sub>2</sub> with dilute HCI	
		$NaHSO_3 + HCI \longrightarrow NaCI + SO_2 + H_2O$	
(iv)	By hea	ating sulphides (metal sulphide ores) in excess of air. $2 \text{ZnS} + 3O_2 \longrightarrow 2 \text{ZnO} + 2 \text{SO}_2$	
<i>(</i> <b>)</b>	Prope	rties :	
(1) (ii)	Colour It is he $SO_2.6I$	less gas with burning sulphur smell. eavier than air and is highly soluble in water. $SO_2$ in solution is almost completely present as $H_2O$ and only traces of $H_2SO_3$ .	
(iii)	Neithe	r burns nor helps in burning but burning magnesium and potassium continue to burn in its atmosphere. $3Mg + SO_2 \longrightarrow 2 MgO + MgS$ ; $4K + 3SO_2 \longrightarrow K_2SO_3 + K_2S_2O_3$	
(iv)	Acidic	<b>Nature :</b> Acidic oxide and thus dissolve in water forming sulphurous acid. SO <sub>2</sub> + H <sub>2</sub> O $\longrightarrow$ H <sub>2</sub> SO <sub>3</sub>	
(v)	Additi	on Reaction :	
		$SO_2 + CI_2 \xrightarrow{Sun \ light} SO_2CI_2$ (sulphuryl chloride)	
		$SO_2 + O_2 \xrightarrow{\text{platinised}} SO_3 ; PbO_2 + SO_2 \longrightarrow PbSO_4$	
(vi)	Reduc	sing Nature :	
	It is a r	nore powerful reducing agent in alkaline medium than in acidic medium. $H_2O + SO_2 \longrightarrow H_2SO_3$ ; $H_2SO_3 + H_2O \longrightarrow H_2SO_4 + 2H$	
	$\succ$	Reducing character is due to the liberation of nascent hydrogen.	
	(a)	Reduces halogens to corresponding halides. SO <sub>2</sub> + 2H <sub>2</sub> O $\longrightarrow$ H <sub>2</sub> SO <sub>4</sub> + 2H	
		$2H + Cl_2 \longrightarrow 2HCl^2$	
		$\overline{\text{SO}_2 + 2\text{H}_2\text{O} + \text{Cl}_2} \longrightarrow \text{H}_2\text{SO}_4 + 2\text{HCl}$	
	(b)	Reduces acidified iodates to iodine	
		$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H] \times 5$ 2KIO + H SO $\longrightarrow$ K SO + 2HIO	
		$2HIO_3 + 10H \longrightarrow I_2 + 6H_2O$	
		$\frac{1}{2 \text{KIO}_{2} + 5 \text{SO}_{2} + 4 \text{H}_{2} \text{O}_{2} \longrightarrow \text{K}_{2} \text{SO}_{2} + 4 \text{H}_{2} \text{SO}_{2} + 1}$	
	$\triangleright$	It also reduces acidified $KMnO_4 \longrightarrow Mn^{2+}$ (decolourises),	
		Acidified $K_2 Cr_2 O_7 \longrightarrow Cr^{3+}$ (green coloured solution) & Ferric Sulphate $\longrightarrow$ Ferrous sulphate	
(vii)	Oxidis	sing nature : Acts as oxidising agent with strong reducing agent	
	(a) (b)	$2\operatorname{SnCl}_{2} + \operatorname{SO}_{2}  2\operatorname{SnCl}_{2} + 2\operatorname{H}_{2} \operatorname{O} + \operatorname{SO}_{2}$ $2\operatorname{SnCl}_{2} + \operatorname{SO}_{2} + 4\operatorname{HCl}  2\operatorname{SnCl}_{2} + 2\operatorname{H}_{2} \operatorname{O} + \operatorname{SO}_{2}$	
(viii)	Bleac	hing Action :	
	<b>T</b> I ''.	$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H_4$	
		add to the reducing nature of $SO_2$ red matter + H colourless matter	
	Thorof	Air oxidation	
	merel	טוב, טובמטוווויץ ום נבוויףטומו א.	



## SULPHUR TRIOXIDE (SO $_3$ ):

**Preparation** :

(i)  $6H_2SO_4 + P_4O_{10} \longrightarrow 6SO_3 + 4H_3PO_4$ 

 $P_4O_{10}$  is dehydrating agent

(ii)  $\operatorname{Fe}_2(\operatorname{SO}_4)_3 \xrightarrow{\Delta} \operatorname{Fe}_2\operatorname{O}_3 + 3\operatorname{SO}_3$ 

Properties :

(i) Acidic Nature : Dissolves in water forming sulphuric acid  $SO_3 + H_2O \longrightarrow H_2SO_4$ 

(ii)  $H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$  (oleum)

- (iii) Oxidising Nature :
  - (a)  $2SO_3 + S \xrightarrow{100^\circ C} 3SO_2$
  - (c)  $SO_3 + PCI_5 \longrightarrow POCI_3 + SO_2 + CI_2$

b) 
$$5SO_3 + 2P \longrightarrow 5SO_2 + P_2O_5$$
  
d)  $SO_2 + 2HBr \longrightarrow H_2O + Br_2 + SO_2$ 

## **OXYACIDS OF SULPHUR :**

Sulphur forms a number of oxoacid such as  $H_2SO_3$ ,  $H_2S_2O_4$ ,  $H_2S_2O_5$ ,  $H_2S_2O_6$  (x = 2 to 5,)  $H_2SO_4$ ,  $H_2S_2O_7$ ,  $H_2SO_8$ . 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.



Structures of some important oxoacids of sulphur

## SULPHURIC ACID $(H_2SO_4)$ :

## Manufacture :

(a)

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

Sulphuric acid is manufactured by the contact process which involves three steps :

(i) burning of sulphur or sulphide ores in air to generate  $SO_2$ 

(ii) conversion of SO<sub>2</sub> to SO<sub>3</sub> by the reaction with oxygen in the presence of a catalyst ( $V_2O_5$ ), and (iii) absorption of SO<sub>2</sub> in H<sub>2</sub>SO<sub>4</sub> to give Oleum (H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>)

The SO<sub>2</sub> produced is profiled by removing dust and other impurities such as arsenic compounds.

The key step in the manufacture of  $H_2SO_4$  is the catalytic oxidation of  $SO_2$  with  $O_2$  to give  $SO_3$  in the presence of  $V_2O_5$  (catalyst).

 $2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g) D_r H^{\Theta} = -196.6 \text{ kJ mol}^{-1}.$ 

The reaction is exothermic reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favourable conditions for maximum yield. But the temperature should not be very low other wise rate of reaction will become slow.

In practice the plant is operated at a pressure of 2 bar and a temperature of 720 K. The SO<sub>3</sub> gas from the catalytic converter is absorbed in concentrated  $H_2SO_4$  to produce oleum. Dilution of oleum with water gives  $H_2SO_4$  of the desired concentration. In the industry two steps are carried out simultaneously to make the process a continuous one and also to reduce the cost.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$
 (Oleum)

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

(b) Lead chamber process :

 $2SO_2 + O_2$  (air) +  $2H_2O + [NO]$  (catalyst)  $\longrightarrow 2H_2SO_4 + [NO]$  (catalyst). Acid obtained is 80% pure and is known as brown oil of vitriol.



#### **Properties :**

Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K. The acid freezes at 283 K and boils at 611 K. It dissolves in water with the evolution of a larger quantity of heat.

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,

(i) Sulphuric acid ionises in two steps.

 $H_2SO_4(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + HSO_4^-(aq) ; Ka_1 = very larger (K_{a1} > 10)$ 

 $H_2SO_4^{-}(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq)$ ; Ka<sub>2</sub> = 1.2 × 10<sup>-2</sup>

The larger value of  $K_{a1}$  ( $K_{a1} > 10$ ) means that  $H_2SO_4$  is largely dissociated into  $H^+$  and  $HSO_4^-$ . 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 in to  $CO_2$ .

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$
;  $NaHCO_3 + H_2SO_4 \longrightarrow NaHSO_4 + H_2O + CO_2$ 

(c) Sulphuric acid, because of its low volatility can be used to manufacture more volatile acid from their corresponding salts.

$$2MX + H_2SO_4 \rightarrow 2HX + M_2SO_4(X = F, CI, NO_3); NaCI + H_2SO_4 \longrightarrow NaHSO_4 + HCI$$
(M = Metal)

(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.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O; H_2C_2O_4 \xrightarrow{H_2SO_4} CO + CO_2$$

(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 SO<sub>2</sub>.

 $\begin{array}{l} \text{Cu} + 2\text{H}_2\text{SO}_4(\text{concentrated}) \longrightarrow \text{CuSO}_4 + 2\text{H}_2\text{O} \\ 3\text{S} + 2\text{H}_2\text{SO}_4(\text{concentrated}) \longrightarrow 3\text{SO}_2 + 2\text{H}_2\text{O} \\ \text{C} + 2\text{H}_2\text{SO}_4(\text{concentrated}) \longrightarrow \text{CO}_2 + 2\text{SO}_2 + 2\text{H}_2\text{O} \end{array}$ 

 $\begin{array}{ll} \text{(iv)} & \text{With PCI}_{5} \text{ forms mono and di-acid chlorides.} \\ & \text{HO} - \text{SO}_{2} - \text{OH} + \text{PCI}_{5} \longrightarrow \text{CI} - \text{SO}_{2} - \text{OH} + \text{POCI}_{3} + \text{HCI} \\ & \text{HO} - \text{SO}_{2} - \text{OH} + 2\text{PCI}_{5} \longrightarrow \text{CI} - \text{SO}_{2} - \text{CI} + 2\text{POCI}_{3} + 2\text{HCI} \\ & \text{HO} - \text{SO}_{2} - \text{OH} + 2\text{PCI}_{5} \longrightarrow \text{CI} - \text{SO}_{2} - \text{CI} + 2\text{POCI}_{3} + 2\text{HCI} \\ & \text{W} & 3\text{KCIO}_{3} + 3\text{H}_{2}\text{SO}_{4} \longrightarrow 2\text{KHSO}_{4} + \text{HCIO}_{4} + 2\text{CIO}_{2} + \text{H}_{2}\text{O} \end{array}$ 

#### Uses :

Sulphuric acid is a very important industrial chemical. A nation's industrial strength can be judged by the quantity of sulphuric acid it produces and consumes .It is needed for the manufacture of hundreds of other compounds also in many industrial processes .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.

#### SODIUM THIOSULPHATE (Na2S2O3.5H2O):

#### Preparation :

- (i)  $Na_2SO_3 + S \xrightarrow{boiled} Na_2S_2O_3$
- (ii)  $Na_2CO_3 + 2SO_2 + H_2O \longrightarrow 2NaHSO_3 + CO_2$ ;  $2NaHSO_3 + Na_2CO_3 \longrightarrow 2Na_2SO_3 + H_2O + CO_2$  $Na_2SO_3 + S \xrightarrow{\Delta} Na_2S_2O_3$
- (iii)  $Na_2S + Na_2SO_3 + I_2 \longrightarrow Na_2S_2O_3 + 2 Nal$
- (iv)  $6\text{NaOH} + 4\text{S} \xrightarrow{\Delta} \text{Na}_2\text{S}_2\text{O}_3 + 2\text{Na}_2\text{S} + \text{H}_2\text{O}$



#### **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.

 $Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 8HCI$ Therefore , it is known as antichlor.

### (iii) Reaction with HCI :

 $S_2O_3^{2-} + H^+ \longrightarrow S^{\downarrow}$  (white) +  $SO_2 + H_2O$  (disproportionation reaction) This test is used for distinction between  $S_2O_3^{2-}$  and  $SO_3^{2-}$  ions as  $SO_3^{2-}$  ions give only  $SO_2$  with HCI.

#### (iv) Complex formation reactions :

(a) Reaction with silver salts (AgNO<sub>3</sub>, AgCl, AgBr or Agl) :

 $\begin{array}{l} S_2O_3^{2-} + 2Ag^{+} \longrightarrow Ag_2S_2O_3 \downarrow \text{ (white)} \\ Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S \downarrow \text{ (black)} + H_2SO_4 \end{array}$ 

This hydrolytic decomposition can be accelerated by warming.

If hypo is in excess, then soluble complex is formed.

 $2S_2O_3^{2-} + Ag^{+} \longrightarrow [Ag(S_2O_3)_2]^{3-} \text{ (soluble complex) or } [Ag(S_2O_3)_3]^{5-}$ 

This reaction is utilized in photography where hypo is used as fixer.

#### (b) Reaction with $\text{FeCl}_3$ :

It develops a pink or dark violet colour which soon vanishes on standing according to following reaction.

$$Fe^{3+} + 2S_2O_3^{2-} \longrightarrow [Fe(S_2O_3)_2]^- (Pink \text{ or violet})$$
  
$$[Fe(S_2O_3)_2]^- + Fe^{3+} \longrightarrow 2Fe^{2+} + S_4O_6^{2-}$$

Over all reaction is

$$2S_2O_3^{2-} + 2Fe^{3+} \longrightarrow 2Fe^{2+} + S_4O_6^{2-}$$

## (c) Reaction with AuCl<sub>3</sub> (Soluble in water) :

$$\begin{aligned} &\text{AuCl}_3 + \text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{AuCl} \downarrow + \text{Na}_2\text{S}_4\text{O}_6 + 2\text{HCl} \\ &\text{AuCl} + \text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Na}_3 \left[\text{Au}(\text{S}_2\text{O}_3)_2\right] \text{ (soluble complex)} + \text{NaCl} \end{aligned}$$

#### (d) Reaction with CuCl<sub>2</sub>:

$$\begin{split} & 2 \operatorname{CuCl}_2 + 2\operatorname{Na}_2\operatorname{S}_2\operatorname{O}_3 \longrightarrow 2\operatorname{CuCl} \downarrow + \operatorname{Na}_2\operatorname{S}_4\operatorname{O}_6 + 2\operatorname{NaCl} \\ & \operatorname{CuCl} + \operatorname{Na}_2\operatorname{S}_2\operatorname{O}_3 \longrightarrow \operatorname{Cu}_2\operatorname{S}_2\operatorname{O}_3 \downarrow + 2\operatorname{NaCl} \\ & 3 \operatorname{Cu}_2\operatorname{S}_2\operatorname{O}_3 + 2\operatorname{Na}_2\operatorname{S}_2\operatorname{O}_3 \longrightarrow \operatorname{Na}_4\left[\operatorname{Cu}_6(\operatorname{S}_2\operatorname{O}_3)_5\right] \text{ (soluble complex)} \end{split}$$

#### (v) Reaction with potassium tri-iodite solution i.e. Kl<sub>3</sub>

$$I_3^- + S_2O_3^{2-} \longrightarrow 3I^- + S_4O_6^{2-}$$

This reaction finds application in the iodometric and iodimetric methods of titrimetric analysis.

(vi) 
$$4\operatorname{Na}_2\operatorname{S}_2\operatorname{O}_3.5\operatorname{H}_2\operatorname{O} \xrightarrow{215^\circ\operatorname{C}} 4\operatorname{Na}_2\operatorname{S}_2\operatorname{O}_3 \xrightarrow{220^\circ\operatorname{C}} 3\operatorname{Na}_2\operatorname{SO}_4 + \operatorname{Na}_2\operatorname{S}_5$$

#### (vii) Reaction with soluble salt of lead :

$$S_2O_3^{2-} + Pb^{2+} \longrightarrow PbS_2O_3 \downarrow (white)$$
  
 $PbS_2O_3 \downarrow + H_2O \longrightarrow PbS\downarrow (black) + 2H^+ + SO_4^{2-}$ 

Uses :

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





## **PART - I : OBJECTIVE QUESTIONS**

\* Marked Questions are having more than one correct option.

## Group 15<sup>th</sup>

- **1.** In group 15, the melting points of the elements :
  - (A) increase regularly on moving down the group.
  - (B) decrease regularly on moving down the group.
  - (C) first decrease upto As and then increase to Bi.
  - (D) first increase from N to As and then decrease to Bi.
- 2. Which out of the following gases is obtained when ammonium dichromate is heated -(A) Oxygen (B) Ammonia (C) Nitrogen (D) Nitrous oxide 3. Among the trihalides of nitrogen which one is most basic -(A) NF<sub>2</sub> (B) NCl<sub>3</sub> (D) NBr<sub>3</sub>  $(C) NI_3$ The correct sequence of decrease in the bond angle of the following hydrides is - : 4. (A)  $NH_3 > PH_3 > AsH_3 > SbH_3$ (B)  $NH_3 > AsH_3 > PH_3 > SbH_3$ (C) SbH<sub>3</sub> > AsH<sub>3</sub> > PH<sub>3</sub> > NH<sub>3</sub> (D)  $PH_3 > NH_3 > AsH_3 > SbH_3$ 5. The thermal stability of the hydrides of group 15 follows the order : (A)  $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$ (B)  $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$ (C)  $PH_3 > NH_3 > AsH_3 > SbH_3 < BiH_3$ (D)  $AsH_3 < PH_3 > SbH_3 > BiH_3 > NH_3$ The hydrides of group 15 elements act as : 6. (A) lewis acids (B) lewis bases (C) both (D) none 7. The basic strength of the hydrides of group 15 elements : (A) decreases on moving down the group (B) increases on moving down the group (C) first decreases upto AsH<sub>3</sub> and then increases (D) first increases upto AsH<sub>3</sub> and then decreases 8. The low reactivity of nitrogen is due to -(A) Small atomic radius (B) High electronegativity (C) Stable configuration (D) High bond dissociation energy 9. Which one of the following does not undergo hydrolysis -(A) AsCl<sub>3</sub> (B) SbCl<sub>2</sub> (C) PCl<sub>2</sub> (D) NF<sub>3</sub> 10. Which one of the following properties of white phosphorous are shared by red phosphorous -(B) It burns when heated in air (A) It dissolves in CS<sub>2</sub> (C) It reacts with NaOH to give PH<sub>3</sub> (D) It phosphorescences in air 11. Which of the following acids is monobasic? (A) Hypophosphorous acid  $(H_3PO_2)$ (B) Orthophosphoric acid  $(H_3PO_4)$ (C) Pyrophosphoric acid  $(H_4P_2O_7)$ (D) Hypophosphoric acid  $(H_4P_2O_6)$ 12. Red and white phosphorus will differ but not in : (A) smell (B) solubility in CHCl<sub>3</sub> (C) exhibiting phosphorescence (D) reaction with concentrated HNO<sub>3</sub>



13.	Which of the following c (A) $N_2O_3$	oxides is amphoteric in na (B) P <sub>4</sub> O <sub>6</sub>	ature ? (C) Sb <sub>4</sub> O <sub>6</sub>	(D) Bi <sub>2</sub> O <sub>3</sub>
14.	Which of the following is (A) White phosphorus	s least reactive ? (B) Yellow phosphorus	(C) Red phosphorus	(D) Black phosphorus
15.	is obtained when am	monium dichromate is h	eated.	
	(A) nitrogen	(B) oxygen	(C) ammonia	(D) none
16.	Which one of the follow (A) $PF_5$	ing pentafluorides canno (B) AsF <sub>5</sub>	t be formed - (C) SbF <sub>5</sub>	(D) BiF <sub>5</sub>
17.	The dimerisation of NO (A) An increase in press (C) A decrease in paran	<sub>2</sub> as the temperature is lo sure nagnetism	owered is accompanied b (B) A darkening in colou (D) The formation of a c	ay - Ir colloid
18.	Which of the following r (A) Sodium nitroprussid (C) Nessler's reagent	eagents can separate nit e solution	ric oxide from nitrous oxi (B) Ferrous sulphate so (D) Tollen's reagent	ide - Iution
19.	Phosphine is not obtaine (A) White P is heated w (C) $Ca_3P_2$ reacts with w	d by the reaction when - ith NaOH ater	(B) Red P is heated with (D) $P_4O_6$ is boiled with	h NaOH water
20.	In P <sub>4</sub> O <sub>6</sub> the number of c (A) 1.5	oxygen atoms bonded to (B) 2	each phosphorus atom is (C) 3	s - (D) 4
21.	In the ostwald's process (A) $N_2$	s, nitric acid is prepared b (B) NH <sub>3</sub>	by the catalytic oxidation (C) $N_2O_5$	of : (D) NO <sub>2</sub>
22.	$NH_4CI$ (s) is heated in to blue and then to red. It is	est tube. Vapours are bro s because of :	bught in contact with red	litmus paper, which changes to
	(A) formation of $NH_4OH$	and HCI	(B) formation of $NH_3$ and (D) greater diffusion of (D)	d HCl HCl than NH
	(C) greater and son of i		(D) greater unusion of	
23.	Which of the following v (A) N <sub>2</sub> O	vill combine with Fe(II) io (B) NO	n to form a brown compl (C) N <sub>2</sub> O <sub>3</sub>	ex compound ? (D) NO <sub>2</sub>
24.	NO <sub>2</sub> can be prepared by	y heating :		
	(A) NH <sub>4</sub> NO <sub>3</sub>	(B) NaNO <sub>3</sub>	(C) Pb(NO <sub>3</sub> ) <sub>2</sub>	(D) KNO <sub>3</sub>
25.	The wrong statement al (A) it is nitrous oxide	pout N <sub>2</sub> O is :	(B) it is least reactive ov	kide of nitrogen
	(C) it is not a linear mole	ecule	(D) it is known as laugh	ing gas
26.	Following are neutral ox (A) NO	ides except : (B) N <sub>2</sub> O	(C) CO	(D) NO <sub>2</sub>
27.	Which of the following statements are not correct about the hydrides of group 15 elements - (A) The hydrides of the elements of group 15 are ionic and have planar triangular shape (B) The thermal stability of the hydrides decreases down the group (C) the basic character of the hydrides decreases down the group (D) The reducing nature of the hydrides increases down the group			
28.	Which of the following is	s basic in nature -		

(A)  $H_3PO_3$  (B)  $H_3BiO_3$  (C)  $H_3AsO_3$  (D)  $H_3SbO_3$ 



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29.	Acidic nitrogen hydride (A) $N_2H_4$	is - (B) N <sub>3</sub> H	(C) NH <sub>2</sub> OH	(D) NH <sub>3</sub>
30.	PCI <sub>5</sub> exists but NCI <sub>5</sub> do (A) Nitrogen has no vac (C) Nitrogen atom is mu	es not because - cant d-orbitals uch smaller	(B) NCI <sub>5</sub> is unstable (D) Nitrogen is highly in	ert.
31.	$HNO_3 + P_4O_{10} \longrightarrow H$ in the above reaction th (A) $NO_2$	IPO <sub>3</sub> + X e product X is : (B) N <sub>2</sub> O <sub>3</sub>	(C) N <sub>2</sub> O <sub>4</sub>	(D) N <sub>2</sub> O <sub>5</sub>
32.	Which of the following $(A) NO_2$	oxides of nitrogen is solid (B) N <sub>2</sub> O <sub>3</sub>	at or below 273 K ? (C) N <sub>2</sub> O	(D) N <sub>2</sub> O <sub>5</sub>
33.	Cold solution of barium (A) $BaSO_4 + HNO_2$	nitrite on mixing with sul (B) BaSO <sub>4</sub> + HNO <sub>3</sub>	phuric acid produces : (C) BaSO <sub>4</sub> + NO <sub>2</sub>	(D) $BaSO_4 + N_2 + O_2$
34.	The mixture of concent (A) CIO <sub>2</sub>	rated HCl and HNO <sub>3</sub> mac (B) NOCl	de in 3 : 1 ratio contains : (C) NCl <sub>3</sub>	(D) N <sub>2</sub> O <sub>4</sub>
35.	Which of the following a (A) Hyponitrous acid	acids can form two types (B) Nitrous acid	of salts? (C) Nitric acid	(D) Pernitric acid
36.	Nitric acid usually turns (A) absorption of yellow (C) its oxidation by atme	yellow on standing. This wavelength ospheric air	is due to : (B) slow decomposition (D) absorption of moistu	of HNO <sub>3</sub> into NO <sub>2</sub> ure by it
37.	Concentrated nitric acid (A) PH <sub>3</sub>	l oxidises phasphours (P (B) P <sub>2</sub> O <sub>5</sub>	) into : (C) HPO <sub>3</sub>	(D) H <sub>3</sub> PO <sub>4</sub>
38.	Which of the following r (A) Pb	netals does not dissolve (B) Cu	in concentrated HNO <sub>3</sub> ? (C) Au	(D) Hg
39.	The compound which h (A) PCI <sub>5</sub>	as molecular nature in ga (B) POCl <sub>3</sub>	as phase but ionic in solic (C) P <sub>4</sub> O <sub>10</sub>	d state is : (D) PCl <sub>3</sub>
40.	When $P_4O_{10}$ is dissolve (A) $H_3PO_2$	d in water, the acid forme (B) H <sub>3</sub> PO <sub>4</sub>	ed finally is : (C) H <sub>3</sub> PO <sub>3</sub>	(D) H <sub>4</sub> P <sub>2</sub> O <sub>7</sub>
41.	The substance used as (A) Na <sub>3</sub> PO <sub>4</sub>	a fast drying agent in the (B) P <sub>4</sub> O <sub>10</sub>	e laboratory is : (C) charcoal	(D) anhydrous calcium chloride
42.	On heating a mixture of (A) $NH_4NO_3$	$^{\rm NH_4Cl}$ and ${\rm KNO_2}$ we ge (B) ${\rm N_2}$	t - (C) NO	(D) N <sub>2</sub> O
43.	Which of the following $\mu$ (A) H <sub>3</sub> PO <sub>3</sub>	phosphorus oxyacids car (B) H <sub>3</sub> PO <sub>4</sub>	n act as a reducing agent (C) H <sub>4</sub> P <sub>2</sub> O <sub>6</sub>	t ? (D) H <sub>4</sub> P <sub>2</sub> O <sub>7</sub>
44.	When white pnosphor (A) PH <sub>3</sub> + NaH <sub>2</sub> PO <sub>3</sub>	ous is heated with caus (B) PH <sub>3</sub> + NaH <sub>2</sub> PO <sub>2</sub>	tic soda, the compound (C) PH <sub>3</sub> + Na <sub>2</sub> HPO <sub>3</sub>	ds formed are - (D) PH <sub>3</sub> + NaH <sub>2</sub> PO <sub>4</sub>
45.	The P – P – P bond a (A) 120°	ngle in white phosphorus (B) 90°	s is - (C) 60°	(D) 109°, 28'
46.	Phosphine produces s (A) It reacts with wate (C) It burns in air	moky rings when it con r vapour	nes in contact with air b (B) It reacts with nitrog (D) It contains impuriti	because - gen es of P <sub>2</sub> H <sub>4</sub>



47.	PCl <sub>5</sub> is kept in well stop (A) It is highly volatile (C) It reacts readily wi	pered bottles because - th moisture	<ul><li>(B) It reacts with oxyg</li><li>(D) It is explosive</li></ul>	en
48.	Which of the following (A) $P_4O_6$	oxides will be least ac (B) $P_4O_{10}$	idic - (C) As <sub>4</sub> O <sub>6</sub>	(D) As <sub>4</sub> O <sub>10</sub>
49.	Which of the following (A) $H_3PO_2$	oxy acids of Phosphor (B) H <sub>3</sub> PO <sub>3</sub>	rus is a reducing agent (C) H <sub>3</sub> PO <sub>4</sub>	and monobasic - (D) H <sub>4</sub> P <sub>2</sub> O <sub>6</sub>
50.	Which of the following i (A) $NH_3$	s used as anaesthetic - (B) NO	(C) N <sub>2</sub> O	(D) NO <sub>2</sub>
51.	Which pair of oxides $(A)$ NO, $N_2O$	of nitrogen is paramagn (B) N <sub>2</sub> O <sub>5</sub> , NO <sub>2</sub>	etic ? (C) N <sub>2</sub> O <sub>5</sub> , N <sub>2</sub> O	(D) NO, NO <sub>2</sub>
52.	What is false about N (A) It is anhydride of $R$ (C) Solid $N_2O_5$ is call	<sub>2</sub> O <sub>5</sub> ? HNO <sub>3</sub> ed nitronium nitrate	(B) It is a powerful ox (D) Structure of N <sub>2</sub> O <sub>5</sub>	idizing agent contains no [N $ ightarrow$ O] bond
53.	Which of the following (A) $As_2O_3$	oxides is most acidic ? (B) P <sub>2</sub> O <sub>3</sub>	(C) Sb <sub>2</sub> O <sub>3</sub>	(D) N <sub>2</sub> O <sub>3</sub>
54.	Least acidic and most (A) $N_2O$ , $N_2O_5$	acidic oxides of nitroge (B) $N_2O$ , $N_2O_4$	en are - (C) N <sub>2</sub> O, NO	(D) N <sub>2</sub> O, N <sub>2</sub> O <sub>3</sub>
55.	Aqua regia is mixture (A) 3HCl + HNO <sub>3</sub>	of – (B) 3HNO <sub>3</sub> + HCI	(C) H <sub>3</sub> PO <sub>4</sub> + HCI	(D) PH <sub>3</sub> + HCIO
56.	The number of molecu	les of water needed to c	convert one molecule of	P <sub>2</sub> O <sub>5</sub> into orthophosphoric acid
	IS – (A) 2	(B) 3	(C) 4	(D) 5
57.	On heating ammonium (A) oxygen	dichromate, the gas evol (B) ammonia	ved is : (C) nitrous oxide	(D) nitrogen
58.	One mole of calcium ph (A) one mole of phosph (C) two moles of phosph	osphide on reaction with ine hine	excess water gives : (B) two moles of phospl (D) one mole of phosph	horic acid orus pentoxide
59.	Which statement is no (A) It is obtained by he (C) It is a typical non-n	t correct for nitrogen ? eating (NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> netal	(B) It does not readily (D) d-orbitals are avail	react with O <sub>2</sub> able for bonding
60.	Nitrogen is obtained by (A) $NH_4CI$	the thermal decomposition (B) NH <sub>4</sub> NO <sub>3</sub>	on of : (C) AgNO <sub>3</sub>	(D) none of these
61.	Nitrogen gas is prepare (A) by heating ammoniu (C) by passing HNO <sub>3</sub> va	d : ım nitrate. ıpours on red hot copper	<ul><li>(B) by reacting excess of</li><li>(D) by heating lead nitra</li></ul>	chlorine with liquor ammonia. ate.
62.	Which of the following (A) $H_3PO_2$	compound is tribasic ac (B) H <sub>3</sub> PO <sub>3</sub>	cid ? (C) H <sub>3</sub> PO <sub>4</sub>	(D) H <sub>4</sub> P <sub>2</sub> O <sub>7</sub>



## Group 16<sup>th</sup>

1.	Which of the following h (A) H <sub>2</sub> O	nydrides of the oxygen fa (B) H <sub>2</sub> S	mily shows the lowest bo (C) H <sub>2</sub> Se	illing point? (D) H <sub>2</sub> Te
2.	Which of the following s (A) Superoxides give hy (B) $CrO_3$ is an acidic ox (C) $SnO_2$ is an amphote (D) $KO_2$ is peroxide whi	statement is false ? /drogen peroxide and ox ide. eric oxide. ich with H <sub>2</sub> O forms hydro	ygen with water. gen peroxide only.	
3.*	The compound which o (A) AgNO <sub>3</sub>	n strong heating gives ox (B) BaO <sub>2</sub>	kygen is : (C) Pb(NO <sub>3</sub> ) <sub>2</sub>	(D) CaCO <sub>3</sub>
4.	In the reaction $O_3 + 2I^-$ (A) $I_2$	+ $H_2O \longrightarrow 2OH^- + (X B) IO_3^-$	$(C) + O_2$ . The compound ( $(C) IO_4^-$	X) is : (D) I <sub>2</sub> O <sub>5</sub>
5.	Ozone is - (A) An isobar of oxyge (C) A polymer of oxyg	en	(B) An isotope of oxy (D) An allotrope of oxy	gen ygen
6.	Ozone reacts with dry (A) $IO_2$	iodine to give - (B) $I_2O_3$	(C) I <sub>2</sub> O <sub>4</sub>	(D) I <sub>4</sub> O <sub>9</sub>
7.	Which of the following (A) O <sup>16</sup>	isotopes is present in (B) O <sup>17</sup>	largest amount - (C) O <sup>18</sup>	(D) All in equal amounts
8.	Hydrogen sulphide rea another compound. Th (A) Black	cts with lead acetate for ne colour of the compo (B) Yellow	ming a black compound und is - (C) White	which reacts with H <sub>2</sub> O <sub>2</sub> to form (D) Pink
9.	Oxygen is gas but sulphur is solid because - (A) Oxygen is composed of discrete molecules while sulphur is polymeric (B) Molecular weight of sulphur is much higher than that of oxygen (C) Oxygen is a stronger oxidising agent than sulphur (D) Boiling point of sulphur is much higher than that of oxygen			
10.	One gas bleaches the (A) CO and $CO_2$	colour of the flowers by (B) $H_2S$ and $Br_2$	reduction while the othe (C) $SO_2$ and $Cl_2$	er by oxidation. The gases are-(D) $\rm NH_3$ and $\rm SO_3$
11.	The commercial name (A) Sulphuric acid (C) Sulphuric acid crys	e for peroxodisulphuric a stals	acid is - (B) Marshall's acid (D) Sulphurous acid	
12.	<ul> <li>Estimation of ozone can be made quantitatively by :</li> <li>(A) decomposition into O<sub>2</sub> and absorption of O<sub>2</sub> into pyrogallol</li> <li>(B) volumetric method using KI and titration of the liberated iodine using hypo solution</li> <li>(C) oxidative ozonolysis method</li> <li>(D) all methods given above</li> </ul>			
13.	Sulphur on oxidation wi (A) SO <sub>3</sub>	th hot sulphuric acid give (B) SO <sub>2</sub>	s : (C) H <sub>2</sub> SO <sub>3</sub>	(D) H <sub>2</sub> S <sub>2</sub> O <sub>3</sub>
14.	Which one of the follow (A) ZnSO <sub>4</sub>	ing gives mixture of SO <sub>2</sub> (B) CuSO <sub>4</sub>	and SO <sub>3</sub> on heating ? (C) $Fe_2(SO_4)_3$	(D) FeSO <sub>4</sub>



15.*	Which of the following s (A) $SO_3^{2-}$	pecies is basic and redu (B) SO <sub>4</sub> <sup>2-</sup>	cing ? (C) $S_2O_4^{2-}$	(D) HSO <sub>4</sub> <sup>-</sup>
16.*	$SO_2$ can reduce : (A) HCIO <sub>3</sub> to HCI	(B) $\operatorname{Cr}_2 \operatorname{O}_7^{2-} / \operatorname{H}^+$ to $\operatorname{Cr}^{3+}$	(C) $MnO_4^- / H^+$ to $Mn^{2+}$	(D) $IO_3^-$ to $I_2$
17.	Which of the following   charcoal ?	product is formed by the	reaction of sulphur diox	ide with chlorine in presence of
	(A) SO <sub>2</sub> CI	(B) SO <sub>2</sub> Cl <sub>2</sub>	(C) SOCI <sub>2</sub>	(D) SO <sub>3</sub> Cl
18.	$H_2S$ is far more volatile (A) sulphur atom is mor (B) oxygen being more (C) $H_2O$ has bond angl (D) hydrogen atom is lo	than water because : e electronegative than over electronegative than sulp e of nearly 105°. osely bonded with sulphu	kygen atom. hur forms hydrogen bon ır.	d.
19.	When H <sub>2</sub> S is passed the (A) yellow	rough acidified K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> s (B) blue	solution, the solution turn (C) green	s : (D) white
20.	The following catalyst is (A) NO	used in the manufacturi (B) NO <sub>2</sub>	ng of sulphuric acid by le (C) Pt	ad chamber process. (D) V <sub>2</sub> O <sub>5</sub>
21.	$H_2SO_4$ has very corrosi (A) it reacts with protein (B) it acts as an oxidisin (C) it acts as a dehydrat (D) it acts as a dehydrat	ive action on skin becaus s ig agent ting agent ting agent and absorptior	se : n of water is highly exothe	ermic.
22.	Concentrated $H_2SO_4$ dis (A) it is stronger than hy (C) Sulphates are more	splaces hydrogen chlorid /drochloric acid. soluble than chlorides	e from chlorides because (B) HCI is a gas while H (D) Sulphates are less s	e: $I_2SO_4$ is a liquid. soluble than chlorides
23.	Which of the following r (A) $2PCI_5 + H_2SO_4$ (B) $2NaOH + H_2SO_4$ (C) $NaCI + H_2SO_4$ (D) $2HI + H_2$	eactions depict the oxidis $\rightarrow 2POCl_3 + 2HCl + SO_2$ $\longrightarrow Na_2SO_4 + 2H_2O$ $\rightarrow NaHSO_4 + HCl$ $\Rightarrow I_2 + SO_2 + 2H_2O$	sing behaviour of H <sub>2</sub> SO <sub>4</sub> <sub>2</sub> Cl <sub>2</sub>	?
24.	Out of $H_2S_2O_3$ , $H_2S_4O_6$ (A) $H_2S_2O_3$ , $H_2S_4O_6$	, $H_2SO_5$ and $H_2S_2O_8$ perc (B) $H_2S_4O_6$ , $H_2SO_5$	exy acids are : (C) $H_2SO_5$ , $H_2S_2O_8$	(D) H <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , H <sub>2</sub> S <sub>2</sub> O <sub>8</sub>
25.	The term 'thio' is used in (A) $Na_2S_2O_3$	n the names of all of the t (B) Na <sub>2</sub> S <sub>2</sub> O <sub>6</sub>	following compounds exc (C) NaSCN	cept : (D) Na <sub>2</sub> SO <sub>3</sub>
26.	The reaction between diminishes. The pink co	ferric salt and aqueous lour is due to the formati	sodium thiosulphate pro	oduces pink colour which soon
	(A) [Fe(S <sub>2</sub> O <sub>3</sub> ) <sub>3</sub> ] <sup>4–</sup>	(B) [Fe(S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>	(C) $Fe_2 (S_4O_6)_3$	(D) none of these
27.	The decreasing order (A) O > S > Se > Te	of catenation of group (B) S > O > Se > Te	16 elements is - (C) S > Se > O > Te	(D) O > S > Te > Se
28.	The correct increasing $(A) H_2O < H_2S < H_2Se < (C) H_2Se < H_2Te < H_2O$	order of dipole moments < $H_2Te$ < $H_2S$	of the following is - (B) H <sub>2</sub> Te < H <sub>2</sub> Se < H <sub>2</sub> S (D) H <sub>2</sub> S < H <sub>2</sub> O < H <sub>2</sub> Se	< H <sub>2</sub> O < H <sub>2</sub> Te
29.	Low volatile neture of H (A) Hydrogen bonding (C) Strong bonds	$_2$ SO <sub>4</sub> is due to -	(B) Vander Waals' force (D) None of these	PS



30.	Oxygen is more electronegative than sulphur, yet $H_2S$ is acidic while $H_2O$ is neutral. This is because- (A) Water is a highly associated compound (B) $H - S$ bond is weaker than $H - O$ bond (C) $H_2S$ is a gas while $H_2O$ is a liquid (D) The molecular weight of $H_2S$ is more than that of $H_2O$			
31.	The acidic character of (A) $SeO_2 > SO_2 > TeO_2$ (C) $PoO_2 > TeO_2 > SeO_2$	dioxides of members of $0 > PoO_2$ $O_2 > SO_2$	bxygen family decreases (B) $SO_2 > SeO_2 > Te O_2$ (D) $TeO_2 > PoO_2 > SeO_2$	in the order - > $PoO_2$ $P_2 > SO_2$
32.	A solution of $SO_2$ in wat (A) An oxidising agent	er reacts with H <sub>2</sub> S precip (B) A reducing agent	itating sulphur. Here SO (C) An acid	$_{2}$ acts as - (D) A catalyst
33.	Which of the following of (A) $N_2O_5$	oxides is the most acidic? (B) P <sub>2</sub> O <sub>5</sub>	(C) As <sub>2</sub> O <sub>5</sub>	(D) Sb <sub>2</sub> O <sub>5</sub>
34.	Hydrolysis of one mole (A) two moles of sulphu (B) two moles of peroxy (C) one mole of sulphur (D) one mole of sulphur	of peroxy disulphuric acid ric acid monosulphuric acid. ric acid and one mole of p ric acid, one mole of hydr	d produces beroxy monosulphuric ac ogen peroxide.	id.
35.	The oxidation number $c$ (A) 0, + 1 and – 2	of sulphur in S <sub>8</sub> , S <sub>2</sub> F <sub>2</sub> and (B) + 2, + 1 and – 2	$H_2S$ respectively are : (C) 0, + 1 and + 2	(D) - 2, + 1 and - 2
36.	Which one has the high $(A) O - O$	est bond energy - (B) S – S	(C) Se – Se	(D) Te – Te
37.	Caro's acid is - (A) H <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	(B) H <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	(C) H <sub>2</sub> SO <sub>3</sub>	(D) H <sub>2</sub> SO <sub>5</sub>
38.	On heating ozone, its ve	olume -		
	(A) Increases to $1\frac{1}{2}$ tim	nes	(B) Decreases to half	
	(C) Remains unchange	d	(D) Becomes double	
39.	Concentrated H <sub>2</sub> SO <sub>4</sub> is (A) Oxidizes HBr (C) Causes disproportio	not used to prepare HBr pnation of HBr	from KBr because it - (B) Reduces HBr (D) Reacts too slowly w	ith KBr
40.	Vegetable colouring ma (A) Oxidation	tter in presence of moist (B) Reduction	ure is bleached by SO <sub>2</sub> d (C) Sulphonation	ue to - (D) Unsaturation
41.	When water is added in (A) $H_2SO_4$ is viscous (C) $H_2SO_4$ is corrosive	conc. $H_2SO_4$ the reactio	n is exothermic because (B) Hydrates of H <sub>2</sub> SO <sub>4</sub> a (D) None of these	- are formed
42.	$H_2SO_4$ reacts with suga (A) A dehydrating agent (C) A sulphonating ager	r and acts as - nt	(B) An oxidizing agent (D) None of these	
43.	Which of the following h	has $p\pi$ –d $\pi$ bonding ?		
	(A) NO <sub>3</sub>	(B) SO <sub>3</sub> <sup>2-</sup>	(C) BO <sub>3</sub> <sup>3-</sup>	(D) CO <sub>3</sub> <sup>2-</sup>
44.	The decreasing tenden (A) S > Se > Te > Po	cy to exist in puckered 8- (B) Se > S > Te > Po	membered ring structure (C) S > Te > Se > Po	is - (D) Te > Se > S > Po
45.	The increasing thermal (A) $H_2O < H_2S < H_2Se$ (C) $H_2S < H_2O < H_2Se$	stability of the hydrides c < H <sub>2</sub> Te < H <sub>2</sub> Te	f group 16 follows seque (B) $H_2$ Te < $H_2$ Se < $H_2$ S (D) $H_2$ Se < $H_2$ O < $H_2$ S	ence - 5 < H <sub>2</sub> O < H <sub>2</sub> Te
46.	In SF <sub>4</sub> , sulphur is - (A) dsp <sup>2</sup> -Hybridized	(B) sp <sup>3</sup> d-Hybridized	(C) d <sup>2</sup> sp <sup>3</sup> -Hybridized	(D) sp <sup>3</sup> -Hybridized
47.	The correct order of det (A) $SF_6 > SeF_6 > TeF_6$ (C) $SF_6 > TeF_6 > SeF_6$	creasing stability of hexa	fluorides of group 16 mer (B) $TeF_6 > SeF_6 > SF_6$ (D) $TeF_6 > SF_6 > SeF_6$	nbers is -



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## **PART - II : MISCELLANEOUS QUESTIONS**

## MATCH THE COLUMN

Group 15 <sup>th</sup>			
1.	. Column I		Column II
	(a)	Acid hydride of nitrogen	(i) Nitrous oxide
	(b)	Laughing gas	(ii) [Fe(H <sub>2</sub> O) <sub>5</sub> NO]
	(c)	Nitrolim	(iii) Dinitrogen trioxide
	(d)	Brown ring	(iv) Ammonia
	(e)	Deep blue liquid	(v) Calcium cyanamide and carbon
	(f)	lodide of Millon's base	(vi) Hydrazoic acid
			(vii) Diphenyl amine

#### 2. Column I (a) $H_3PO_3$ (Unbalanced) $\_^{\Delta}$ $HNO_3(50\%) + As_2O_3 + H_2O (Unbalanced) \longrightarrow (ii) NO_2$ (b) $Pb(NO_3)_2$ (Unbalanced) $\_^{\Delta}$ (c)

- (d)  $NH_4NO_3$  (Unbalanced)  $\_$
- $P_4$  + NaOH + H<sub>2</sub>O (Unbalanced)  $\xrightarrow{\Lambda}$ (e)

## Column – II

Column II

(i)  $N_2O$ 

(iii) PH<sub>3</sub>

(v) NO

(vi) H<sub>3</sub>PO<sub>4</sub>

(iv) NaH<sub>2</sub>PO<sub>2</sub>

(A) $PCI_5 \xrightarrow{Moist}_{Air}$	(P) Hydrolysis
(B) $P_4$ + NaOH (conc.) + $H_2O \xrightarrow{\Delta} CO_2$	(Q) At least one of the products has tetrahedral hybridisation
(C) $H_3PO_3 \xrightarrow{\Delta}$ (D) $P_2O_3 + H_2O \xrightarrow{\Delta}$	(R) Disproportionation (S) At least one of the products has $p\pi$ –d $\pi$ bonding.

## Group 16<sup>th</sup>

4.

3.

Column – I

Column I	Column II
(a) Fish like smell	(i) iodometric titration
(b) $Na_2CO_3$ (aq.) + $SO_2$ (excess)	(ii) Sulphur
(c) Kipp's apparatus	(iii) contact process
(d) Alkali waste	(iv) Ozone
(e) $I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{-2-} + 2I^-$	(v) Hydrogen Sulphide
(f) Vulcanised rubber	(vi) Calcium Sulphide
(g) Vanadium pentoxide	(vii) Sodium thiosulphate



5.	Column I	Column II
	(a) Hydrogen sulphide	(i) Brown colour with alcoholic benzidine
	(b) Hydrogen peroxide	(ii) Pink colour with ferric chloride
	(c) Ozone	(iii) Green colour with acidfied potassium dichromate
	(d) Sodium thiosulphate	(iv) Anhydride of sulphuric acid
	(e) Sulphur dioxide	(v) Frasch process
	(f) Sulphur trioxide	(vi) Yellow ppt with cadmium
	(g) Sulphuric acid	(vii) Orange colour with titanium sulphate solution
	(h) Sulphur	(viii) Salt cake insoluble in water
	(i) sodium bisulphate	(ix) Absorbs water from organic compound
6.	Column – I	Column – II
	(A) $(NH_4)_2S_2O_8 + H_2O \xrightarrow{\text{Distillation}}$	(P) Hydrolysis
	(B) NaBO <sub>2</sub> + H <sub>2</sub> O + H <sub>2</sub> O <sub>2</sub> $\xrightarrow{OH^-}$	(Q) One of the product has peroxide linkage
	(C) Na <sub>2</sub> SO <sub>3</sub> $\xrightarrow{\text{fusion}}_{\text{temperature}}$	(R) Disproportionation.
	(D) 2–Ethyl anthraquinol + Air $\longrightarrow$	(S) In one of the products the central atom has $sp^3$ hybridisation.

## **ASSERTION / REASONING**

## **DIRECTIONS**:

The following questions consist of two statements one labelled ASSERTION (A) and the another labelled REASON (R). Select the correct answers to these questions from the codes given below :

- (A) Both Assertion and Reason are true and Reason is the correct explanation of Assertion.
- (B) Both Assertion and Reason are true but Reason is not correct explanation of Assertion
- (C) Assertion is true but Reason is false
- (D) Assertion is false but Reason is true

## Group 15<sup>th</sup>

- 7. Assertion : Ammonium nitrite on heating gives  $N_2O$ . Reason :  $N_2O$  is a neutral oxide.
- Assertion: H<sub>3</sub>PO<sub>3</sub> is a dibasic acid and shows reducing character.
   Reason: H<sub>3</sub>PO<sub>3</sub> contains two OH<sup>-</sup> groups and one hydrogen atom directly attached to P atom.
- **Assertion :** Liquid NH<sub>3</sub> is used for refrigeration.
   **Reason :** Enthalpy of vaporisation of ammonia is very large.
- **10.** Assertion :  $PCI_5$  is covalent in gaseous and liquid state but ionic in solid state. **Reason :**  $PCI_5$  in solid state consists of tetrahedral  $PCI_4^+$  cation and octahedral  $PCI_6^-$  anion.
- Assertion : Among nitrogen halides NX<sub>3</sub>, the dipole moment is highest for NI<sub>3</sub> and lowest for NF<sub>3</sub>.
   Reason : Nitrogen halides NX<sub>3</sub>, have trigonal pyramidal structure.



- 12. Assertion :  $NO_3^-$  is planar while  $NH_3$  is pyramidal. Reason : N in  $NO_3^-$  is sp<sup>2</sup> hybridised but in  $NH_3$  it is sp<sup>3</sup> - hybridised.
- **13. Assertion** : NaH<sub>2</sub>PO<sub>2</sub> is the acid salt. **Reason** : It contains no ionisable protons.
- Assertion : Both H<sub>3</sub>PO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> have the same number of hydrogen atoms but H<sub>3</sub>PO<sub>4</sub> is a tribasic acid and H<sub>3</sub>PO<sub>3</sub> is a diabasic acid.
   Reason : 1 mol of H<sub>3</sub>PO<sub>3</sub> is neutralised by 2 mol of NaOH while 1 mol of H<sub>3</sub>PO<sub>4</sub> is neutralised by 3 mol of NaOH.

## Group 16<sup>th</sup>

- Assertion : Covalency of oxygen is two (O<sup>2-</sup>)
   Reason : Dinegative anion of oxygen (O<sup>2-</sup>) is quite common but dinegative anion of sulphur (S<sup>2-</sup>) is less common.
- **16. Assertion :** At room temperature oxygen exists as a diatomic gas, where as sulphur exists as solid. **Reason :** The catenated O O O changes are less stable as compared to O = O molecule.
- 17. Assertion : Anhydrous  $BaO_2$  is not used for preparing  $H_2O_2$ . Reason :  $H_2O_2$  is prepared on large scale by air oxidation of 2-Ethyl anthraquinol.
- Assertion : Tailing of mercury occurs on passing O<sub>3</sub> thorugh it.
   Reason : Due to oxidation of mercury in to mercury suboxide (Hg<sub>2</sub>O) mercury starts sticking to glass wall.
- **19. Assertion :** Sulphuric acid is less viscous than water due to intramolecular hydrogen bonding. **Reason :** Concentrated sulphuric acid has a great affinity for water.
- 20. Assertion : In caro's acid the oxidation state of sulphur is +6 Reason : In caro's acid, there is one peroxolinkage. ( - O - O -)
- 21. Assertion : Ozone is a stronger oxidising agent in acidic medium. Reason :  $O_3 + 2H^+ + 2\overline{e} \rightarrow O_2 + H_2O$ ; SRP = + 2.07V  $O_3 + H_2O + O\overline{e} \rightarrow O_2 + 2OH^-$ ; SRP = + 1.24V
- 22. Assertion : A pink coloured solution of potassium permangnate turns green on passing  $O_3$  through it. Reason :  $K_2MnO_4$  is oxidised by  $O_3$  to  $KMnO_4$
- **23.** Assertion :  $H_2O_2$  is stored in wax-lined glass Reason : Presence of traces of alkali metal ions from the glass catalyse the decomposition of  $H_2O_2$ .
- 24. Assertion : Reaction of SO<sub>2</sub> and H<sub>2</sub>S in the presence of  $Fe_2O_3$  catalyst gives elemental sulphur. Reason : SO<sub>2</sub> acts as a reducing agent.
- 25. Assertion :  $S_8$  molecule has puckered ring structure Reason :  $S_8$  molecules contains eight lone pairs of electrons
- 26. Assertion : Sulphur exhibits paramagnetic behaviour in vapour state. Reason : In vapour state sulphur partly exists as  $S_2$  molecule which has two unpaired electrons in antibonding  $\pi^*$  orbitals.



## TRUE / FALSE Group 15<sup>th</sup>

- 27. Conc. HNO<sub>3</sub> renders iron passive probably because of the formation of an oxide film.
- 28. Nitrous acid acts both as an oxidising and a reducing agent.
- **29.** The bond angle in ammonia is smaller than bond angle in phosphine.
- **30.** Phosphorus acid is a tribasic acid.
- **31.** Red phosphorus is less volatile than white phosphorus because the former has a tetrahedral structure.
- **32.**  $PH_3$  is less basic than ammonia.
- **33.** Quick lime is used for drying ammonia.
- **34.** Nitric oxide, though an odd electron molecule is diamagnetic in liquid state.
- **35.** Ammonia has extensive hydrogen bonding.
- **36.** Phosphorus (white) is usually stored under water to prevent it catching fire.
- **37.** Dinitrogen tetraoxide is paramagnetic.
- **38.**  $PCI_5$  is an ionic solid at room temperature.
- **39.** The dipole moment of  $NF_3$  is higher than that of  $NH_3$ .
- **40.**  $NF_3$  is stable but  $NCI_3$  and  $NI_3$  are explosive in nature.

## Group 16th

- **41.** SO<sub>2</sub> does not help in combustion but burning magnesium continues burning in its atmosphere.
- 42. Concentrated sulphuric acid must be slowly added to water with constant stirring for dilution.
- 43. Marshall's acid has S-S linkage
- 44. High boiling point and high viscocity of sulphuric acid is due to intra molecular hydrogen bonding
- **45.** Sodium thiosulphate is used as antichlor during the dyeing process
- **46.** In  $SO_4^{2-}$  all S-O bond lengths are not equal.
- **47.** Dry  $SO_2$  does not bleach dry flowers.
- 48. Sulphur in vapour state exhibit paramagnetic behaviour.
- **49.** In the solid state, SO<sub>3</sub> exists in several modifications having a cyclic trimeric or a linear polymeric chain structure.
- 50. Alkaline KI is oxidised to potassium iodadte and periodate by ozone.



## FILL IN THE BLANKS

Group 15<sup>th</sup>

51.	is a neutral oxide of nitrogen.		
52.	Nitrolim is a mixture of carbon and		
53.	Phosphorus is reactive because of its highly strained tetrahedral structure.		
54.	Phosphorus pentoxide reacts witn nitric acid to formand		
55.	Laughing gas is formed by heating ammonium		
56.	A mixture of conc. HNO <sub>3</sub> and is used for the nitration of organic compounds.		
57.	The basicity of phosphorus acid is		
58.	In $P_4O_{10}$ , the number of oxygen atoms bonded to each phosphorus atom is		
59.	The angle P–P–P in $P_4$ molecule is degree.		
60.	Among $PCl_3$ , $CH_3^+$ , $NH_2^-$ and $NF_3$ is least reactive towards water.		
61.	The use of ammonia in refrigeration is based on its		
62.	The formula of hydrazine is the oxidation state of nitrogen in hydrazine is		
63.	The acidic hydride of nitrogen is its formula is		
64.	There are single bonds and double bonds in P <sub>4</sub> O <sub>10</sub> molecule.		
65.	The molecules of $PCI_5$ in solid state are in nature consisting tetrahedral cations and [PCI_6] <sup>-</sup> ions.		
66.	Red phosphorus is reactive than white phosphorus as red phosphorus is		
67.	The maximum valency, that the element nitrogen exhibits, is		
68.	Thermal decomposition of ammonium dichromate produces gas and steam.		
69.	In $P_4O_6$ , each phosphorus is linked with oxygen atoms.		
70.	Ammonia is made dry by the use of		
71.	NO <sub>2</sub> is the mixed anhydride of and acids.		



## Group 16<sup>th</sup>

- **72.** The lead chamber process involves the oxidation of ..... by atmospheric oxygen under the influence of ...... as catalysts.
- 73. Sulphur acts as ..... agent in vulcanization of rubber.
- 74. Monoclinic sulphur is stable above .....<sup>0</sup>C
- **75.** An oxide,..... liberates chlorine with HCl and oxygen with conc.  $H_2SO_4$ .
- **76.**  $2\text{NaHSO}_3 + 2\text{H}_2\text{S} \rightarrow \dots + 3\text{S} + 3\text{H}_2\text{O}$
- 77. Aqueous solution of sodium chlorate reacts with sulphur dioxide to form...... acid and sodium chloride.
- 78. Fluorine reacts with water at very low temp. when mixture of .....is formed
- 79. When ...... gas is passed through dry KOH a deep orange coloured compound ..... is formed.
- 80. CuO is..... oxide whereas CO is ..... oxide.
- 81. Bleaching action of SO<sub>2</sub> is due to ..... and is .....

## **EXERCISE** # 2

## **PART - I : MIXED OBJECTIVE**

## Single choice type Group 15<sup>th</sup>

1.	The H–MH bond angle in the hydrides of grou (A) $NH_3 > PH_3 > AsH_3 > SbH_3$ (B) N (C) $NH_3 < PH_3 = AsH_3 = SbH_3$ (D) P		f group (B) NH <sub>3</sub> (D) PH <sub>3</sub>	jroup 15 elements follows the order ) NH <sub>3</sub> < PH <sub>3</sub> < AsH <sub>3</sub> < SbH <sub>3</sub> ) PH <sub>3</sub> > NH <sub>3</sub> > AsH <sub>3</sub> > SbH <sub>3</sub>			
2.	When $NH_3$ is oxidised w (A) $NCI_3$	vith excess NaOC (B) NH <sub>2</sub> OH	l, the co	ompound formed is (C) N <sub>3</sub> H	(D) NO <sub>2</sub>		
3.	The gas obtained on he (A) $N_2O$	ating lead nitrate t (B) NO	to 400°(	C is (C) NO <sub>2</sub>	(D) N <sub>2</sub> O <sub>5</sub>		
4.	Which of the following c (A) $NH_4NO_2$	ompounds does g (B) NH <sub>4</sub> NO <sub>3</sub>	give N <sub>2</sub>	on heating? (C) NaN <sub>3</sub>	(D) Both (A) and (C)		
16 <sup>TH</sup> 5.	<b>Group</b> The oxide which on stro (A) AgNO <sub>3</sub>	ng heating gives o (B) BaO <sub>2</sub>	oxygen	is : (C) Both (A) and (B)	(D) Na <sub>2</sub> O		
6.	In the reaction $O_3 + I_2 + H_2O - I_3$ The compound (X) is (A) HIO <sub>3</sub>	→ (X) + O <sub>2</sub> (B) HI		(C) HIO <sub>4</sub>	(D) I <sub>2</sub> O <sub>5</sub>		
7.	The aqueous solution of (A) converts blue litmus (C) converts red litumus	f hydrogen peroxic pink s blue	de	(B) converts blue litumus white (D) None of these			
8.	The process of obtainin (A) the Frasch process (C) the Calcaroni proces	g sulphur by the b ss	orehole	e method is called : (B) the Lablanc process (D) the Mannheium process			



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# More than one choice type Group 15<sup>th</sup>

- 9. As, Sb and Bi show little or no tendency to form negative ions of the type M<sup>3-</sup>. This is because
  - (A) these elements are less electronegative
  - (B) their atoms have larger size
  - (C) they are unable to hold the added electrons due to inert pair effect
  - (D) they do not posses half filled np subshells
- **10.** Which of the following statements is (are) correct ?
  - (A) The hydrides of group 15 elements act as oxidising agents
  - (B) The hydrides of group 15 elements act as reducing agents
  - (C) The oxidising power increases in going from  $\rm NH_3$  to  $\rm BiH_3$
  - (D) The reducting power increases in going from  $\rm NH_3$  to  $\rm BiH_3$
- **11.** Which of the following statements is (are) correct ?
  - (A) Antimony on reaction with conc.  $\ensuremath{\mathsf{HNO}_3}$  gives antimonic acid.
  - (B) manganese on reaction with dilute  $\mathrm{HNO}_3$  gives  $\mathrm{NO}_2$  gas.
  - (C)  $HNO_2$  disproportionate to give  $HNO_3$  and NO
  - (D)  $\mathrm{HNO}_3$  on reaction with  $\mathrm{P_4O}_{10}$  gives  $\mathrm{N_2O}_5$
- 12. Which of the following statements is (are) correct ?
  - (A)  $SbH_3 > NH_3 > ASH_3 > PH_3$  (boiling point)

(B)  $H_3PO_4 > H_3PO_3 > H_3PO_2$  (reducing character)

- (C)  $N_2O < NO < N_2O_3 < N_2O_5$  (oxidation state on nitrogen atom)
- (D)  $NH_3 > PH_3 > ASH_3 > SbH_3 \ge BiH_3$  (Basicities)

## Group 16<sup>th</sup>

- **13.** Which of the following statement (s) is/are true for sodium thiosulphate ?
  - (A) it acts as an antichlor
  - (B) it is used as an reducing agent in iodometric titration.
  - (C) it reacts with hydrochloric acid to form  $SO_2$  and sulphur.

(D) it is used in photography as hypo to dissolves excess of AgBr as soluble complex.

- **15.** Select the correct statement (s) from the following
  - (A) Alcoholic benzidine gives brown colour with  $H_2O_2$  but not with  $O_3$ .
  - (B) Lead gives white precipitate with hypo but on boiling with water it turns black.
  - (C) Acidified solution of  $H_2O_2$  is used for restoring the colour of lead painting.
  - (D) Sulphur when dissolves in oleum gives bright coloured solution.
- **16.** Which of the following is/are true for oxygen.
  - (A) KMnO<sub>4</sub>(s) on strong heating gives oxygen gas
  - (B) Oxygen mixed with helium or CO<sub>2</sub> is used for artificial respiration.
  - (C) It has two unpaired electrons in bonding  $\boldsymbol{\pi}$  molecular orbitals.
  - (D) Brins process is used as industrial method for the preparation of oxygen gas.
- **17.** Sulphuric acid acts as

(A) hygroscopic agent (B) sulphonating agent (C) reducing agent

(D) oxidising agent.

- **18.** What is true for hydrogen peroxide and ozone ?
  - (A)  $H_2O_2$  acts as a stronger reducing agent in alkaline medium than in acidic medium
  - (B)  $H_2O_2$  and  $O_3$  both are oxidising agents as well as bleaching agent
  - (C)  $H_2O_2$  forms a hydrate,  $H_2O_2.H_2O$
  - (D) Ozonc is wed in the manfacture of potassium permangnate from pyrolusite.



## **PART - II : SUBJECTIVE QUESTIONS**

#### Group 15<sup>th</sup>

- 1.  $NO_2$  can not be dried by an alkali, why?
- 2. Nitrogen cannot be stored as liquid in sealed containers but ammonia can be, why?
- 3. Concentrated HNO<sub>3</sub> turns yellow in sun light. Explain ?
- 4. Anhydrous CaCl<sub>2</sub>, P<sub>4</sub>O<sub>10</sub> or conc. H<sub>2</sub>SO<sub>4</sub> can not be used as drying agent for ammonia. why ?
- 5. Red phosphorus is denser, less volatile and chemically less reactive than yellow phosphorus. Explain ?
- 6. How many P–O bonds are there in  $P_4O_6$  and  $P_4O_{10}$ ?
- 7. What happens when molten mixture of  $KNO_3$  and  $KNO_2$  reacts with  $Cr_2O_3$ ?
- **8.** How NO,  $N_2O_5$  and NO<sub>2</sub> can be differentiate ?
- **9.** What happens when PCl<sub>3</sub> reacts with amino methane.
- **10.** Complete and balance the following chemical equations : (a)  $HSO_3 NH_2 + HNO_3 (Conc.) \longrightarrow$ 
  - (b)  $Ag_2N_2O_2 + HCI \xrightarrow{\text{ether}}$
  - (c)  $HNO_3$  (50%) +  $As_2O_3$  +  $H_2O \longrightarrow$
  - (d) AgNO<sub>3</sub> + Cl<sub>2</sub>  $\xrightarrow{60-90^{\circ}C}$

(e)  $HPO_3 + H_3PO_4 \xrightarrow{100^{\circ}C}$ (taken in equimolar) (f)  $Ca_3 (PO_4)_2 + SiO_2 + C \longrightarrow$ 

- 11. What products are formed when H<sub>3</sub>PO<sub>2</sub> is heated at 415 K and at 435 K respectively.
- **12.** Which is stronger  $H_3PO_3$  or  $H_3PO_4$ ?
- 13. What happens when phosphoric acid is heated ?
- **14.** Write the chemical reactions of  $P_4O_6$  with cold and hot water.
- **15.** Give the equations for preparation of :
  - (A) Superphosphate of lime
  - (B) Nitrolim
  - (C) Phosphine (by  $P_4$  and  $I_2$ (aq)
- **16.** Why does  $NO_2$  dimerise ?



- 17. Why is BiH<sub>3</sub> the strongest reducing agent among all the hydrides of group 15 elements ?
- **18.** In what way can it be proved that  $PH_3$  is basic in nature ?
- **19.** Why does PCl<sub>3</sub> fumes in air ?
- 20. What happens when
  (A) PCI<sub>5</sub> is heated.
  (B) PCI<sub>5</sub> is reacted with heavy water.
  (C) H<sub>3</sub>PO<sub>3</sub> is heated.
- **21.** Explain why NH<sub>3</sub> is basic while BiH<sub>3</sub> is only feebly basic ?
- **22.** Nitrogen exists as diatomic molecule and phosphorus as  $P_4$ ?
- **23.** Give the resonating structure of  $NO_2$  and  $N_2O_5$ ?
- **25.** Give reasons for the following:
  - (a) Formation of NH<sub>3</sub> from its elements at constant pressure is accompanied by a decrease in volume.
  - (b) Nitric oxide turns brown in air.
  - (c) Copper dissolves in HNO<sub>3</sub> but not in HCI.
  - (d)  $Pb(NO_3)_2$  on heating produces a pale yellow gas which on strong heating produces brown gas.
- **26.** State the property of ammonia due to which it is used in refrigeration.
- 27. What happens when:
  - (a) NH<sub>4</sub>CI & NaNO<sub>3</sub> is heated strongly
  - (b)  $NH_4NO_3$  is heated
  - (c)  $NH_4NO_2$  is heated
  - (d)  $Mg_3N_2$  reacts with water
  - (e)  $NaNO_3$  is heated with NaOH and Zn powder in water
  - (f) Mg is burnt in air and the product is treated with water
- **28.** State the conditions under which  $NH_3$  is manufactured from  $N_2$  and  $H_2$ .
- **29.** How will you obtain  $N_2$  from a mixture of  $N_2$  and CO?
- **30.** Commercial nitrogen is passed through copper chips kept in ammonia solution for removing oxygen. Explain.
- **31.** Nitric acid acts only as an oxidising agent while nitrous acid can act both as an oxidising and reducing agent.
- **32.** Write down a reaction showing action of  $N_2O_4(\ell)$  as non-aqeous solvent.
- **33.** A waxy crystalline solid (A) with a garlic odour is obtained by buring white P in a stream of air. (A) reacts vigorously with hot water forming a gas (B) and an acid (C). Gas (B) has unplesant odour of rotten fish and is neutral towards litmus. When passed through CuSO<sub>4</sub> solution gas (B) produced a black ppt. (D) What are (A) to (D) ? Give chemical equations of the reactions.
- **34.** Why does  $H_3PO_3$  act as a reducing agent but  $H_3PO_4$  does not?



## Group 16<sup>th</sup>

- 35. Which allotropic form of sulphur is stable at room temp?
- 36. Explain why the liquid oxygen stickes to the magnet pole but liquid nitrogen does not ?
- **37.** Write the names of substances which have higher oxidation potential than ozone.
- **38.** Write the allotropic forms of oxygen
- **39.** Why sulphur is able to show oxidation state of +4 and +6 with fluorine and oxygen ?
- 40. How oxygen is prepared in large scale by Brin's process
- 41. What happens when
  - (a)  $K_2Cr_2O_7$  is strongly heated
  - (b) Silent electric discharge is passed through pure and dry O<sub>2</sub>
  - (c) Ozone reacts with dry iodine
  - (d) 2-Ethyl anthraquinol undergoes air oxidation
  - (e) Reaction between formaldehyde and hydrogen peroxide is carried out in dark.
  - (f) Sodium thiosulphate reacts with ferric chloride solution.
  - (g) H<sub>2</sub>S and SO<sub>2</sub> react in presence of moisture
  - (h) Burning magnesium is kept in the atmosphere of SO<sub>2</sub>
  - (i) Acidified iodates react with SO<sub>2</sub>
  - (j) Conc. H<sub>2</sub>SO<sub>4</sub> is made to react with phosphorus pentaoxide
- **42.** Why in  $SO_4^{2-}$  all S O bonds have equal bond lengths ?
- **43.** How pure hydrogen sulphide is prepared ?
- **44.** Concentrated  $H_2SO_4$  can not be used for drying  $H_2$ .
- **45.**  $H_2S$  is stronger acid than  $H_2O$ . Why?
- **46.** Explain the following :

(i) An acidified  $K_2Cr_2O_7$  paper turns green when exposed to  $SO_2$ 

(ii)  $H_2S$  acted only as reducing agent while  $SO_2$  can act both as a reducing agent and oxidising agent (iii)  $SO_2$  acts as a bleacing agent.

- 47. Why is dioxygen a gas but sulphur a solid ?
- **48.**  $H_2S$  is less acidic than  $H_2Te$ , why?
- 49. Which of the following do not react with oxygen directly ? Zn, Fe, Au,Kr.
- **50.** Why is  $Ka_2 \ll Ka_1$  for  $H_2SO_4$  in water ?
- **51.** How is  $O_3$  estimated quantitatively ?
- 52. Out of following forms of sulphur which one is paramagnetic in nature and why ?  $S_8$ ,  $S_6$  and  $S_2$
- **53.** How is the presence of  $SO_2$  detected ?
- **54.** How is  $SO_2$  an air pollutant ?
- 55. Which aerosols deplete ozone ?
- 56. Describe the changes which occur on heating sulphur .
- **57.** What happens when one mole (partial hydrolysis) and excess of water (complete hydrolysis) reacts with one mole of per oxodisulphuric acid ?
- **58.** Why are sulphurous acid and sulphites redcuing ?.
- **58.** Describe the action of heat on NaHSO<sub>3</sub>.



- **59.** What happens when  $Na_2S_3$  is heated in air ?
- **60.** Oxygen almost invariably exhibits an oxidation state of -2 but other members of the family exhibit negative as well as positive oxidation state of +2, +4 and +6.
- 61. Sulphur dioxide acts as a strong reducing agent in alkaline medium.
- **62.** Among the hydrides,  $H_2O$ ,  $H_2S$ ,  $H_2Se$  which has highest bond angle.
- **63.** Which of the following has highest boiling point and why (a)  $H_2O$  (b)  $H_2S$
- 64. What do you understand by tailing of mercury ?
- **65.** An inorganic halide (A) reacts with water to form two acids (B) and (C). Also aqueous solution of (A) reacts with KOH to form two salts (D) and (E) Which are soluble in water. The solution gives white precipitates with both AgNO<sub>3</sub> and BaCl<sub>2</sub> solutions respectively. Identify (A) to (E) and write the chemical reactions involved.
- 66. From the reactions given below, identify (A), (B), (C) and (D) and write their formulae. (A) + dil.  $H_2SO_4 + K_2Cr_2O_7 \rightarrow$  (B) Green Solution (A) + dil.  $H_2SO_4 +$  (C)  $\rightarrow$  MnSO<sub>4</sub> (A) + O<sub>2</sub>  $\xrightarrow{H_2O}$  (D) (D) + BaCl<sub>2</sub>  $\rightarrow$  White ppt.
- **67.** Arrange the following in increasing order
  - (a)  $H_2O$ ,  $CO_2$ ,  $SO_3$ ,  $N_2O_5$ ,  $SiO_2$  Acidic character
  - (b)  $H_2O, H_2S, H_2Se, H_2Te$  Thermal stability
- **68.** On heating rhombic sulpur it melts but viscosity of liquid increases upto 200<sup>0</sup>C and beyond that it decreases why ?
- **69.** O O bond length is more in  $H_2O_2$  than in  $O_2F_2$ . Explain.
- **70.** For drying  $H_2S$  gas conc.  $H_2SO_4$  can not be used why?
- 71. Draw the structure of following acids.(a) Marshall's acid(b) Dithionic acid(c) Caro's acid
- **72.** Complete the following equations
  - (i)  $I_2 + O_3 + H_2O \rightarrow HIO_3 + \dots$
  - (ii) NaHS + .....  $\rightarrow$  Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> + H<sub>2</sub>O
  - (iii)  $(NH_4)_2S_2O_8 + H_2O + MnSO_4 \rightarrow \dots + \dots + \dots$
  - (iv)  $Sb_2S_3 + HCI \rightarrow \dots + \dots$
  - (v)  $Hg_2CI_2 + SO_2 + HCI \rightarrow \dots + \dots + \dots$
  - (vi)  $CaS + H_2O + CO_2 \rightarrow \dots + \dots$
- 73. What happens when
  - (A) FeCl<sub>3</sub> reacts with hypo solution
  - (B)  $Mn_2O_7$  dissolves in water.
  - (C)  $CuCl_2$  reacts with aqueous  $Na_2S_2O_3$
  - (D) Sulphuric acid is heated with potassium.



#### ETOOS ACADEMY Pvt. Ltd

F-106, Road No.2 Indraprastha Industrial Area, End of Evergreen Motor, BSNL Lane, Jhalawar Road, Kota, Rajasthan (324005) Tel. : +91-744-242-5022, 92-14-233303 (d) Thiosulphuric acid



## PART - I : IIT-JEE PROBLEMS (PREVIOUS YEARS)

Marked Questions are having more than one correct option.

### Group 15<sup>th</sup>

1.	The number of P—O—	The number of P—O—P bonds in cyclic trimetaphosphoric acid is :						
	(A) zero	(B) two	(C) three	(D) fou	r			
2.	The correct order of aci (A) $Cl_2O_7 > SO_2 > P_4O_{10}$ (C) $Na_2O > MgO > Al_2O$	dic strength is :	(B) CO <sub>2</sub> > N <sub>2</sub> O <sub>5</sub> > SO <sub>3</sub> (D) K <sub>2</sub> O > CaO > MgO		[JEE 2000,(S) 3/35]			
3.	Ammonia can be dried (A) conc. $H_2SO_4$	by : (B) P <sub>4</sub> O <sub>10</sub>	(C) CaO	(D) anh	[ <b>JEE 2000,(S) 3/35]</b> ydrous CaCl <sub>2</sub>			
4.	Give Statement-2(s) wh is a tetra-atomic molecu	ly elemental nitrogen exis ule.	sts as diatomic molecule	whereas	elemental phosphorus [JEE 2000 (M), 2/100]			
5.	Polyphosphates are use (A) form soluble complet (B) precipitate anionic s (C) form soluble complet (D) precipitate cationic s	ed as water softening age exes with anionic species pecies exes with cationic species species	ents because they:		[JEE 2002(S), 3/90]			
6.	For $H_3PO_3$ and $H_3PO_4$ , (A) $H_3PO_3$ is dibasic an (C) $H_3PO_4$ is tribasic ar	the correct choice is : ad reducing (B) $H_3F$ ad reducing (D) $H_3F$	$PO_3$ is dibasic and non-re $PO_3$ is tribasic and non-re	educing educing	[JEE 2003 (S), 3/84]			
7.	$(NH_4)_2 Cr_2O_7$ on heating (A) heating $NH_4NO_2$ (C) treating $Mg_3N_2$ with	[ <b>JEE 2004 (S)</b> , 3/84] H <sub>2</sub> O <sub>2</sub>						
8.	A pale blue liquid is obta (A) $N_2O$	ained by equimolar mixtu (B) N <sub>2</sub> O <sub>3</sub>	re of two gases at –30°C (C) N <sub>2</sub> O <sub>4</sub>	(D) N <sub>2</sub> C	[JEE 2005 (S), 3/84] ) <sub>5</sub>			
9.	Thermodynamically mo (A) Red	st stable allotrope of pho (B) White	sphorus is : (C) Black	(D) Yell	<b>[JEE 2005 (S), 3/84]</b> ow			
10.	<ul><li>(a) What amount of Ca</li><li>(b) Write the structure of</li></ul>	O in grams is required to of $P_4O_{10}$ .	neutralise 852 g of $P_4O_1$	0 •	[JEE 2005 (M), 1/60]			

#### Paragraph for Question Nos. 11 to 13

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of  $NH_3$  and  $PH_3$ . Phosphine is a flammable gas and is prepared from white phosphorous.

- **11.** Among the following, the correct statement is :
  - (A) phosphates have no biological significance in humans.
  - (B) between nitrates and phosphates, phosphates are less a abundant in earth's crust.
  - (C) between nitrates and phosphates, nitrates are less abundant in earth's crust.
  - (D) oxidation of nitrates is possible in soil.



[JEE 2008 (P-I), 4/82]

- 12. Among the following, the correct statement is :
  - [JEE 2008 (P-I), 4/82] (A) between NH<sub>3</sub> and PH<sub>3</sub>, NH<sub>3</sub> is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional.
  - (B) between NH<sub>3</sub> and PH<sub>3</sub>, PH<sub>3</sub> is a better electron donor because the lone pair of electrons occupies sp<sup>3</sup> orbital and is more directional.
  - (C) between NH<sub>3</sub> and PH<sub>3</sub>, NH<sub>3</sub> is a better electron donor because the lone pair of electrons occupies sp<sup>3</sup> orbital and is more directional.
  - (D) between NH<sub>3</sub> and PH<sub>3</sub>, PH<sub>3</sub> is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional.
- 13. White phosphorus on reaction with NaOH gives PH<sub>a</sub> as one of the products. This is a :

[JEE 2008 (P-I), 4/82]

(A) dimerization reaction	(B) disproportionation reaction
(C) condensation reaction	(D) precipitation reaction

14. The reaction of  $P_4$  with **X** leads selectively to  $P_4O_6$ . The **X** is : [JEE 2009 (P-I), 3/80] (A) Dry O<sub>2</sub> (B) A mixture of O<sub>2</sub> and N<sub>2</sub> (D) O<sub>2</sub> in the presence of aqueous NaOH (C) Moist O<sub>2</sub>

15. Match each of the reactions given in column I with the corresponding products (s) given in column II. [ IEE 2000 (D II) 0/001

	Column			[JEE 2009 (P-II), 8/80]
(A)	$Cu + dil HNO_3$	(p)	NO	
(B)	Cu + conc $HNO_3$	(q)	NO <sub>2</sub>	
(C)	Zn + dil HNO <sub>3</sub>	(r)	N <sub>2</sub> O	
(D)	$Zn + conc HNO_3$	(s)	Cu(NO <sub>3</sub> ) <sub>2</sub>	
_		(t)	Zn(NO <sub>3</sub> ) <sub>2</sub>	
Extra pure $N_2$ can be obtained by heating : (A) $NH_3$ with CuO (B) $NH_4NO_3$		(C) (N	NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	[ <b>JEE 2011 (P-I), 3/80</b> ] (D) Ba(N <sub>3</sub> ) <sub>2</sub>

Among the following the number of compounds than can react with PCI<sub>2</sub> to give POCI<sub>3</sub> is 17. [JEE 2011 (P-II), 4/80] O<sub>2</sub>, CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>, P<sub>4</sub>O<sub>10</sub>

## Group 16<sup>th</sup>

16.

18.	Amongest $H_2O$ , $H_2S$ , $H_2$ (A) $H_2O$ because of H-b (C) $H_2S$ because of H-b	Se and $H_2$ Te the one with onding.	h highest boiling point is : [JEE 2000 (S), (B) $H_2$ Te because of higher molecular weight. (D) $H_2$ Se because of lower molecular weight.			
18.	The number of S–S bor (A) three	nds, in sulphur trioxide tri (B) two	mer (S <sub>3</sub> O <sub>9</sub> ) is : (C) one	(D) Zero	<b>[JEE 2001 (S), 3/35]</b>	
19.	Which of the following c (A) $H_2 S_2 O_3$	xoacids of sulphur has – (B) H <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	O–O– linkage ? (C) H <sub>2</sub> S <sub>2</sub> O <sub>6</sub>	(D) H <sub>2</sub> S	[ <b>JEE 2004 (S), 3/84</b> ] S <sub>2</sub> O <sub>8</sub>	
20.	Which of the following is (A) KI	s not oxidised by O <sub>3</sub> ? (B) KMnO <sub>4</sub>	(C) K <sub>2</sub> MnO <sub>4</sub>	(D) FeS	<b>[JEE 2005 (S), 3/84]</b>	
21.	Which gas is evolved w (A) $NO_2$	hen PbO <sub>2</sub> is treat (B) O <sub>2</sub>	ed with concentrated HN (C) N <sub>2</sub>	O <sub>3</sub> ? (D) N <sub>2</sub> O	[JEE 2005 (S), 3/84]	
22.	Aqueous solution of Na $_{2}$ (A) Na $_{2}$ S $_{4}$ O $_{6}$	${}_{2}S_{2}O_{3}$ on reaction with CI (B) NaHSO <sub>4</sub>	<sup>2</sup> gives : (C) NaCl	(D) NaC	<b>[JEE 2008 (P-I), 3/82]</b> )H	

23. The difference in the oxidation numbers of the two types of sulphur atoms in Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub> is. [JEE 2009 (P-I), 4/80]



## PART - II : AIEEE PROBLEMS (PREVIOUS YEARS)

1.	In case of nitrogen, NCl <sub>3</sub> is possible but no NCl <sub>5</sub> while in case of phosphorus, PCl <sub>3</sub> as well as PCl <sub>5</sub> a possible. It is due to : [AIEEE 2002] (1) availability of vacant d-orbital in P but not in N.							
	<ul><li>(2) lower ele</li><li>(3) lower ten</li><li>(4) occurrent</li></ul>	dency of H bonc ce of P in solid v	formation in F while N in gase	P than N. ous state at room	temperature.			
2.	The substand (1) $CaC_2 + Ca$	the used in holmes $a_{3}P_{2}$ (2) Ca	s singnals of the $a_3(PO_4)_2 + Pb_3C$	e ship is a mixture $\theta_4$ (3) $H_3PO_4 + Ca$	of: aCl <sub>2</sub> (4)NH	[AIEEE 2003] <sub>3</sub> + HOCI		
3.	What would acid ?	happen when a	solution of pota	assium chromate	is treated with a	n excess of dilute nitric [AIEEE 2003]		
	(1) $Cr^{3+}$ and (3) $CrO_4^{2-}$ is	$Cr_2O_7^{2-}$ are form reduced to + 3 s	ed state of Cr	(2) $\operatorname{Cr}_2 \operatorname{O}_7^{2^-}$ and (4) $\operatorname{Cr}\operatorname{O}_4^{2^-}$ is o	$d H_2 O are formedxidized to + 7 st$	d ate of Cr		
4.	The number	of hydrogen ato	m (s) attached	to phosphorus at	om in hypophos	phorus acid is : [AIEEE 2005]		
	(1) zero	(2) two	(3) (	one	(4) three			
5.	Which of the (1) $2HI + H_2S$ (3) NaCI + $H_2$	following chemic $O_4 \rightarrow I_2 + SO_2 + SO_4 \rightarrow NaHSO_4$	al reactions dep 2H <sub>2</sub> O + HCI	bicts the oxidizing b (2) $Ca(OH)_2$ + (4) $2PCI_5$ + H <sub>2</sub> S	behaviour of $H_2SO_4 \rightarrow CaSO_4$ SO <sub>4</sub> $\rightarrow$ 2POCl <sub>3</sub> +	D <sub>4</sub> ? <b>[AIEEE 2006]</b> , + 2H <sub>2</sub> O 2HCI + SO <sub>2</sub> CI <sub>2</sub>		
6.	Which of the (1) $H_3PO_3$ is a (3) $HCIO_4$ is a	following stateme a stronger acid th a weaker acid tha	ents is true? an H <sub>2</sub> SO <sub>3</sub> an HClO <sub>3</sub>	(2) In aqueous (4) HNO <sub>3</sub> is a s	medium HF is a stronger acid that	[AIEEE 2006] stronger acid than HCI n HNO <sub>2</sub>		
7.	Regular use ( (1) Superpho (3) Potassium	of which of the fo sphate of lime n nitrate	llowing fertilizer	s increases the ac (2) Ammonium (4) Urea	idity of soil? a sulphate	[AIEEE 2007, 3/120]		
8.	In context wit the correct st (1) CO is rem (2) $H_2$ is rem (3) CO is oxid (4) CO and H	h the industrial platement ? noved by absorptioved through occ dized to $CO_2$ with $I_2$ are fractionally	reparation of hy ion in aqueous ( lusion with Pd. steam in the pr separated using	drogen from water $Cu_2Cl_2$ Solution. resence of a cataly g differences in the	gas (CO + H <sub>2</sub> ), v st followed by ab ir densities.	which of the following is [AIEEE 2008, 3/105] sorption of CO <sub>2</sub> in alkali.		
9.	Which of the (1) The stabil (2) Nitrogen of (3) Single N– (4) N <sub>2</sub> O <sub>4</sub> has	following stateme ity of hydrides ind cannot form $d\pi$ –p N bond is weake two resonance s	ent is wrong ? creases from NI π bond r than the single tructures	H <sub>3</sub> to BiH <sub>3</sub> in group è P–P bond	15 of the period	[AIEEE 2010] ic table.		
10.	Which of the (1) $S_2$ molecu (2) The vapor (3) At 600° C (4) The oxida	following stateme ule is paramagne ur at 200°C consi the gas mainly c ttion state of sulp	ents regarding s tic ist mostly onsist of S <sub>2</sub> mol hur is never less	sulphur is incorrect lecules s than +4 in its con	? npounds	[AIEEE 2011]		
11.*	Which of the (1) ONCI and (3) Ozone is y	following is the w I ONO <sup>-</sup> are not is violet-black in sol	vrong statement oelectronic lid state	: ? (2) O <sub>3</sub> molecul (4) Ozone is di	e is bent. amagnetic gas	[JEE Mains2013]		
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## **PART-I: NCERT QUESTIONS**

- **1.** Discuss the general characteristics of Group 15 elements with reference to their electronic configuration, oxidation state, atomic size, ionisation enthalpy and electronegativity.
- 2. Why does the reactivity of nitrogen differ from phosphorus?
- **3.** Discuss the trends in chemical reactivity of group 15 elements.
- 4. Why does NH, form hydrogen bond but PH, does not?
- 5. How is nitrogen prepared in the laboratory? Write the chemical equations of the reactions involved.
- 6. How is ammonia manufactured industrially?
- 7. Illustrate how copper metal can give different products on reaction with HNO<sub>3</sub>.
- 8. Give the resonating structures of NO<sub>2</sub> and  $N_2O_5$ .
- **9.** The HNH angle value is higher than HPH, HAsH and HSbH angles. Why? [Hint : Can be explained on the basis of  $sp^3$  hybridisation in NH<sub>3</sub> and only s-p bonding between hydrogen and other elements of the group].
- **10.** Why does  $R_3P = O$  exist but  $R_3N = O$  does not (R = alkyl group)?
- **11.** Explain why NH<sub>3</sub> is basic while BiH<sub>3</sub> is only feebly basic.
- **12.** Nitrogen exists as diatomic molecule and phosphorus as  $P_{a}$ . Why?
- **13.** Write main differences between the properties of white phosphorus and red phosphorus.
- 14. Why does nitrogen show catenation properties less than phosphorus?
- **15.** Give the disproportionation reaction of H<sub>3</sub>PO<sub>3</sub>.
- **16.** Can PCl<sub>2</sub> act as an oxidising as well as a reducing agent? Justify.
- **17.** Justify the placement of O, S, Se, Te and Po in the same group of the periodic table in terms of electronic configuration, oxidation state and hydride formation.
- 18. Why is dioxygen a gas but sulphur a solid?
- **19.** Knowing the electron gain enthalpy values for  $O \rightarrow O^-$  and  $O \rightarrow O^{2-} \rightarrow$  as 141 and 702 kJ mol<sup>-1</sup> respectively, how can you account for the formation of a large number of oxides having  $O^{2-}$  species and not  $O^-$ ? (Hint: Consider lattice energy factor in the formation of compounds).
- 20. Which aerosols deplete ozone?
- **21.** Describe the manufacture of  $H_2SO_4$  by contact process?
- **22.** How is  $SO_2$  an air pollutant?
- **23.** What are the oxidation states of phosphorus in the following : (i)  $H_3PO_3$  (ii)  $PCI_3$  (iii)  $Ca_3P_2$  (iv)  $Na_3PO_4$  (v)  $POF_3$ ?
- Write balanced equations for the following :
  (i) NaCl is heated with sulphuric acid in the presence of MnO<sub>2</sub>.
  (ii) Chlorine gas is passed into a solution of Nal in water.
- **25.** Arrange the following in the order of property indicated for each set:  $NH_3$ ,  $PH_3$ ,  $AsH_3$ ,  $SbH_3$ ,  $BiH_3$  increasing base strength.



## **PART-II : ADVANCED LEVEL QUESTIONS**

1.	$NH_3 + O_2 \xrightarrow{Pt} (A)$ (A) + O <sub>2</sub> $\longrightarrow$ (B) (brown fumes).										
	(B) + $H_2O \longrightarrow (C)$ (nitrogen in lower oxidation state) + (D) (nitrogen in higher oxidation state)										
	(C) and (D) both are oxoacids of nitrogen.										
	(C) + I <sup>-</sup> $\longrightarrow$ (E) (violets vapours). Identify (A) (B) (C) (D) and (E)										
2	Explain the high reactivity of white pheenberg $c_{2}$ compared to red pheenberg										
2.	Explain the high reactivity of white phosphorus as compared to red phosphorus.										
3.	What happens ? (a) When phosphine is heated at 150°C. (b) When phosphine is dissolved in water in presence of light.										
4.	$P_4$ + NaOH $\longrightarrow$ Products. Explain the reducing character of one of the products obtained by taking the example of copper sulphate.										
5.	Starting with phosphorite, $Ca_{3}(PO_{4})_{2}$ , show how you would prepare phosphoric acid.										
6.	Give the names and formulae of the compounds in which sulphur exhibits an oxidation state of : (A) $-2$ (B) $+4$ (C) $+6$										
7.	$O_3$ is a powerful oxidising agent. Write equation to represent oxidation of (a) I <sup>-</sup> to I <sub>2</sub> in acidic solutions. (b) sulphur to sulphuric acid in the presence of moisture.										
8.	Give the important applications of $O_3$ .										
9.	$SO_2$ and $CI_2$ both are used as bleaching agent. What factors cause bleaching ?										
10.	Colourless salt (A) decolourises $I_2$ solution and gives white precipitate (changing to black) with AgNO <sub>3</sub> solution. (A) also produces pink colour with FeCl <sub>3</sub> solution. Identify (A) and explain reactions.										
11.	<ul> <li>Arrange the following in the increasing order of the properties stated against them.</li> <li>(a) (i) NH<sub>3</sub>, (ii) PH<sub>3</sub>, (iii) AsH<sub>3</sub>, (iv) SbH<sub>3</sub> - boiling point.</li> <li>(b) (i) Bi<sup>3+</sup>, (ii) Sb<sup>3+</sup>, (iii) As<sup>3+</sup> - stability of +3 oxidation state.</li> <li>(c) (i) NH<sub>3</sub>, (ii) PH<sub>3</sub>, (iii) AsH<sub>3</sub>, (iv) SbH<sub>3</sub>, (v) BiH<sub>3</sub> - reducing character.</li> </ul>										
12.	Ammonia can not be prepared by: (A) heating $NH_4NO_3$ or $(NH_4)_2 Cr_2O_7$ (B) heating of $NH_4CI$ or $(NH_4)_2CO_3$ (C) heating of $NaNO_3$ or $NaNO_2$ with zinc dust or aluminium and sodium hydroxide (D) reaction of AIN or $CaCN_2$ with $H_2O$										
13.	(A) Colourless salt + NaOH $\xrightarrow{\Delta}$ (B) gas + (C) alkaline solution										
	(C) + Zn (dust) $\xrightarrow{\text{Warm}}$ gas (B); (A) $\xrightarrow{\Delta}$ $\underbrace{gas(D) + liquid(E)}_{\text{both triatomic}}$										
	Gas (B) gives white fumes with HCI. Identify (A) to (E) and write the chemical reactions involved.										
14.	Titanium (IV) ions give an orange-red colouration in slightly acidic solution with hydrogen peroxide because of the formation of : (A) perove disulphatetitanium (IV) ions										
	(C) titanium (IV) sulphate (D) none of these										
15.	Aqueous solution of Na S O, gives white precipitate with Aq <sup>+</sup> ions: the precipitate dissolves in excess of										

- 15. Aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> gives white precipitate with Ag<sup>+</sup> ions; the precipitate dissolves in excess of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. If the precipitate is boiled with water it changes to black and the supernatant liquid then gives a white precipitate with a solution containing Ba<sup>2+</sup> ions. Explain by writing the chemical equations involved.
- **16.**  $HNO_3$  can not be used for the preparation of  $H_2S$  from metal sulphides. Why ?
- **17.** How will you obtain sodium thiosulphate from aqueous solution of Na<sub>2</sub>CO<sub>3</sub> using SO<sub>2</sub> gas and sulphur ? (only in three steps)



ANSWERS													
EXERCISE # 1													
Group 15 <sup>h</sup>													
1.	(D)	2.	(C)	3.	(C)	4.	(D)	5.	(B)	6.	(B)	7.	(A)
8.	(D)	9.	(D)	10.	(B)	11.	(A)	12.	(D)	13.	(C)	14.	(D)
15.	(A)	16.	(D)	17.	(C)	18.	(B)	19.	(B)	20.	(C)	21.	(B)
22.	(C)	23.	(B)	24.	(C)	25.	(C)	26.	(D)	27.	(A)	28.	(B)
29.	(B)	30.	(A)	31.	(D)	32.	(D)	33.	(A)	34.	(B)	35.	(A)
36.	(B)	37.	(D)	38.	(C)	39.	(A)	40.	(B)	41.	(B)	42.	(B)
43. 50	(A) (C)	44. 51	(B) (D)	45. 52	(C) (D)	46. 53	(D)	47. 54	(C)	48. 55	(C)	49. 56	(A) (B)
50. 57.	(D)	58.	(D) (C)	52. 59.	(D) (D)	60.	(D) (D)	61.	(A) (C)	62.	(A) (C)	50.	(D)
Grou	p 16 <sup>th</sup>		( )		( )								
1.	(B)	2.	(D)	3.*	(ABC)	4.	(A)	5.	(D)	6.	(D)	7.	(A)
8.	(C)	9.	(A)	10.	(C)	11.	(B)	12.	(B)	13.	(B)	14.	(D)
15.*	(AC)	16.*	(ABC	D) <b>17.</b>	(B)	18.	(B)	19.	(C)	20.	(A)	21.	(D)
22.	(B)	23.	(D)	24.	(C)	25.	(D)	26.	(B)	27.	(C)	28.	(B)
29. 36	(A) (B)	30. 37	(B)	31. 39	(B) (A)	32. 30	(A)	33. 40	(A) (B)	34. 1	(C) (B)	35. 42	(A)
43.	(B) (B)	44.	(D) (A)	45.	(A) (B)	46.	(A) (B)	40. 47.	(B) (A)	41.	(D)	42.	(~)
	( )		( )			PA	RT - I		( )				
Group	0 15 <sup>th</sup>												
1.	(a – v	i), (b — i)	, (c – iv,	v), (d –	ii) (e – iii)	(f – iv)	2.	(a – ii	i, vi), (b	— ii, v), (	c – ii), (d	– i) (e –	- iii, iv)
3.	(A – F	?,Q,S) ; (	B – P,Q,	R,S) ; (0	C –Q,R,S)	; (D –	P,Q,R,S	)					
Group	0 16 <sup>th</sup>												
4.	(a - iv	) , (b - vi	i), (c - v)	, (d - ii, <sup>-</sup>	vi), (e - i)	, (f - ii)	, (g - iii)						
5.	(a - vi	), (b - vii	), (c - i),	(d - ii), (	e - iii), (f -	iv), (g	- ix), (h -	· v), (i - v	riii)				
6.	(A) P,0	Q,S ; (B)	) P,Q,S ;	(C) R,S	; (D) Q, S	5							
Group	15 <sup>th</sup>	0	( ^ )	•	( ^ )	40	(D)	44	(D)	40	( • •	40	
1. 11	(D) (B)	ð.	(A)	9.	(A)	10.	(B)	11.	(B)	12.	(A)	13.	(D)
Grour	(D). 16 <sup>th</sup>												
15.	(B)	16.	(B)	17.	(B)	18.	(A)	19.	(D)	20.	(A)	21.	(A)
22.	(D)	23.	(A)	24.	(B)	25.	(C)	26.	(A)		( )		( )
वर्ग 15	th												
27.	Т	28.	Т	29.	F	30.	F	31.	F	32.	Т	33.	Т
34.	Т	35.	Т	36.	Т	37.	F	38.	Т	39.	F	40.	Т
Group	• 16 <sup>th</sup>		_		_		_		_		_		_
41.	T	42.	T	43.	F T	44.	F	45.	Т	46.	F	47.	Т
48.	I	49.	I	50.	I								
FILL	IN T	HE BL		S									
Group	Group 15 <sup>th</sup>												

51.  $N_2O$  or NO. 52. CaCN<sub>2</sub> 53. White 54. N<sub>2</sub>O<sub>5</sub>, H<sub>3</sub>PO<sub>4</sub> 55. Nitrate 56. Conc.  $H_2SO_4$ 57. Two 58. Four 59. 60 60.  $NF_3$ 61. High heat of vaporisation. 62.  $NH_2NH_2$ , -2 63. Hydrazoic acid, N<sub>3</sub>H Less, Polymeric, Chains 64. 12, 4 65. Ionic, [PCl<sub>4</sub>]<sup>+</sup>, Octahedral 66. 67. + 5 68. 69. Three 70. CaO 71. nitrous, nitric  $N_2$ 



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#### Group 16<sup>th</sup>

72. 75. 79.	SO <sub>2</sub> , ox MnO <sub>2</sub> ozone,	ides of r KO <sub>3</sub>	nitrogen 76. 80.	Na <sub>2</sub> SO <sub>3</sub> basic, r	<b>73.</b> 3 <b>77.</b> neutral	cross lir sulphur <b>81.</b>	nking ic acid reduction, temp	74. 78. porary	95.6 <sup>0</sup> C ozonise	d oxygen
				<u>EXERCISE # 2</u>			<u>ISE # 2</u>			
						PAR	T - I			
Group	15 <sup>th</sup>									
1.	(A)	2.	(A)	3.	(C)	4.	(D)			
16 <sup>⊤н</sup> Gı	roup									
5.	(C)	6.	(A)	7.	(B)	8.	(A)			
Group	15 <sup>th</sup>									
9.	(AB)	10.	(BD)	11.	(ACD)	12.	(BD)			
Group	16 <sup>th</sup>									
13.	(ABCD)	14.	(BD)	15.	(BCD)	16.	(ABD) <b>17.</b>	(ABD)	18.	(ABD)

## PART - II

#### Group 15<sup>th</sup>

- 1. NO<sub>2</sub> being acidic in nature is absorbed by alkali.
- 2. Critical tempt of nitrogen is very low where as the critical tempt. of ammonia is higer than the ordinary tempt. So NH<sub>3</sub> is easily liquified.
- **3.**  $4HNO_3 \xrightarrow{\text{Sun light}} 4NO_2 \uparrow + 2H_2O + O_2$

NO<sub>2</sub> formed dissolves in HNO<sub>3</sub> to produce yellow colour.

- 4.  $NH_3$  being basic reacts with  $P_4O_{10}$  or  $H_2SO_4$ . CaCl<sub>2</sub> forms addition compound with  $NH_3$ .
- 5. Red phosphorus exists as polymeric chains of  $P_4$  tetrahedron linked together, whereas in yellow phosphorus individual  $P_4$  molecules are held together by weak van der Walls force (has angle strain).
- 6.  $P_4O_6 = 12$ ;  $P_4O_{10} = 16$
- 7.  $3KNO_2 + KNO_3 + Cr_2O_3 \xrightarrow{\Delta} 2K_2CrO_4 + 4NO_3$
- 8. NO colourless, turns brown in air ;  $N_2O_5$  is volatile solid which forms HNO<sub>3</sub> with water ; NO<sub>2</sub> is brown gas which condenses to yellow liquid  $N_2O_4$  at  $-20^{\circ}$ C
- 9. A crystalline compound  $[P_2N_3 (CH_3)_3]_2$  is formed.  $4PCI_3 + 6CH_3NH_2 \longrightarrow [P_2N_3(CH_3)_3]_2 + 12HCI$
- **10.** (a) HSO<sub>3</sub>N H<sub>2</sub>(sulphamic acid) + HNO<sub>3</sub> (conc.)  $\xrightarrow{\Delta}$  N<sub>2</sub>O + H<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O
  - (b)  $Ag_2N_2O_2 + 2HCI \longrightarrow 2AgCI \downarrow + H_2N_2O_2$
  - (c)  $2HNO_3$  (50%) +  $As_2O_3 + 2H_2O \longrightarrow NO + NO_2 + 2H_3AsO_4$
  - (d)  $4\text{AgNO}_3 + 2\text{Cl}_2 \xrightarrow{60-90^\circ\text{C}} 4\text{AgCl} \downarrow + 2\text{N}_2\text{O}_5 + \text{O}_2$
  - (e)  $HPO_3 + H_3PO_4 \xrightarrow{100^{\circ}C} H_4P_2O_7$
  - (f)  $2Ca_3 (PO_4)_2 + 6SiO_2 \longrightarrow 6CaSiO_3 + P_4O_{10}$  $P_4O_{10} + 10C \longrightarrow P_4 + 10 CO$
- 11. At 415 K;  $3H_3PO_2 \longrightarrow 2H_3PO_3 + PH_3 \uparrow$ At 435 K;  $2H_3PO_2 \longrightarrow H_3PO_4 + PH_3 \uparrow$



**12.**  $H_3PO_3 > H_3PO_4$ 

**13.** Undergoes dehydration.

$$2H_{3}PO_{4} \xrightarrow{525 \text{ K}} H_{4}P_{2}O_{7} + H_{2}O$$
$$H_{3}PO_{4} \xrightarrow{875 \text{ K}} HPO_{3} + H_{2}O$$

**14.** 
$$P_4O_6 + 6H_2O$$
 (cold)  $\longrightarrow 4H_3PO_3$   
 $P_4O_6 + 6H_2O$  (hot)  $\underline{\quad vigorous\ reaction} \rightarrow 3H_3PO_4 + PH_3$ 

**15.** (A) 
$$Ca_3(PO_4)_2 + 2H_2SO_4 \longrightarrow Ca(H_2PO_4)_2 + 2CaSO_4$$
  
Super phosphate of lime

(B)  $CaO + 3C \xrightarrow{2800-2900^{\circ}C} CaC_2 + CO$ 

$$CaC_2 + N_2 \xrightarrow{500-600^{\circ}C} \underbrace{CaCN_2 + C}_{Nitrolim}$$

(C)  $P_4 + 2I_2 + 8H_2O \longrightarrow 2PH_4I + 2HI + 2H_3PO_4$ 

$$PH_4I + NaOH \longrightarrow PH_3 + NaI + H_2O$$

- **16.**  $NO_2$  being odd molecule, on dimerisation is converted to stable  $N_2O_4$  molecule with even number of electrons.
- 17. Lowest bond dissociation energy (i.e., least stable), so breaking of B H bond is easier.
- **18.**  $PH_3$  + HI  $\longrightarrow$   $PH_4I$ (Lewis base) (acid) (salt)
- **19.** PCl<sub>3</sub> hydrolyses in the presence of moisture giving fumes of HCl

$$PCI_3 + H_2O \longrightarrow H_3PO_3 + 3 HCI$$

- **20.** (A)  $PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$ 
  - (B)  $PCl_5 + D_2O \longrightarrow POCl_3 + 2 DCl$
  - (C) 4  $H_3PO_3 \longrightarrow 3 H_3PO_4 + PH_3$
- **21.** Lone pair of electrons is present in more concentrated s–orbital and due to decrease in bond (E H) dissociation enthalpy down the group acts as acid rather then a base.
- **22.** Nitrogen has unique ability to form  $p\pi$ - $p\pi$  multiple bond. Phosphorus does not form  $p\pi$   $p\pi$  bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping.





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NITROGEN & OXYGEN FAMILY ADVANCED # 52 25. (a) Refer text

(b)  $2NO + O_2 \longrightarrow 2NO_2$  (Brown)

(c) Copper is placed below hydrogen in electrochemical series and does not liberate  $H_2$  from acid. However, HNO<sub>3</sub> oxidises copper due to its strong oxidant nature.

(d)  $Pb(NO_3)_2 \xrightarrow{\Delta} N_2O_4 \xrightarrow{\Delta} NO_2 \uparrow (Brown)$ 

- **26.** Due to its high heat of vaporisation.
- 27. Refer text.
- 28. Refer text.
- 29. Refer text.
- **30.**  $2Cu + 8NH_3 + O_2 + 2H_2O \longrightarrow 2[Cu(NH_3)_4 (OH)_2; O_2 \text{ is removed in the form of cupra-ammonium hydroxide complex.}$
- 31.
   HNO3 में N अधिकतम ऑक्सीकरण अवस्था में

   HNO2 में
   N, +3 ऑक्सकरण अवस्था में है जो बढ़ व घट सकती है।
- 32.  $N_2O_4(\ell) \implies NO^+ (acid) + NO_3^- (base)$

 $ZnCl_2 + 2N_2O_4(\ell) \longrightarrow Zn(NO_3)_2 + 2NOCI.$ 

- **33.** (A)  $P_4O_6$ ; (B)  $PH_3$ ; (C)  $H_3PO_4$ ; (D)  $Cu_3P_2$
- **34.**  $H_3PO_3$  contains one P–H bond and hence acts as a reducing agent but  $H_3PO_4$  does not contain a P–H bond.

## Group 16th

- **35.** Rhombic Slphur **36.** O<sub>2</sub> is paramagnetic where as N<sub>2</sub> is dimagnetic
- **37.** F<sub>2</sub>, Atomic oxygen, OF<sub>2</sub>. **38.** Ordinary oxygen and ozone
- **39.** Due to presence of empty d-orbitals.

**40.**  $2BaO + O_2 \xrightarrow{500^{\circ}C} 2BaO_2$ ;  $2BaO_2 \xrightarrow{800^{\circ}C} 2BaO + O_2$ 

**41.** (a) 
$$4K_2Cr_2O_7 \xrightarrow{\Lambda} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$
 (b)

(c) 
$$2I_2 + 9O_3 \rightarrow I_4O_9 + 9O_2$$

(d) 
$$OH \qquad C_2H_5 \qquad air \qquad O_2 \qquad C_2H_5 + H_2O_2$$

- (e)  $2HCHO + H_2O_2 \rightarrow 2HCOOH + H_2$ yellow coloured light is emitted
- (f)  $Fe^{3+} + 2S_2O_3^{2-} \rightarrow [Fe(S_2O_3)_2]^-$  (pink or violet)  $Fe^{3+} + [Fe(S_2O_3)]^- \rightarrow 2Fe^{2+} + S_4O_6^{-2-}$ pink colour produced soon vanishes
- (g)  $2H_2S + SO_2 \xrightarrow{\text{moisture}} 2H_2O + 3S$
- (h)  $3Mg + SO_2 \rightarrow 2MgO + MgS$
- (i)  $2\text{KIO}_3 + 5\text{SO}_2 + 4\text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 + 4\text{H}_2\text{SO}_4 + \text{I}_2$
- (j)  $H_2SO_4 + P_2O_5 \rightarrow 2HPO_3 + SO_3$



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NITROGEN & OXYGEN FAMILY ADVANCED # 53

 $3O_2 \xrightarrow{\text{silent}} 2O_3$ 

- 42. Due to resonance
- **43.** Sb<sub>2</sub>S<sub>3</sub> (pure) + 6HCl (pure)  $\rightarrow$  2SbCl<sub>3</sub> + 3H<sub>2</sub>S
- 44. As hydrogen catches fire due to heat liberated when water is absorbed by acid.
- 45. H-S bond length is bigger than H-O thus H<sup>+</sup> is more easily released.
- (i) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + H<sub>2</sub>SO<sub>4</sub> + 3SO<sub>2</sub> → K<sub>2</sub>SO<sub>4</sub> + Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + H<sub>2</sub>O
  (ii) In H<sub>2</sub>S the oxidation state of sulphur is -2 and it can increase its oxidation state, thus acts as only reducing agent. In SO<sub>2</sub> the oxidation state is +4 which can be increased as well as decreased . Thus SO<sub>2</sub> acts as reducing as well as oxidising agent

(iii)  $SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$ . Then nascent hydrogen bleaches the coloured substance.

- **47.** Dioxygen exists as diatomic molecules (weak van der Waal's force) where as sulphur as polyatomic molecules (strong van der Waal's forces.).
- **48.** Due to the decrease in bond (E H) dissociation enthalpy down the group acidic character increases.
- 49. Au and Kr.
- **50.** First ionisation to  $H_3O^+$  and  $HSO_4^-$  is larger whereas ionisation of  $HSO_4^-$  to  $H_3O^+$  and  $SO_4^{-2-}$  is very small.
- 51.  $2 I^{-} (aq) + H_2O(\ell) + O_3(g) \rightarrow 2OH^{-} (aq) + I_2(s) + O_2(g)$ . It is buffered with a borate buffer (PH 9.2) lodine liberated is titrated against a standard solution of sodium thiosulphate.
- **52.** Sulphur exist as S<sub>2</sub> in vapour state which has two unpaired electrons in the anti-bonding  $\pi^*$  orbitals like O<sub>2</sub>

**53.** Ca (OH)<sub>2</sub> + SO<sub>2</sub> 
$$\longrightarrow$$
 CaSO<sub>3</sub>  $\downarrow$  (white) + H<sub>2</sub>O

 $CaSO_3 + H_2O + SO_2$  (excess)  $\longrightarrow Ca(HSO_3)_2$  milkiness disappears.

- 54. Dissolves in rain water and produce acid rain .
- 55. Freons .
- 56.  $S_8$  (melt)  $\stackrel{\text{at 160°C}}{\underset{2160°C}{\longrightarrow}} S_8$  ring break and diradical so formed polymerises to forms long chain polymer and

viscocity starts to increase  $\xrightarrow{At 200^{\circ}C}$  Viscosity further  $\uparrow \xrightarrow{At 444^{\circ}C}_{\text{boilingpoint}}$  viscosity  $\downarrow$  shorter chains

and rings are formed  $\xrightarrow{At 600^{\circ}}$  in vapour state exist as S<sub>2</sub> molecules (paramagnetic like O<sub>2</sub>).

57. 
$$H_2 S_2 O_8 + H_2 O \rightarrow H_2 SO_5 + H_2 SO_4$$
  
 $H_2 SO_5 + H_2 O (excess) \longrightarrow H_2 SO_4 + H_2 O_2$ 

- **58.**  $H_2SO_3 + H_2O \longrightarrow H_2SO_4 + 2 H.$  $SO_3^{2-} \xrightarrow{H_+} SO_2$
- 58.  $2NaHSO_3 \xrightarrow{\Lambda} H_2SO_3 + Na_2SO_3$  $4Na_2SO_3 \xrightarrow{} Na_2S + 3Na_2SO_4$
- **59.**  $2 \operatorname{Na}_2 S_3 + 3 \operatorname{O}_2 \xrightarrow{\operatorname{air}} 2 \operatorname{Na}_2 S_2 \operatorname{O}_3 + 2 \operatorname{S}_2 \operatorname{O}_3$



## Group 16<sup>th</sup>

- **60.** Oxygen has no d-orbitals while other have d-orbitals. Therefore, the paired electrons can be made unpaired by exciting electrons to d-orbitals.
- 61.  $SO_2 + 2OH^- \implies SO_4^{2^-} + 2H^+ + 2\overline{e}$ : reaction proceeds in forward direction as  $OH^-$  concentration increases  $SO_2 + 2H_2O \implies SO_4^{2^-} + 4H^+ + 2\overline{e}$ : as  $H^+$  concentration increases the reaction proceeds in backward direction.
- **62.**  $H_2O = 104.5^\circ$ ;  $H_2S = 92.5^\circ$ ;  $H_2Se = 91^\circ$  **63.**  $H_2O$ ; intermolecular hydrogen bonding.
- **64.** Mercury is a mobile liquid but in presence of ozone it loses its mobility due to the formation of mercury suboxide and starts sticking to the glass. This is called as tailing of mercury.  $2Hg + O_3 \rightarrow Hg_2O + O_2$ .
- **65.** (A)  $SO_2CI_2$ ; (B)  $H_2SO_4$ ; (C) HCI; (D)  $K_2SO_4$ ; (E) KCI
- **66.** (A)  $Na_2SO_3$ ; (B)  $Cr_2(SO_4)_3$ ; (C)  $KMnO_4$ ; (D)  $Na_2SO_4$

**67.** (a) 
$$H_2O < SiO_2 < CO_2 < N_2O_5 < SO_3$$
 (b)  $H_2Te < H_2Se < H_2S < H_2O_5$ 

**68.** On heating,  $S_8$  rings are broken and long chain polymers are formed up to 200<sup>o</sup>C. Thus due to polymerisation, liquid becomes viscous but beyond 200<sup>o</sup>C long chains are broken into short chains and ultimately  $S_2$  molecules are formed in the vapour phase, so viscosity of liquid decreases.

**70.**  $H_2SO_4$  acts as strong oxidising agent and, therefore, following reaction takes place.  $H_2S + H_2SO_4 \rightarrow SO_2 + S + 2H_2O$ 

- **72.** (i)  $I_2 + 5O_3 + H_2O \rightarrow 2HIO_3 + 5O_2$ 
  - (ii)  $2NaHS + 4NaHSO_3 \rightarrow 3Na_2S_2O_3 + 3H_2O_3$
  - (iii)  $(NH_4)_2S_2O_8 + 2H_2O + MnSO_4 \rightarrow (NH_4)_2SO_4 + MnO_2 + 2H_2SO_4$
  - (iv)  $Sb_2S_3 + 6HCI \rightarrow 2SbCl_3 + 3H_2S$
  - (v)  $2Hg_2CI_2 + SO_2 + 4HCI \rightarrow 4HgCI_2 + 2H_2O + S$
  - (vi)  $CaS + H_2O + CO_2 \rightarrow CaCO_3 + H_2S$
- 73. (A) Refer text (B) Refer text (C) Refer text (D) Refer text.

### Group 15<sup>th</sup>

- **1.** (C) **2.** (A) **3.** (C)
- 4. 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=N) because of small size of nitrogen atom. Heavier elements of this group do not able to 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 as tendency to under go catenation.

$$\mathsf{N} \equiv \mathsf{N} (\mathsf{N}_2) \xrightarrow{\mathsf{P}}_{\mathsf{P}} (\mathsf{P}_4)$$



NITROGEN & OXYGEN FAMILY ADVANCED # 55



## <u>EXERCISE # 4</u> PART-I

- 1. 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.
- **2.** Because BiH<sub>3</sub> is the least stable among the hydrides of Group 15.
- **3.** Because of strong  $p\pi$ - $p\pi$  overlap resulting into the triple bond,  $N \equiv N$ .
- **6.** From the structure of  $N_2O_5$  it is evident that covalence of nitrogen is four.
- **7.** Both are sp<sup>3</sup> hybridised. In  $PH_4^+$  all the four orbitals are bonded whereas in  $PH_3$  there is a lone pair of electrons on P, which is responsible for lone pair-bond pair repulsion in  $PH_3$  reducing the bond angle to less than 109° 28.
- **10.**  $PCl_5 + D_2O \rightarrow POCl_3 + 2DCl$
- **11.** Three P–OH groups are present in the molecule of  $H_3PO_4$ . Therefore, its basicity is three.
- **15.** Because of small size and high electronegativity of oxygen, molecules of water are highly associated through hydrogen bonding resulting in its liquid state.
- 21. Both the S–O bonds are covalent and have equal strength due to resonating structures.
- **23.** In general, interhalogen compounds are more reactive than halogens due to weaker  $X-X^1$  bonding than X–X bond. Thus, ICI is more reactive than  $I_2$ .

## **PART-II**

**1.**  $4\text{NH}_3 + 5\text{O}_2 \xrightarrow{\text{Pt}} 4\text{NO} + 6\text{H}_2\text{O}.$ 

 $\begin{array}{l} \mathsf{NO}+\mathsf{1/2O}_2 \longrightarrow \mathsf{NO}_2 \text{ (brown fumes).} \\ \mathsf{NO}_2+\mathsf{H}_2\mathsf{O} \longrightarrow \mathsf{HNO}_2+\mathsf{HNO}_3 \text{ (both oxoacids).} \\ \mathsf{2HNO}_2+\mathsf{2I}^-+\mathsf{2H}^+ \longrightarrow \mathsf{I}_2 \text{ (violets vapours)}+\mathsf{2NO}+\mathsf{2H}_2\mathsf{O}. \\ \mathsf{So,} (\mathsf{A})=\mathsf{NO}, (\mathsf{B})=\mathsf{NO}_2, (\mathsf{C})=\mathsf{HNO}_2, (\mathsf{D})=\mathsf{HNO}_3 \text{ and } (\mathsf{E})=\mathsf{I}_2. \end{array}$ 

2. 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.





- (a) Phosphine on heating at 150°C burns forming H<sub>3</sub>PO<sub>4</sub> PH<sub>3</sub> + 2O<sub>2</sub> → H<sub>3</sub>PO<sub>4</sub>
   (b) The solution of PH, in water decomposes in presence of light giving red phosphorus and H
  - (b) The solution of  $PH_3$  in water decomposes in presence of light giving red phosphorus and  $H_2$ .
- 4.  $P_4 + 3 \text{ NaOH} + 3 \text{ H}_2 \text{O} \longrightarrow PH_3 + 3 \text{ NaH}_2 PO_2$ (sodium hypothosphite)

 $4Cu^{2+} + PH_3 + 4H_2O \longrightarrow H_3PO_4 + 4Cu \downarrow + 8H^+$ Sodium hypophosphite also acts as a strong reducing agent and reduces copper sulphate to Cu<sub>2</sub>H<sub>2</sub>.

5.  $Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 2CaSO_4 + 2H_3PO_4.$ 

**6.** (A) 
$$H_2S^{2-}$$
 (B)  $S^{4+}O_2$  (C)  $S^{+6}O_3$ 

- 7. (a)  $O_3 + 2I^- + 2H^+ \longrightarrow O_2 + I_2 + H_2O$  (b)  $3O_3 + S + H_2O \longrightarrow H_2SO_4 + 3O_2$ .
- 8. (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, KMnO<sub>4</sub> etc. It is also used for bleaching oil, ivory, flour starch etc.
- **9.**  $SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H.$

 $Cl_2 + H_2O \longrightarrow 2HCl + O.$ 

Bleaching action of  $SO_2$  is due to H (that causes reduction) and that of  $CI_2$  is due to O (that causes oxidation).

(a) ) PH<sub>3</sub> < AsH<sub>3</sub> < NH<sub>3</sub> < SbH<sub>3</sub> - boiling point. NH<sub>3</sub> has higher boiling point due to H-bonding. In rest of the hydrides the boiling point increases down the group with increasing atomic number on account of the increasing magnitude of van der Waal's attraction. van der Waal attraction ∞ molecular weight.
(b) Bi<sup>3+</sup> < Sb<sup>3+</sup> < As<sup>3+</sup> - stability of +3 oxidation state decreases down the group due to inert pair effect.

(c)  $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$  - reducing character increases down the group as bond dissociation energy decreases.

12. Except (A) all gives ammonia

 $\mathsf{NH_4NO_3} \xrightarrow{ \Delta} \mathsf{N_2O+2H_2O} ; (\mathsf{NH_4})_2 \mathsf{Cr_2O_7} \longrightarrow \mathsf{N_2+Cr_2O_3+4H_2O}$ 

- **13.**  $NH_4NO_3 + NaOH \xrightarrow{\Delta} NH_3 + NaNO_3 + H_2O$ ;  $NH_3 + HCI \longrightarrow NH_4CI$  (white fumes)  $NaNO_3 + 7NaOH + 4Zn \longrightarrow 4Na_2ZnO_2 + NH_3\uparrow + 2H_2O$  $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$  So, (A) =  $NH_4NO_3$ , (B) =  $NH_3$ , (C) =  $NaNO_3$ , (D) =  $N_2O$  and (E) =  $H_2O$ .
- **14.** The colour is attributed to peroxotitanic acid, HCOO-Ti(OH)<sub>3</sub> or peroxodisulphatotitanium (IV) ions,  $[TiO_2(SO_4)_2]^{2-}$

**15.** 
$$2Ag^+ + S_2O_3^{2-} \longrightarrow Ag_2S_2O_3 \downarrow \text{ (white)}; Ag_2S_2O_3 + 3S_2O_3^{2-} \longrightarrow 2[Ag(S_2O_3)_2]^{3-}$$
  
 $Ag_2S_2O_3 \downarrow + H_2O \xrightarrow{\text{boiled}} AgS \downarrow \text{ (black)} + H_2SO_4; H_2SO_4 + Ba^{2+} \longrightarrow BaSO_4 \downarrow \text{ (white)} + 2H$ 

- 16. FeS + 2H<sup>+</sup>  $\longrightarrow$  Fe<sup>2+</sup> + H<sub>2</sub>S HNO<sub>3</sub> being strong oxidising agent oxidises H<sub>2</sub>S to sulphur. 2HNO<sub>3</sub>  $\longrightarrow$  2NO<sub>2</sub> + H<sub>2</sub>O + [O] ; H<sub>2</sub>S + [O]  $\longrightarrow$  H<sub>2</sub>O + S
- **17.**  $Na_2CO_3 + 2SO_2 \longrightarrow 2NaHSO_3 + CO_2$

$$2NaHSO_3 + Na_2CO_3 \longrightarrow 2Na_2SO_3 + CO_2 + H_2O \Rightarrow Na_2SO_3 + S \xrightarrow{\Delta} Na_2S_2O_3$$

