p-BLOCK ELEMENTS (NITROGEN & OXYGEN FAMILY)

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JEE(ADVANCED) SYLLABUS

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

JEE (MAIN) SYLLABUS

Group - 15 : Properties and uses of nitrogen and phosphorus; Allotrophic forms of phosphorus; Preparation, properties, structure and uses of ammonia, nitric acid, phosphine and phosphorus halides, (PCI₃, PCI₅); Structures of oxides and oxoacids of nitrogen and phosphorus.

Group - 16 : Preparation, properties, structures and uses of dioxygen and ozone; Allotropic forms of sulphur; Preparation, properties, structures and uses of sulphur dioxide, sulphuric acid (including its industrial preparation); Structures of oxoacids of sulphur.

P-BLOCK ELEMENTS (NITROGEN AND OXYGEN FAMILY)

NITROGEN FAMILY

GROUP-15 ELEMENTS (N, P, As, Sb, Bi)

(i) As we go down the group, there is a shift from non-metallic to metallic through metalloidic character.

(ii) Nitrogen and phosphorus are **non-metals**, arsenic and antimony **metalloids** and bismuth is a **typical metal**.

Occurrence :

Nitrogen : Molecular nitrogen comprises 78% by volume of the atmosphere. It is 33^{rd} most abundant element in the earth's crust. In the earth's crust, it occurs as sodium nitrate, NaNO₃ (called Chile saltpetre) and potassium nitrate (Indian saltpetre). It is found in the form of proteins and nucleic acid in plants and animals.

Phosphorus :

(i) It is eleventh most abundant element in earth's crust occurs in minerals of the apatite family, $Ca_9(PO_4)_6$. CaX_2 (X = F, Cl or OH) (e.g., fluorapatite $Ca_9(PO_4)_6$. CaF_2) and also found as chlorapatite $Ca_9(PO_4)_6$. $CaCl_2$). (ii) It is also present in nucleic acid (in DNA and RNA) which are the main components of phosphate rocks. (iii) Arsenic, antimony and bismuth are found mainly as sulphide minerals.

Electronic Configuration :

The valence shell electronic configuration of these elements is ns²np³.

Atomic and Ionic Radii :

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

Explanation :

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 :**

$$N > P > As > Sb > Bi$$
 (IE₁ values)

Explanation :

Ionisation enthalpy decreases down the group due to gradual increase in atomic size. Because of the extra stable half-filled p orbitals electronic configuration and smaller size, the ionisation enthalpy of the group 15 elements is much greater than that of group 14 elements in the corresponding periods. The order of successive ionisation enthalpies, as expected is $\Delta_1 H_1 < \Delta_1 H_2 < \Delta_1 H_3$.

Electronegativity:

$$N > P > As > Sb = Bi$$

(1.9) (1.9)

Explanation :

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.

Metallic Character

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

Physical Properties :

(i) All the elements of this group are polyatomic. Dinitrogen is a diatomic gas while all others are solids.

(ii) Metallic character increases down the group.

(iii) 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.

(iv) 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.

B. Pt. : N < P < As < Bi < Sb,

(v) Except nitrogen all the elements show allotropy.

 $\mathsf{P} \to \text{exists}$ in three allotropic form as white, red and black

As, Sb \rightarrow exist as yellow and grey

 $\text{Bi} \rightarrow \text{exist} \text{ as } \alpha, \, \beta, \, \gamma, \delta \, \text{allotropic form}$

Catenation

- The group 15 elements also show catenation property but to much smaller extent than carbon.
- Among group 15 elements P has the maximum tendency for catenation forming cyclic as well as open chain compounds consisting of many phosphorous atoms.
 - P_2H_4 has two P atoms bonded together the lesser tendency of elements of group 15 to show catenation in comparison to carbon is their low dissociation enthalpies.
 - C C 353.3 kJ /mole
 - N N 160.8 kJ / mole
 - P P 201.6 kJ / mole

As – As 147.4 kJ / mole

Anomalous properties of nitrogen

- (i) 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).
- (ii) Heavier elements of this group do not form p_{π} - p_{π} bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping.
- (iii) Nitrogen exists as a diatomic molecule with a triple bond (one σ and two π) between the two atoms. N₂ bond enthalpy (941.4 kJ mol⁻¹) is very high.
- (iv) Phosphorus, arsenic and antimony form single bonds as P–P, As–As and Sb–Sb while bismuth forms metallic bonds in elemental state.
- (v) The single N–N bond is weaker than the single P–P bond because of high interelectronic repulsion of the nonbonding electrons, owing to the small bond length. As a result the catenation tendency is weaker in nitrogen.
- (vi) 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 $d_{\pi}-p_{\pi}$ bond as the heavier elements can e.g., $R_{3}P=O$ or $R_{3}P=CH_{2}$ (R=alkyl group).
- (vii) Phosphorus and arsenic can form $d_{\pi}-d_{\pi}$ bond also with transition metals when their compounds like $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands.

Chemical Properties :

(A) Oxidation states and trends in chemical reactivity

- (i) The common oxidation states of these elements are -3, +3 and +5.
- (ii) The tendency to exhibit –3 oxidation state decreases down the group due to increase in size and metallic character. Bismuth hardly forms any compound in –3 oxidation state.
- (iii) The stability of +5 oxidation state decreases down the group. The only well characterised Bi (V) compound is BiF_{5} .
- (iv) The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group.
- (v) Nitrogen exhibits + 1, + 2, + 4 oxidation states also when it reacts with oxygen. Phosphorus also shows +1 and +4 oxidation states in some oxoacids.
- (vi) In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution. For example,

(i) $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$

(vii) Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and –3 both in alkali and acid.

(ii) $4H_3PO_3 \xrightarrow{Heat} 3H_3PO_4 + PH_3$

- (viii) +3 oxidation state in case of arsenic, antimony and bismuth becomes increasingly stable with respect to disproportionation.
- (ix) Nitrogen is restricted to a maximum covalency of 4 since only four (one s and three p) orbitals are available for bonding.
- (x) The heavier elements have vacant d orbitals in the outermost shell which can be used for bonding (covalency) and hence, expand their covalency as in PF_{6}^{-} .

(B) Reactivity towards hydrogen:

- (i) All the elements of Group 15 form hydrides of the type EH_3 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.
- (ii) The stability of hydrides decreases from NH₃ to BiH₃ 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 BiH₃ is the strongest reducing agent amongst all the hydrides.
- (iii) Basicity (or K_b) also decreases in the order $NH_3 > PH_3 > AsH_3 > SbH_3 \ge BiH_3$.

Property	NH ₃	PH ₃	AsH ₃	SbH ₃	BiH ₃
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 (°)	107.8	93.6	91.8	91.3	—
$\Delta_{\rm f} {\rm H} {}^{\bullet}\!\!\!\! {\rm kJ} {\rm mol}^{-1}$	- 46.1	13.4	66.4	145.1	278
$\Delta_{diss} H \ (E - H)/kJ \ mol^{-1}$	389	322	297	255	_

Table : Properties of Hydrides of Group 15 Elements

(C) Reactivity towards oxygen:

- (i) All these elements form two types of oxides: E_2O_3 and E_2O_5 .
- (ii) The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state.
- (iii) Their acidic character decreases down the group.
- (iv) 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 predominantly basic.

(D) Reactivity towards halogens:

- (i) These elements react to form two series of halides: EX_3 and EX_5 .
- (ii) Nitrogen does not form pentahalide due to non-availability of the d orbitals in its valence shell.
- (iii) Pentahalides are more covalent than trihalides.
- (iv) All the trihalides of these elements except those of nitrogen are stable. In case of nitrogen, only NF_3 is known to be stable. Trihalides except BiF_3 are predominantly covalent in nature.
- (E) Reactivity towards metals: All these elements react with metals to form their binary compounds exhibiting -3 oxidation state, such as, Ca_3N_2 (calcium nitride) Ca_3P_2 (calcium phosphide), Na_3As (sodium arsenide), Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2 (magnesium bismuthide).

SOLVED EXAMPLE_

- **Ex.-1** Arrange the following in the increasing order of the properties stated against them.
 - (a) (i) NH_3 , (ii) PH_3 , (iii) AsH_3 , (iv) SbH_3 boiling point.
 - (b) (i) Bi^{3+} , (ii) Sb^{3+} , (iii) As^{3+} stability of +3 oxidation state.
 - (c) (i) NH₃, (ii) PH₃, (iii) AsH₃, (iv) SbH₃, (v) BiH₃ reducing character.
- **Sol.** (a)) $PH_3 < AsH_3 < NH_3 < SbH_3$ boiling point.

 \dot{NH}_{a} 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 \propto molecular weight.

(b) $Bi^{3+} < Sb^{3+} < As^{3+}$ - 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.

DINITROGEN (N₂):

(i) Dinitrogen comprises 78% of the earth atmosphere but it is not a very abundant element in the earth's crust.

(ii) Nitrates are all very soluble in water so they are not wide spread in the earth's crust. $NaNO_3$ (Chile saltpetre) is found together with small amounts of KNO_3 (Indian saltpetre) $CaSO_4$ and $NaIO_3$ along the coast of southern Chile under a thin layer of sand or soil.

(iii) Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily.

(iv) 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 :

 $NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + H_2O(\ell) + NaCl_{(aq)}$

 $\mathrm{N_2}$ 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 : $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 \uparrow + 4H_2O + Cr_2O_3$

(iii) Very pure nitrogen :

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

Sodium azide also gives N_2 on heating.

 $2NaN_3 \xrightarrow{300^{\circ}C} 3N_2 + 2Na$

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 CO₂ which is absorbed in alkalies & N_2 remains which is collected in gas cylinders.

PROPERTIES :

- (i) N_2 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 NH₃.

(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.

 $N_2 + 3H_2 \longrightarrow 2NH_3$

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

 $N_2 + O_2 \longrightarrow 2NO$

Reaction with CaC₂ and BaC₂: At 1100°C, these carbides react with N₂ forming CaCN₂ and Ba(CN)₂ (V) respectively.

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

CaCN, reacts with H₂O in the soil to produce NH₃ gas. NH₃ 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.)

Uses of Dinitrogen

- For providing an inert atmosphere during many industrial processes where presence of air or O₂ is to be 1. avoided.
- 2. For manufacture of NH₃ by the Haber's process.
- 3. For manufacture of HNO,
- For manufacture of nitrolim. 4.

AMMONIA (NH₃):

PREPARATION:

(ii)

(v)

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

 $NH_4NO_3 + NaOH \longrightarrow NH_3\uparrow + NaNO_3 + H_2O$

 $(NH_{4})_{2}SO_{4} + CaO \longrightarrow 2NH_{3}\uparrow + CaSO_{4} + H_{2}O$

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

By the hydrolysis of metal nitrides like AIN or Mg₂N₂.

AIN + NaOH + $H_2O \longrightarrow NaAlO_2 + NH_3$

(iii) The ammonia evolved is passed through quick lime to dry it and collected by the downward displacement of air. Ammonia cannot be dried using CaCl₂, P₂O₅ or concentrated H₂SO₄ because NH₃ reacts with all of these.

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

$$P_2O_5 + 6NH_3 + 3H_2O \longrightarrow 2(NH_4)_3PO_4$$

CaO + H_2O \longrightarrow Ca(OH)_2

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

$$NH_2CONH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3 \implies 2NH_3 + H_2O + CO_2$$

Quantitative estimation of nitrogen :

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

NaNO₃ + 7NaOH + 4Zn \rightarrow 4Na₂ZnO₂ + NH₃ \uparrow + 2H₂O

$$NaNO_2 + 3Zn + 5NaOH \longrightarrow 3Na_2ZnO_2 + H_2O + NH_3^{\uparrow}$$

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

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)
- (ii) Cyanamide process :

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

Physical properties :

- Ammonia is a colourless gas with a pungent odour. Its freezing point and boiling point are 198.4 and 239.7 K (i) respectively.
- (ii) In the solid and liquid states, it is associated through hydrogen bonds as in the case of water and that accounts for its higher melting and boiling points than expected on the basis of its molecular mass.
- (iii) Ammonia gas is highly soluble in water. Its aqueous solution is weakly basic due to the formation of OH-ions. $NH_{3}(g) + H_{2}O(\ell) \longrightarrow NH_{4}^{+}(aq) + OH^{-}(aq)$

Chemical properties :

NH, as weak base : (i)

It forms ammonium salts with acids, e.g., NH₄Cl, (NH₄)₂ SO₄ etc. As a weak base, it precipitates the hydroxides of many metals from their salt solutions. For example,

(a) 2 FeCl₂ (aq) + 3 NH₄OH (aq) \longrightarrow Fe₂O₂ . xH₂O (s) + 3 NH₄Cl (aq)

(b) $ZnSO_{4}(aq) + 2 NH_{4}OH(aq) \longrightarrow Zn(OH)_{2}(s) + (NH_{4})_{2} SO_{4}(aq)$

White precipitate is soluble in excess of ammonia solution forming $[Zn(NH_3)_{a}]^{2+}$, soluble complex.

- (c)
- $\begin{array}{l} \mathsf{NiCl}_{_{2}}\left(\mathsf{aq.}\right) + 2\mathsf{NH}_{_{4}}\mathsf{OH}\left(\mathsf{aq.}\right) \longrightarrow \mathsf{Ni}(\mathsf{OH})_{_{2}} \downarrow \left(\mathsf{green}\right) + 2\mathsf{NH}_{_{4}}\mathsf{CI} \\ \mathsf{CrCl}_{_{3}}\left(\mathsf{aq.}\right) + 3\mathsf{NH}_{_{4}}\mathsf{OH}\left(\mathsf{aq.}\right) \longrightarrow \mathsf{Cr}(\mathsf{OH})_{_{3}} \downarrow \left(\mathsf{green}\right) + 3\mathsf{NH}_{_{4}}\mathsf{CI} \\ \mathsf{CoCl}_{_{2}}\left(\mathsf{aq.}\right) + 2\mathsf{NH}_{_{4}}\mathsf{OH}\left(\mathsf{aq.}\right) \longrightarrow \mathsf{Co}(\mathsf{OH})_{_{2}} \downarrow \left(\mathsf{pink}\right) + 2\mathsf{NH}_{_{4}}\mathsf{CI} \\ \end{array}$ (d)
- (e)
- Cr(OH)₂ (precipitate) is partially soluble in excess ammonia whereas

Ni(OH), (precipitate), Co(OH), (precipitate) are soluble in excess of ammonia forming soluble complex.

(ii) Complex formation by NH, :

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 Cu²⁺, Ag⁺; Cd²⁺, Ni²⁺ etc.

[Cu(NH₃)₂]²⁺ (aq), [Cr(NH₃)₂]³⁺, [Ni(NH₃)₂]²⁺, [Co(NH₃)₂]²⁺, [Ag (NH₃)₂]⁺ (aq), [Cd(NH₃)₂]²⁺ (aq) (deep blue) (purple) (blue) (pale yellow) (colourless) (colourless)

[Co(NH₃)₆]³⁺ (yellow but appears dark brown due to other compounds)

(iii) Thermal dicompostion of ammonium salts :

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.

 $NH_4CI \xrightarrow{\Lambda} NH_3 + HCI;$ $(NH_{4})_{2}SO_{4} \xrightarrow{\Delta} 2NH_{3} + H_{2}SO_{4}$

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 .

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

$$NH_4CIO_4 \xrightarrow{\Delta} N_2 + CI_2 + O_2 + H_2O$$

Test of Ammonia and Ammonium salts : (iv)

When NH₂ gas is passed into the colourless solution of Nessler's reagent a brown precipitate or coloration is formed. This is a test for NH₃ gas.

 $2K_2Hgl_4 + 3KOH + NH_3 \longrightarrow H_2N HgO Hgl \downarrow (brown) + 7KI + 2H_2O$

(Millon base)

Uses of NH₂:

- 1. Used as a refrigeration fluid.
- For the production of ammonium fertilizers such as ammonium sulphate, ammonium phosphate, 2. ammonium nitrate, urea etc.
- 3. For removing grease because NH₂OH dissolves grease.
- For manufacture of HNO, by the Ostwald process. 4.
- As a laboratory reagent. 5.
- In the production of artificial rayon, silk, nylon etc. 6.

OXIDES OF NITROGEN :

Nitrogen forms a number of oxides, N_2O , NO, N_2O_3 , NO₂ or N_2O_4 and N_2O_5 , and also very unstable NO₃ and N_2O_6 . All these oxides of nitrogen exhibit $p\pi$ - $p\pi$ multiple bonding between nitrogen and oxygen.

Oxides of Nitrogen					
Name	Formula	Oxidation state of	Common methods of	Physical appearance and	
		nitrogen	preparation	chemical nature	
Dinitrogen oxide [Nitrogen oxide]	N ₂ O	+1	$NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$	Colourless gas, neutral	
Nitrogen monoxide	NO	+2	2NaNO ₂ + 2FeSO ₄ + 3H ₂ SO ₄	Colourless gas,	
[Nitrogen (II) oxide]	110		\rightarrow Fe ₂ (SO ₄) ₃ + 2NaHSO ₄	neutral	
			$+ 2H_{2}O + 2NO$		
Dinitrogen trioxide [Nitrogen (III) oxide]	N_2O_3	+3	$2NO + N_2O_4 \xrightarrow{-30^\circ C} 2N_2O_3$	Pale Blue solid (MP = -100.1°C), acidic, Intense blue liquid (-30°C)	
Nitrogen dioxide [Nitrogen (IV) oxide]	NO ₂	+4	$\frac{2Pb(NO_3)_2}{4NO_2 + 2PbO + O_2}$	brown gas, acidic	
Dinitrogen tetroxide [Nitrogen (IV) oxide]	N_2O_4	+4	$2NO_2 \xrightarrow{Cool} N_2O_4$	Colourless solid/ liquid, acidic	
Dinitrogen pentaoxide [Nitrogen(V) oxide]	N_2O_5	+5	$4\text{HNO}_3 + P_4O_{10}$ $\rightarrow 4\text{HPO}_3 + 2N_2O_5$	colourless solid, acidic	

Structure of Oxides of Nitrogen

Formula	Resonance structures	Bond Parameters
N ₂ O	$\dot{N} = N = \ddot{O} \leftrightarrow : N \equiv N - \ddot{O}:$ $N = \ddot{O} \leftrightarrow : \ddot{N} = \ddot{O}:$	N—N—O 113 pm 119 pm Linear
N ₂ O ₃	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N_0 115 pm 115 pm 115 pm 115 pm 110° 112 pm 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110° 110°
No ₂		N 120 pm O 134° O Angular
N_2O_4	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} O \\ 135^{\circ} \\ O \end{array} \begin{array}{c} N \\ Planar \end{array} \begin{array}{c} N \\ O \end{array} \begin{array}{c} O \\ V \\ O \end{array} \end{array} \begin{array}{c} O \\ V \\ O \end{array} \begin{array}{c} O \\ V \\ O \end{array} \end{array} \begin{array}{c} O \\ V \\ O \end{array} \begin{array}{c} O \\ V \\ O \end{array} \end{array} \begin{array}{c} O \\ V \\ O \end{array} \begin{array}{c} O \\ V \\ O \end{array} \end{array} $
N ₂ O ₅	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} 0 \\ N \\ 0 \\ 0 \\ \end{array} \begin{array}{c} 112^{\circ} \\ 112^{\circ} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ $

Oxide	Preparation	Properties
N ₂ O	$NH_4NO_3 \rightarrow N_2O + 2H_2O$	$Cu(hot) + N_2O \rightarrow CuO + N_2$
NO	$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$	$2NO + X_2 \rightarrow 2NOX (X = Cl or Br)$
	$2HNO_2 + 2I^- + 2H^+ \rightarrow 2NO + I_2 + 2H_2O$	
N ₂ O ₃	$NO + NO_2 \rightarrow N_2O_3; 4NO + O_2 \rightarrow 2N_2O_3$	$N_2O_3 + KOH \rightarrow 2KNO_2 + H_2O$
NO ₂	$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$	$2NO_2 + F_2 \rightarrow 2NO_2F$ (nitryl fluoride)
N_2O_5	$4HNO_3 + P_4O_{10} \xrightarrow{250 \text{ K}} 2N_2O_5 + 4HPO_3$	$N_2O_5 + Na \rightarrow NaNO_3 + NO_2$

OXY ACIDS OF NITROGEN : NITROUS ACID (HNO,) :

PREPARATION:

By acidifying an aqueous solution of a nitrite

 $Ba(NO_2)_2 + H_2SO_4 \longrightarrow 2HNO_2 + BaSO_4 \downarrow$

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.

 $2KI + 2HNO_2 + 2HCI \longrightarrow 2H_2O + 2NO + 2KCI + I_2$

(iv) With strong oxidizing agents like KMnO₄ nitrous acid and nitrites function as reducing agents and get oxidized to NO₃⁻ ions : 2KMnO₄ + 5KNO₂ + 6HCl $\longrightarrow 2$ MnCl₂ + 5KNO₃ + 3H₂O + 2KCl

NITRIC ACID (HNO₃) :

PREPARATION:

(i) In the laboratory :

4

Nitric acid is prepared by heating KNO_3 or $NaNO_3$ and concentrated H_2SO_4 in a glass retort. NaNO₃ + $H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

(ii) On a large scale it is prepared mainly by **Ostwald's process.** This method is based upon catalytic oxidation of NH_3 by atmospheric oxygen.

$$NH_3(g) + 5O_2(g) \text{ (from air)} \xrightarrow{PtrRh gauge catalyst}{500 \text{ K}, 9 \text{ bar}} 4 \text{ NO}(g) + 6 H_2O(g)$$

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 HNO3.

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

NO thus formed is recycled and the aqueous HNO₃ can be concentrated by distillation upto ~ 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4 .

Physical properties :

It is a colourless liquid. Freezing point is 231.4 K and boiling point is 355.6 K. Laboratory grade nitric acid contains ~ 68% of the HNO_3 by mass and has a specific gravity of 1.504.

In the gaseous state, HNO, exists as a planar molecule.

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

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

Chemical properties :

(i) Concentrated nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum. The products of oxidation depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation.

Some metals (e.g., Cr, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

Reactions of Elements (Metals/Metalloids with HNO,)

Element	Nature of HNO,	Changes to	Reactions				
(A) Metals plac	A) Metals placed above H in electrochemical series (ECS)						
1. Mg, Mn 2. Zn, Fe	cold and dilute (a) very dilute (b) dilute (c) concentrated	M(NO ₃) ₂ NH ₄ NO ₃ N ₂ O NO ₂	$M + 2HNO_{3} \rightarrow M(NO_{3})_{2} + H_{2}$ $4Zn+10HNO_{3} \rightarrow 4Zn(NO_{3})_{2} + NH_{4}NO_{3} + 3H_{2}O$ $4Zn + 10HNO_{3} \rightarrow 4Zn(NO_{3})_{2} + N_{2}O + 5H_{2}O$ $Zn + 4HNO_{3} \rightarrow Zn(NO_{3})_{2} + 2NO_{2} + 2H_{2}O$				
3 . Sn	(a) dilute (b) concentrated	NH ₄ NO ₃ NO ₂	$4Zn+10HNO_{3} \rightarrow 4Zn(NO_{3})_{2} + NH_{4}NO_{3} + 3H_{2}O$ Sn + 4HNO ₃ \rightarrow H ₂ SnO ₃ + 4NO ₂ + H ₂ O meta stannic acid				
4. Pb	(a) dilute (b) concentrated	NO NO ₂	$3Pb + 8HNO_{3} \rightarrow 3Pb(NO_{3})_{2} + 2NO + 4H_{2}O$ $Zn + 4HNO_{3} \rightarrow Zn(NO_{3})_{2} + 2NO_{2} + 2H_{2}O$				
(B) Metals belo	ow H in ECS						
5. Cu, Ag, Hg	(a) dilute	NO	3Pb + 8HNO ₃ \rightarrow 3Pb(NO ₃) ₂ + 2NO + 4H ₂ O. Hg forms Hg ₂ (NO ₃) ₂				
	(b) concentrated	NO ₂	$Zn + 4HNO_3 \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$				
(C) Metalloids	(C) Metalloids						
Sb, As	concentrated	NO2	Sb + 5HNO ₃ \rightarrow H ₃ SbO ₄ + 5NO ₂ + H ₂ O antimonic acid				

(ii) Concentrated nitric acid also oxidises non-metals and their compounds. Iodine is oxidised to iodic acid, carbon to carbon dioxide, sulphur to H_2SO_4 and phosphorus to phosphoric acid.

$$\begin{split} &I_2 + 10 \text{ HNO}_3 \longrightarrow 2 \text{ HIO}_3 + 10 \text{ NO}_2 + 4 \text{ H}_2\text{O} \\ &C + 4 \text{ HNO}_3 \longrightarrow \text{CO}_2 + 2 \text{ H}_2\text{O} + 4 \text{ NO}_2 \\ &S_8 + 48 \text{ HNO}_3 \text{ (concentrated)} \longrightarrow 8 \text{ H}_2\text{SO}_4 + 48 \text{ NO}_2 + 16 \text{ H}_2\text{O} \\ &P_4 + 20 \text{ HNO}_3 \text{ (concentrated)} \longrightarrow 4 \text{ H}_3\text{PO}_4 + 20 \text{ NO}_2 + 4 \text{ H}_2\text{O} \end{split}$$

(iii) Brown Ring Test :

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

$$NO_{3}^{-} + 3 Fe^{2+} + 4H^{+} \longrightarrow NO + 3Fe^{3+} + 2 H_{2}O$$
$$[Fe (H_{2}O)_{6}]^{2+} + NO \longrightarrow [Fe (H_{2}O)_{5} (NO)]^{2+} + H_{2}O$$

USES OF HNO₃:

(i) The major use of nitric acid is in the manufacture of ammonium nitrate for fertilizers and other nitrates for use in explosives and pyrotechnics.

(ii) It is also used for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds.

(iii) Other major uses are in the pickling of stainless steel, etching of metals and as an oxidiser in rocket fuels.

-Solved Example-

Ex.-2 $NH_3 + O_2 \xrightarrow{Pt} (A)$
 $(A) + O_2 \longrightarrow (B)$ (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.
 $(C) + I^- \longrightarrow (E)$ (violets vapours).
Identify (A),(B),(C),(D) and (E).

Sol. $4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O.$

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

- **Ex.-3** Why NH_3 gas cannot be dried by passing over P_2O_5 , $CaCl_2$ and H_2SO_4 ?

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, $Ca_3(PO_4)_2CaF_2$

ALLOTROPIC FORMS OF PHOSPHORUS :

White or yellow phosphorus (P_{a}), Red phosphorus and black phosphorus :

PREPARATION :

(i) $2Ca_3(PO_4)_2$ (from bone-ash) + 10C + $6SiO_2 \xrightarrow{\Delta} 6CaSiO_3 + 10CO + P_4(s)$ (electric furnace method) (white phosphorus)

(ii) When white phosphorus is heated in the atmosphere of CO_2 or coal gas at 573 K red phosphorus is produced.

(iii) **Black phosphorus** has two forms α -black phosphorus and β -black phosphorous, α -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, β -black phosphorus is prepared by heating white phosphorus at 473 K under high pressure. It does not burn in air upto 673 K.

PHYSICAL PROPERTIES :

Properties	White-Phosphorus	Red-Phosphorus
Physical state	Soft waxy solid	Brittle powder
Colour	White when pure. Attains yellow colour on standing	Red
Odour	Garlic	Odourless
Melting point	44°C	Sublimes in absence of air at 290°C
Solubility in water	Insoluble	Insoluble
Solubility in CS ₂	Soluble	Insoluble
Chemical activity	Very active	Less active
Stability	Unstable	Stable
Phosphorescence	Glows in dark	Does not glow in dark
Burning in air	Forms P ₄ O ₁₀	Form P ₄ O ₁₀
Reaction with	Evolves phosphine	No action



White-P Red-P 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.

Reactants	Products	Special Points
P ₄ + 3O ₂	P_4O_6, P_4O_{10}	Forms P_4O_6 in limited supply of air, Red and other
		forms of phosphorus also burn in air or oxygen but on
		heating.
P ₄ + 10S	P ₄ S ₁₀	
3M + P	M ₃ P	$M_{3}P + 3H_{2}O \rightarrow 3MOH + PH_{3}\uparrow \{where M = Na, K etc.\}$
3CaO + 8P + 9H ₂ O	$3Ca(H_2PO_2)_2 + 2PH_3$	
P + 5NHO ₃	$H_3PO_4 + 5NO_2 + H_2O$	
2P + 5H ₂ SO ₄	$2H_{3}PO_{4} + 5SO_{2} + 2H_{2}O$	

COMPOUNDS OF PHOSPHORUS : PHOSPHINE :

PREPARATION:

- Phosphine is prepared by the reaction of calcium phosphide with water. (i) $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$
- In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert (ii) atmosphere of CO₂.

atmosphere of $\bigcirc \bigcirc_2$. $P_4 + 3 \text{ NaOH} + 3 \text{ H}_2\text{O} \longrightarrow \text{PH}_3 + 3 \text{ NaH}_2\text{PO}_2$ (sodium hypophosphite)

When pure, it is non inflammable but becomes inflammable owing to the presence of P₂H₄ or P₄ vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH,I) which on treating with KOH gives off phosphine.

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

PROPERTIES :

- It is a colourless gas with a slightly garlic or rotten fish smell and is highly poisonous. It explodes in contact (i) with traces of oxidising agents like HNO₃, Cl₂ and Br₂ vapours.
- It is slightly soluble in water but soluble in CS₂ and other organic solvents. The solution of PH₃ in water (ii) decomposes in presence of light giving red phosphorus and H₂.
- When absorbed in copper sulphate or mercuric chloride, the corresponding phosphides are obtained. (iii)

$$\begin{aligned} 3\text{CuSO}_{4} + 2\text{PH}_{3} &\longrightarrow \text{Cu}_{3}\text{P}_{2} \downarrow + 3\text{H}_{2}\text{SO}_{4} \\ 3\text{HgCl}_{2} + 2\text{PH}_{3} &\longrightarrow \text{Hg}_{3}\text{P}_{2} \downarrow \text{(brownish black)} + 6\text{ HCl} \\ \text{Hg}_{3}\text{P}_{2} + \text{H}_{2}\text{O} \xrightarrow{\text{on standing}} \text{Hg} \downarrow \text{(Black)} + \text{H}_{3}\text{PO}_{3} \\ \text{PH}_{3} + 6\text{AgNO}_{3} &\longrightarrow \text{Ag}_{3}\text{P} \cdot 3\text{AgNO}_{3} \downarrow \text{(yellow)} + 3\text{HNO}_{3} \\ \text{Ag}_{3}\text{P} \cdot 3\text{AgNO}_{3} + 3\text{H}_{2}\text{O} \xrightarrow{\text{on standing}} 6\text{Ag} \downarrow \text{(Black)} + 3\text{HNO}_{3} + \text{H}_{3}\text{PO}_{3} \end{aligned}$$

Phosphine is weakly basic and like ammonia, it gives phosphonium compounds with acids e.g., (iv)

$$^{2}H_{3} + HBr \longrightarrow PH_{4}Br$$

Ο Phosphonium compounds are obtained when anhydrous phosphine reacts with anhydrous halogen acids (not in aqueous solution).

(v)
$$PH_3 + O_2 \xrightarrow{150^\circ} P_2O_5 + H_2O$$

P

USES OF PH, :

(i) 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.

(ii) 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_AO_c) :

It is dimeric and has formula P₄O₆

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, P₄O₆ remains in gaseous form whereas P₄O₁₀ 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 $O + 6H O \longrightarrow 4H PO$

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PC$$

(iii) It dissolves in hot water liberating PH_{3}

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

(iv) It slowly gets oxidized in air to form P_4O_{10} $P_4O_6 + 2O_2 \longrightarrow P_4O_{10}$

PHOSPHORUS PENTAOXIDE (P_4O_{10}) :

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

PREPARATION:

It is obtained by burning phosphorus in excess air.

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

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. $P_4O_{10} + 2H_2O \longrightarrow 4HPO_3$; $4HPO_3 + 2H_2O \longrightarrow 2H_4P_2O_7$; $2H_4P_2O_7 + 2H_2O \longrightarrow 4H_3PO_4$
- (iv) It dehydrates concentrated H₂SO₄ and concentrated HNO₃ to SO₃ and N₂O₅ respectively.

 $4HNO_3 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + P_4O_{10} \xrightarrow{distillation} 4HPO_3 + 2SO_3 = 2N_2O_5 ; 2H_2SO_4 + 2N_2O_5 = 2N_2O_5 ; 2H_2SO_5 + 2N_2O_5 = 2N_2O_5 = 2N_2O_5 ; 2H_2SO_5 = 2N_2O_5 = 2$

USES OF P₄O₁₀ :

- 1. For drying acidic gases.
- 2. As a dehydrating agent
- 3. For the preparation of SO_3 and N_2O_5 .
- 4. For the preparation of phosphoric acid.

SOLVED EXAMPLE

- Ex.-4 What happens?
 - (a) When phosphine is heated at 150°C.
 - (b) When phosphine is dissolved in water in presence of light.
- **Sol.** (a) Phosphine on heating at 150°C burns forming H_3PO_4
 - $PH_3 + 2O_2 \longrightarrow H_3PO_4$
 - (b) The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2 .

Ex.-5 P_4 + NaOH $\xrightarrow{\text{warm}}$ Products.

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

Sol. $P_4 + 3 \text{ NaOH} + 3 \text{ H}_2\text{O} \longrightarrow \text{PH}_3 + 3 \text{ NaH}_2\text{PO}_2$

(sodium hypophosphite)

 $4Cu^{2+} + PH_3 + 4H_2O \longrightarrow H_3PO_4 + 4Cu \downarrow + 8H^+$ Sodium hypophosphite also acts as a strong reducing agent and reduces copper sulphate to Cu_2H_2 .

Halides :

Phsophorus forms 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.

$$P_4 + 6 Cl_2 \longrightarrow 4 PCl_3$$

(ii) It is also obtained by the action of thionyl chloride with white phosphorus.

 $P_4 + 8 \text{ SOCl}_2 \longrightarrow 4 \text{ PCl}_3 + 4 \text{ SO}_2 + 2 \text{ S}_2 \text{Cl}_2$

Properties :

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

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

(ii) It reacts with organic compounds containing – OH group such as CH_3COOH, C_2H_5OH . $3 CH_3COOH + PCI_3 \longrightarrow 3 CH_3COCI + H_3PO_3$ $3 C_2H_5OH + PCI_3 \longrightarrow 3 C_2H_5CI + H_3PO_3$

Phosphorus pentachloride :

Preparation:

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

$$P_4 + 10 \text{ Cl}_2 \longrightarrow 4 \text{ PCl}_5$$

It can also be prepared by the action of SO_2CI_2 on phosphorus.

 $P_4 + 10 SO_2CI_2 \longrightarrow 4 PCI_5 + 10 SO_2$

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.

 $\begin{array}{l} \mathsf{PCI}_5 + \mathsf{H}_2\mathsf{O} \longrightarrow \mathsf{POCI}_3 + 2 \ \mathsf{HCI} \\ \mathsf{POCI}_3 + 3 \ \mathsf{H}_2\mathsf{O} \longrightarrow \mathsf{H}_3\mathsf{PO}_4 + 3 \ \mathsf{HCI} \end{array}$

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

 $\mathsf{PCI}_5 \xrightarrow{250^\circ \mathsf{C}} \mathsf{PCI}_3 + \mathsf{CI}_2$

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

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

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

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

$$2 \text{ Ag} + \text{PCl}_5 \longrightarrow 2 \text{ AgCl} + \text{PCl}_3$$

 $\text{Sn} + 2 \text{PCl}_5 \longrightarrow \text{SnCl}_4 + 2 \text{PCl}_3$

It is used in the synthesis of some organic compounds , e.g., C₂H₂CI , CH₂COCI.

OXY ACIDS OF PHOSPHORUS :

Name	Formula	Oxidation state of Phosphorus	Characteristic bonds and their number	Preparation
Hypophosphorus (Phosphinic)	H ₃ PO ₂	+ 1	One P — OH Two P — H	white P_4 + alkali
Orthophosphorous (Phosphonic)	H ₃ PO ₃	+ 3	One $P = O$ Two $P - OH$ One $P - H$	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+ 3	One $P = O$ Two $P - OH$ Two $P - H$	$PCl_3 + H_3PO_3$
Hypophosphoric	$H_4P_2O_6$	+ 4	Two $P = O$ Four $P - OH$	red P_4 + NaClO ₂
Orthophosphoric	H ₃ PO ₄	+ 5	One P — P Three P — OH	$P_4O_{10} + H_2O$
Pyrophosphoric	$H_4P_2O_7$	+ 5	One P = O Four P — OH Two P = O	heat phosphoric acid
Metaphosphoric*	(HPO ₃) _n	+ 5	One $P - O - P$ Three $P - OH$ Three $P = O$	phosphorous acid + Br ₂ , heat in a sealed tube

Oxoacids of Phosphorus



(iv)

(i)

(ii)



Super phosphate

(ii) $[3(Ca_3(PO_4)_2CaF_2) + 14H_3PO_4 \longrightarrow \underbrace{10 Ca(H_2PO_4)_2}_{triple super phosphate} + 2HF$

 H_3PO_4 is used to avoid the formation of the insoluble CaSO₄ (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.

Occurrence:

- (i) 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.
- (ii) 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.
- (iii) 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.

Perodic Properties :

O Electronic Configuration :

The elements of group 16 have six electrons in the outermost shell and have ns² np⁴ general valence shell electronic configuration.

O 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. O < S < Se < Te

O 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. O > S > Se > Te

O 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. Electron affinity : S > Se > Te > Po > O

O 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.

 $O > S \simeq Se > Te > Po$

O Oxidation states :

- (i) 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.
- (ii) 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.
- (iii) 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.
- (iv) 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.
- (v) HNO_3 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.
- (vi) Polonium shows metallic properties since it dissolves in H_2SO_4 , HF, HCl and HNO_3 forming pink solution of Po^{II}. However Po^{II} is strongly radio active and the α -emission decomposes the water and the Po^{II} is quickly oxidised to yellow solution of Po^{IV}.

Anomalous behaviour of oxygen :

- (i) 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 H₂O which is not found in H₂S.
- (ii) 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.

Physical Properties :

- (i) 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).
- (ii) The melting and boiling points increase with an increase in atomic number down the group.
- (iii) 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) .

- (iv) **Catenation**: Tendency for catenation decreases down the group. This property is prominently displayed by sulphur (S_g) . The S—S bond is important in biological system and is found in some proteins and enzymes such as cysteine.
- (v) Selenium has unique property of photo conductivity and is used in photocopying machines and also a decolouriser of glass.
- (vi) Allotropy : All element exhibit allotropy for e.g.

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

Sulphur -

The main allotropic forms are

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

Table : 8 ATOMIC AND PHYSICAL PROPERTIES

Element		0	S	Se	Te
Atomic Number		8	16	34	52
Atomic Mass		16	32.06	78.96	127.6
Electronic configuration		[He] 2s ² 2p ⁴	[Ne] 3s ² 3p ⁴	[Ar] 3d ¹⁰ 4s ² 4p ⁴	[Kr] 4d ¹⁰ 5s ² 5p ⁴
Covalent Radius / pm		74	103	119	142
lonic Radius X ^{−2} / pm		140	184	198	221
lonization enthalpy / (kJ mol ⁻¹)	Ι	1314	1000	941	869
	II	3388	2251	2045	1790
Electronegativity		3.5	2.44	2.48	2.01
Density/[g cm ⁻³ (293 K)]		1.32	2.06	4.19	6.25
Melting point / K		54	393	490	725
Boiling point / K		90	718	958	1260

Chemical Properties :

(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.

Property H₂O H₂S H₂Se H₂Te m.p./K 273 188 208 222 b.p./K 373 213 232 269 H-E distance/pm 96 134 146 169 HEH angle (°) 90 104 92 91 ∆_fH/kJ moĺ¹ -286 -20 73 100 Δ_{diss} H (H-E)/kJ mol¹ 463 347 276 238 1.8×10^{-16} Dissociation constant (K_a) 1.3×10^{-7} 1.3×10^{-4} 2.3×10^{-3}

 Table : 9

 PROPERTIES OF HYDRIDES OF GROUP 16 ELEMENTS

(ii) **Reactivity with oxygen**: All these elements form oxides of the EO₂ and EO₃ types where E = S, Se, Te or Po. Ozone (O₃) and sulphur dioxide (SO₂) are gases while selenium dioxide (SeO₂) is solid. Reducing property of dioxide decreases from SO₂ to TeO₂; SO₂ is reducing while TeO₂ is an oxidising agent. Besides EO₂ type sulphur, selenium and tellurium also form EO₃ type oxides (SO₃, SeO₃, TeO₃). Both types of oxides are acidic in nature.

(iii) Reactivity toward the halogens :

- (a) 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 > Cl > Br > l. Amongst hexahalides, hexafluorides are the only stable halides.
- (b) All hexafluorides are gaseous in nature. They have octahedral structure. Sulphur hexafluoride SF_6 is exceptionally stable for steric reasons.
- (c) Amongst tetrafluorides, SF_4 is a gas, SeF_4 liquid and TeF_4 a solid These fluorides have sp³d 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.
- (d) All elements except selenium form dichlorides and dibromides. These dihalides are formed by sp³ hybridisation and thus have tetrahedral structure. The well known monohalides are dimeric in nature, Examples are S₂F₂, S₂Cl₂, S₂Br₂, Se₂Cl₂ and Se₂Br₂. These dimeric halides undergo disproportionation as given below :

 $2Se_2Cl_2 \longrightarrow SeCl_4 + 3Se.$

SOLVED EXAMPLE_

Ex6	Identify the group 16(VI) (a) the most electronegation (b) semimetal (c) radioactive (d) the most abundant e	A) element that fits each tive lement in the earth's crus	of the following descriptio	on is :
Sol.	(a) Oxygen	(b) Tellurium	(c) Polonium	(d) Oxygen
Ex7 Sol.	Give the names and form (A) – 2 (A) H_2S^{2-}	nulae of the compounds (B) + 4 (B) $S^{4+}O_2$	in which sulphur exhibits (C) + 6 (C) $S^{+6}O_3$	an oxidation state of :

DIOXYGEN (O₂):

It differs from the remaining elements of the VIth group because of the following properties. (A) small size (B) high electronegativity and (C) non-availability of d-orbitals.

PREPARATION:

(i) Laboratory method :

$$2 \text{ KCIO}_3 \xrightarrow{\Delta} 2 \text{ KCI} + 30_2$$

(ii) By thermal decomposition of oxides of metals.

2 HgO $\xrightarrow{450^{\circ}C}$ 2 Hg + O₂; 2 Ag₂O $\xrightarrow{350^{\circ}C}$ 4 Ag + O₂

$$3 \text{ MnO}_2 \xrightarrow{\Lambda} \text{ Mn}_3\text{O}_4 + \text{O}_2; \qquad 2 \text{ Pb}_3\text{O}_4 \xrightarrow{\Lambda} 6 \text{ PbO} +$$

(iii) Thermal decomposion of $K_2 Cr_2 O_7$ and $KMnO_4$

$$4 \text{ K}_2 \text{Cr}_2 \text{O}_7 \xrightarrow{\Delta} 4 \text{ K}_2 \text{Cr} \text{O}_4 + 2 \text{ Cr}_2 \text{O}_3 + 3 \text{O}_2 \text{ ; } 2 \text{ KMnO}_4 \xrightarrow{\Delta} \text{ K}_2 \text{MnO}_4 + \text{MnO}_2 + \text{O}_2$$

0,

(iv) From air (mfg.): Oxygen is obtained by liquefaction of air and then its fractional distillation.

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.

Use of O_2 :

- 1. Oxygen mixed with helium or CO₂ is used for artificial respiration.
- 2. Liquid oxygen is used as oxidising agent in rocket fuels.
- 3. Oxygen is used for production of oxy-hydrogen or oxy-acetylene flames employed for cutting and welding.
- 4. Pure dioxygen is used to convert pig iron into steel in the basic oxygen process which are kaldo and LD process.

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} , Cl_2O_7 , CrO_3 , Mn_2O_7 etc. They are termed as acid anhydride. $Cl_2O_7 + H_2O \longrightarrow 2 HCIO_4$; $Mn_2O_7 + H_2O \longrightarrow 2 HMnO_4$

(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., Na₂O, CaO. CuO, FeO, BaO etc.

 $Na_2O + H_2O \longrightarrow 2 NaOH$; CaO + $H_2O \longrightarrow Ca(OH)_2$; CuO + $H_2SO_4 \longrightarrow CuSO_4 + H_2O$

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_2O_3 amphoteric and CrO_3 acidic.

(iii) Neutral Oxides :

They neither combine with acids nor with the bases to form salts e.g., CO, N₂O, NO etc.

(iv) Amphoteric Oxides :

Many metals yield oxides which combine with both strong acid as well as strong bases e.g., ZnO, AI_2O_3 , BeO, Sb_2O_3 , Cr_2O_3 , PbO, SnO, SnO_2 , Ga_2O_3 etc.

 $\begin{array}{l} \mathsf{PbO}+\mathsf{2}\,\mathsf{NaOH} \longrightarrow \mathsf{Na_2PbO_2}+\mathsf{H_2O}\,;\, \mathsf{PbO}+\mathsf{H_2SO_4} \longrightarrow \mathsf{PbSO_4}+\mathsf{H_2O}\\ \mathsf{Cr_2O_3}+\mathsf{2}\,\mathsf{NaOH} \longrightarrow \mathsf{Na_2Cr_2O_4}+\mathsf{H_2O}\,;\, \mathsf{Cr_2O_3}+\mathsf{3}\,\mathsf{H_2SO_4} \longrightarrow \mathsf{Cr_2(SO_4)_3}+\mathsf{3}\,\mathsf{H_2O} \end{array}$

(v) Mixed Oxides :

They behave as mixture of two simple oxides.

e.g., Pb_3O_4 (2PbO + PbO₂); Fe_3O_4 (FeO + Fe_2O_3); Mn_3O_4 (2 MnO + MnO₂)

(vi) Peroxides :

They react with dilute acids and form H_2O_2 , e.g., Na_2O_2 , K_2O_2 , BaO_2 etc. They contain O_2^{2-} 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 KO₂ + 2 H₂O \longrightarrow 2 KOH + H₂O₂ + O₂.

OZONE (O₃) : PREPARATION :

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

 $\begin{array}{ccc} {\sf O}_2 & & \xrightarrow{\mbox{energy}} & {\sf O} \mbox{ + } {\sf O} \\ {\sf O}_2 \mbox{ + } {\sf O} & & \longrightarrow & {\sf O}_3 \end{tabular}; \end{tabular} \Delta {\sf H} \mbox{ = } 2845 \mbox{ kJ mol}^{-1} \end{array}$

 $3O_2 \implies 2O_3$

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

- O Higher concentration or pure O_3 can be obtained by fractional liquefaction of the mixture.
- O Low concentration of O_3 can be made by UV irradiation of O_2 .

PROPERTIES:

PHYSICAL 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.
- (ii) It also absorbs strongly in the UV region. Thus it protects the people on the earth from the harmful UV radiation from the sun.
- (iii) 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_A . O_3 molecule is diamagnetic but O_3^- is paramagnetic.

CHEMICAL PROPERTIES :

(i) 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) (i) It oxidises I^- to I_2 (from neutral solution of KI)

 $O_{3} \longrightarrow O_{2} + [O]$ $2 \text{ KI} + \text{H}_{2}\text{O} + [O] \longrightarrow 2 \text{ KOH} + \text{I}_{2}$ $2 \text{ KI} + \text{H}_{2}\text{O} + \text{O}_{3} \longrightarrow 2 \text{ KOH} + \text{O}_{2} + \text{I}_{2}$ *used in quantitative estimation of O₃

(ii) Alkaline KI is oxidised to potassium iodate & periodate.

$$\mathsf{KI} + \mathsf{3O}_{_3} \longrightarrow \mathsf{KIO}_{_3} + \mathsf{3O}_{_2} \ ; \qquad \mathsf{KI} + \mathsf{4O}_{_3} \longrightarrow \mathsf{KIO}_{_4} + \mathsf{4O}_{_2}$$

Note : Similarly S²⁻ to SO₄²⁻ (but not H₂S), NO₂⁻ to NO₃⁻ , SO₃²⁻ to SO₄²⁻, AsO₃³⁻ to AsO₄³⁻ , Sn²⁺ to Sn⁴⁺ (acidic medium).

(iii) $O_3 \longrightarrow O_2 + [O]$ $2 K_2 MnO_4 + [O] + H_2 O \longrightarrow 2 KMnO_4 + 2KOH$

$$2 \text{ K}_{2}\text{MnO}_{4} + \text{O}_{3} + \text{H}_{2}\text{O} \longrightarrow 2 \text{ KMnO}_{4} + 2\text{KOH} + \text{O}_{2}$$

(iv) Similarly $[Fe(CN)_{\beta}]^{4-}$ oxidises to $[Fe(CN)_{\beta}]^{3-}$ (basic medium).

(v)
$$2NO_2 + O_3 \longrightarrow N_2O_5 + O_2$$

(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. $H_2S + O_3 \longrightarrow H_2O + S \downarrow (yellow) + O_2$
- (d) Reaction with dry $I_2 : 2 I_2 + 9[O_3] \longrightarrow I_4O_9 + 9O_2$
- **O** I_4O_9 yellow solid has the composition $I^{+3} (IO_3^{-})_3$. Formation of this compound is a direct evidence in favour of basic nature of I_2 (i.e. its tendency to form cations).

(e) Reaction with moist iodine :

$$O_3 \longrightarrow O_2 + [O] \times 5$$

 $I_2 + 5[O] \longrightarrow I_2O_5$
 $I_2O_5 + H_2O \longrightarrow 2HIO_3$
 $\overline{5O_3 + I_2 + H_2O} \longrightarrow 2HIO_3 + 5O_2$

(f) Reaction with Silver :

Silver articles become black in contact with ozone.

 $Ag + O_3 \longrightarrow Ag_2O \downarrow (black) + O_2$

(g) Reaction with H_2O_2 :

 $2e^{-} + 2H^{+} + O_{3} \longrightarrow O_{2} + H_{2}O$ $\frac{H_{2}O_{2} \longrightarrow O_{2} + 2H^{+} + 2e^{-}}{O_{3} + H_{2}O_{2} \longrightarrow 2O_{2} + H_{2}O}$ Oxidising Reducing agent

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

(h) Bleaching Action : O₃ also bleaches coloured substances through oxidation.

(I) 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 Hg₂O (mercury sub-oxide) in Hg.

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

(J) 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)

Uses of ozone :

- 1. As a germicide and disinfectant for sterilising water and improving the atmosphere of crowded places.
- 2. For detecting the position of double bond in the unsaturated organic compounds.
- 3. In mfg. of artificial silk, synthetic camphor, $KMnO_4$ etc.
- 4. It is also used for bleaching oil, ivory, flour, starch etc.

-SOLVED EXAMPLE-

Example-8	O ₃ is a powerful oxidising agent. Write equation to represent oxidation of		
	(a) I^- to I_2 in acidic solutions,		
	(b) sulphur to sulphuric acid in the presence of moisture,		
Solution	(a) $O_3 + 2I^- + 2H^+ \longrightarrow O_2 + I_2 + H_2O$; (b) $3O_3 + S + H_2O \longrightarrow H_2SO_4 + 3O_2$.		

HYDROGEN PEROXIDE (H,O,) :

PREPARATION :

(i) Laboratory Method :

 BaO_2 . $8H_2O + H_2SO_4$ (cold) $\longrightarrow BaSO_4 \downarrow$ (white) $+ H_2O_2 + 8H_2O_4$

BaSO₄ is filtered to get aqueous hydrogen peroxide.

• The reaction between anhydrous BaO_2 and H_2SO_4 is slow and practically ceases after sometimes due to the formation of a protective layer of $BaSO_4$ on BaO_2 . So hydrated barium peroxide is used.

$$\mathsf{Ba}(\mathsf{OH})_2 + \mathsf{H}_2\mathsf{O}_2 + \mathsf{6H}_2\mathsf{O} \longrightarrow \mathsf{BaO}_2 \cdot \mathsf{8H}_2\mathsf{O}$$

O 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_3PO_4 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 : $H^+ + e^- \longrightarrow \frac{1}{2}H_2$ $H_2S_2O_8 + H_2O \xrightarrow{80-90^{\circ}C} H_2SO_5 + H_2SO_4$; $H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2$

(iii) Industrial method (Auto oxidation) :



2- Ethyl anthraquinol

2-Ehtylanthraquinone

PHYSICAL PROPERTIES :

- (i) Colourless viscous liquid which appears blue in the larger quantity and is soluble in water (due to H- bonding) in all proportions and form a hydrate H_2O_2 . H_2O (melting point 221 K).
- (ii) Its boiling point 423 K is more than water but freezing point (-4°C) is less than water. Density and dielectric constant are also higher than H₂O
- (iii) Its aqueous solution is more stable than the anhydrous liquid where it decomposes into water and O_2 slowly on exposure to light. $2H_2O_2 \longrightarrow 2H_2O + O_2$
- **Note :** 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 Na₂CO₂ + H₂O₂ \longrightarrow Na₂O₂ + H₂O + CO₂

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

Chemical Properties :

(i) Oxidising Agent :

 $2e^- + 2H^+ + H_2O_2 \longrightarrow 2H_2O$; SRP = + 1.77 v (in acidic medium) $2e^- + H_2O_2 \longrightarrow 2OH^-$; SRP = + 0.87 v (in alkaline medium)

O 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 PbSO₄.

$$H_2O_2 \longrightarrow H_2O + [O] \times 4$$

PbS + 4[O] \longrightarrow PbSO₄
PbS + 4H₂O₂ \longrightarrow PbSO₄ + 4H₂O

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) $\begin{array}{c} H_2O_2 \text{ oxidises } H_2S \text{ to sulphur.} \\ H_2O_2 \longrightarrow H_2O + [O] \\ H_2S + [O] \longrightarrow H_2O + S\downarrow \\ \hline \\ H_2O_2 + H_2S \longrightarrow 2H_2O + S\downarrow \end{array}$
- O Potassium iodide and starch produces deeper blue colour with acidified H_2O_2 . $H_2O_2 + 2H^+ 2I^- \longrightarrow I_3^- + 2H_2O$

(c)
$$NH_2 - NH_2$$
 (hydrazine) + $2H_2O_2 \longrightarrow N_2 + 4H_2O$

(d)
$$H_2^{\text{FeSO}_4} + H_2^{\text{O}_2} \xrightarrow{\text{FeSO}_4} H_2^{\text{OH}} + H_2^{\text{OH}}$$

(B) In alkaline medium :

(a)
$$Cr(OH)_3(s) + 4 NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4(aq.) + 8H_2O_0$$

or

$$10 \text{ OH}^- + 3 \text{ H}_2\text{O}_2 + 2 \text{ Cr}^{3+} \longrightarrow 2 \text{ Cr}\text{O}_4^{2-} + 8\text{H}_2\text{O}$$

(b)
$$2NaBO_2 + 2H_2O_2 + 6H_2O \longrightarrow Na_2[(OH)_2B(O-O)_2B(OH)_2] 6H_2O$$
 (sodium per oxoborate)

O Used as a brightener in washing powder.

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

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

O 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) Ag₂O is reduced to Ag. Ag₂O + H₂O₂ \longrightarrow 2Ag + H₂O₂ + O₂
- (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). $2 K_3 [Fe(CN)_6] + 2KOH \longrightarrow K_4 [Fe(CN)_6] + H_2O + O$ $H_2O_2 + O \longrightarrow H_2O + O_2$

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

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

$$2 \operatorname{Au}^{3+} + 3\operatorname{H}_2\operatorname{O}_2 \longrightarrow 2\operatorname{Au} \downarrow + 6\operatorname{H}^+ + 3\operatorname{O}_2$$

O It also reduces MnO_4^- to Mn^{2+} (acidic medium), MnO_4^- to MnO_2 (basic medium), OCI^- to CI^- , IO_4^- to IO_3^- and CI_2 to CI^-

TESTS FOR H_2O_2 :

- (i) With $K_2Cr_2O_7$: $Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \xrightarrow{\text{amyl alcohol}} 2CrO_5 + 5H_2O_5$
- O CrO_5 bright blue coloured compound soluble in diethyl ether, amyl alcohol and amyl acetate. $4CrO_5 + 6H_2SO_4 \longrightarrow 2Cr_2(SO_4)_3 + 6H_2O + 7O_2$
- (ii) 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) + $4H^+$
- O Orange red coloured in slightly acid solution and yellow colour with very dilute solution.

USES OF H_2O_2 :

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

SOLVED EXAMPLE.

- **Ex.-9** Give the important applications of O_3 .
- Sol. (A) As a germicide and disinfectant for sterilising water and improving the atmosphere of crowded places.
 (B) For detecting the position of double bond in the unsaturated organic compounds.
 - (C) In mfg. of artificial silk, synthetic camphor, KMnO₄ etc. It is also used for bleaching oil, ivory, flour, starch etc.

SULPHUR (S) :

Allotropic Forms Of Sulphur :

Sulphur forms numerous allotropes of which the **yellow rhombic** (α - sulphur) and **monoclinic** (β - 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.

(a) Rhombic sulphur (α - sulphur) :

(i) This allotrope is yellow in colour, melting point 385.8 K and specific gravity 2.06. (ii) Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in CS_2 . It is insoluble in water but dissolved to some extent in benzene, alcohol and ether. It is readily soluble in CS_2 .

(b) Monoclinic sulphur (β - sulphur) :

(i) Its melting point is 393 K and specific gravity 1.98. It is soluble in CS₂.

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

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

(iv) It is stable above 369 K and transforms into α - sulphur below it . Conversely, α - sulphur is stable below 369 K and transforms into β - sulphur above this. At 369 K both the forms are stable. This temperature is called transition temperature.

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



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

(vi) Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesised in the last two decades.

(C) **Plastic Sulphur:** (i) It is formed when molten sulphur (µ) is poured into cold water. It consists of chain like molecule and has rubber like properties when formed. (ii) On standing it becomes brittle and finally converts to rhombic sulphur. Heating effect on sulphur : S_8 (melt) $\frac{at 160^{\circ}C}{\sqrt{160^{\circ}C}}$ 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 $\xrightarrow{At \ 600^{\circ}C}$ in vapour state exist as S_2 molecules (paramagnetic like O_2). Extraction of sulphur : From hydrocarbons contaminated with H₂S or a stream of gas containing H₂S. It involves two steps : (i) $H_2S + O_2 \xrightarrow{Burn} SO_2 + H_2S$ (ii) $H_2S + SO_2 \xrightarrow{catalyst converter} 3S(g + 2H_2O(g))$ **COMPOUNDS OF SULPHUR :** HYDROGEN SULPHIDE (H_S) : **PREPARATION:** $FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$ (i) It is prepared in kipp's apparatus Preparation of pure H₂S gas (ii) Sb_2S_3 (pure) + 6 HCl (pure) \longrightarrow 2 SbCl₃ + 3 H₂S **Physical Properties :** Colourless gas with rotten egg smell . (i) (ii) Moderately soluble in water but solubility decreases with increasing temperature. Chemical Properties :

(i) 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)
$$H_2O_2 + H_2S \longrightarrow H_2O + S + O_2$$

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

 $H_2S + [O] \longrightarrow H_2O + S$
 $2HNO_2 + H_2S \longrightarrow 2H_2O + NO_2 + S$

$$2HNO_3 + H_2S \longrightarrow 2H_2O + NO_2 + H_2S \longrightarrow 2H_2O + NO_2 + H_2S \longrightarrow 2H_2O + NO_2 + H_2S \longrightarrow 2H_2O + O_2 + H_2O + O_2 + O_2 + H_2O + O_2 +$$

(e)
$$H_2S + O_3 \longrightarrow S + H_2O + O_2$$

O It also reduces
$$MnO_4^-$$
 to Mn^{2+} , H_2SO_4 to $SO_2 \& K_2Cr_2O_7$ to Cr^{3+} (acidic medium)

•
$$MnO_4^-$$
 to MnO_2 (alkaline medium)

(ii) Acidic Nature :

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

 $\mathsf{H}_2\mathsf{S} \mathchoice{\longrightarrow}{\rightarrow}{\rightarrow}{\rightarrow} \mathsf{H}\mathsf{S} + \mathsf{H}^{\scriptscriptstyle +} \between{\rightarrow}{\rightarrow} \mathsf{S}^{2\text{-}} + 2\mathsf{H}^{\scriptscriptstyle +}$

Therefore, It forms two series of salts as given below

NaOH +
$$H_2S \longrightarrow$$
 NaHS + H_2O ; NaOH + $H_2S \longrightarrow$ Na₂S + 2 H_2O

(iii) Formation of Polysulphides :

They are obtained by passing H_2S gas through metal hydroxides.

 $\begin{array}{ccc} \mathsf{NH}_4\mathsf{OH} + \mathsf{H}_2\mathsf{S} & \longrightarrow & (\mathsf{NH}_4)_2\mathsf{S} + 2\mathsf{H}_2\mathsf{O}; \\ (\mathsf{NH}_4)_2\mathsf{S} + \mathsf{H}_2\mathsf{S} \text{ (excess)} & \longrightarrow & (\mathsf{NH}_4)_2\mathsf{S}_{\mathsf{x+1}} + \mathsf{xH}_2 \\ & & \text{yellow ammonium sulphide} \end{array}$

TESTS FOR H₂S :

- (i) Turns acidified lead acetate paper black.
- (ii) Gives violet or purple colouration with alkaline sodium nitroprusside solution (containing NaOH).

USES OF H₂S :

- 1. As a laboratory reagent for the detection of basic radicals in qualitative analysis.
- 2. As reducing agent.

SOLVED EXAMPLE_

 $H_2S + (CH_3COO)_2Pb \longrightarrow PbS (black ppt.) + 2CH_3COOH.$ $Fe^{2+} + K_3[Fe(CN)_6]^{3-} \longrightarrow KFe^{II}[Fe^{III}(CN)_6]$ Turnbull's blue.

SULPHUR DIOXIDE : PREPARATION :

(i) $S + O_2$ or air $\xrightarrow{Burn} SO_2$

(ii)
$$CaSO_4 (gypsum) + C \xrightarrow{\Delta} 2 CaO + SO_2 + CO_2$$

O By this method SO₂ is obtained in large scale

PROPERTIES :

- (i) Colourless gas with burning sulphur smell.
- (ii) It is heavier than air and is highly soluble in water. SO_2 in solution is almost completely present as $SO_2.6H_2O$ and only traces of H_2SO_3 .
- (iii) Neither 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 Nature : Acidic oxide and thus dissolve in water forming sulphurous acid.

 $\begin{array}{ccc} \mathrm{SO}_2 + \mathrm{H}_2\mathrm{O} & \longrightarrow & \mathrm{H}_2\mathrm{SO}_3\\ \mathrm{SO}_2 + \mathrm{Na}_2\mathrm{CO}_3 & \longrightarrow & \mathrm{Na}_2\mathrm{SO}_3 + \mathrm{CO}_2\\ & (\mathrm{excess})\\ \mathrm{2SO}_2 + \mathrm{Na}_2\mathrm{CO}_3 + \mathrm{H}_2\mathrm{O} & \longrightarrow & \mathrm{2NaHSO}_3 + \mathrm{CO}_2\\ & (\mathrm{excess}) \end{array}$

(v) Addition Reaction :

$$SO_{2} + CI_{2} \xrightarrow{Sun light} SO_{2}CI_{2} \text{ (sulphuryl chloride)}$$

$$SO_{2} + O_{2} \xrightarrow{\text{platinised}} SO_{3} \text{ ; } PbO_{2} + SO_{2} \longrightarrow PbSO_{4}$$

(vi) Reducing Nature :

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

$$H_2O + SO_2 \longrightarrow H_2SO_3$$
; $H_2SO_3 + H_2O \longrightarrow H_2SO_4 + 2H$

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

(a) Reduces halogens to corresponding halides. $SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$ $2H + Cl_2 \longrightarrow 2HCl$

 $SO_2 + 2H_2O + CI_2 \longrightarrow H_2SO_4 + 2HCI$

Reduces acidified iodates to iodine (b) $\begin{array}{cccc} \text{SO}_2 + 2\text{H}_2\text{O} & \longrightarrow & \text{H}_2\text{SO}_4 + 2\text{H}] \times 5 \\ 2\text{KIO}_3 + \text{H}_2\text{SO}_4 & \longrightarrow & \text{K}_2\text{SO}_4 + 2\text{HIO}_3 \\ 2\text{HIO}_3 + 10\text{H} & \longrightarrow & \text{I}_2 + 6\text{H}_2\text{O} \end{array}$

 $2\text{KIO}_3 + 5\text{SO}_2 + 4\text{H}_2\text{O} \longrightarrow \text{K}_2\text{SO}_4 + 4\text{H}_2\text{SO}_4 + \text{I}_2$

Ο It also reduces acidified $KMnO_4 \longrightarrow Mn^{2+}$ (decolourises),

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

- $2H_2S + SO_2 \xrightarrow{\text{moisture}} 2H_2O + 3S$ (a)
- (b)
- $\begin{array}{l} 2\text{SnCl}_2 + \text{SO}_2 + 4\text{HCl} \longrightarrow 2\text{SnCl}_4 + 2\text{H}_2\text{O} + \text{S} \\ 2\text{Hg}_2\text{Cl}_2 + \text{SO}_2 + 4\text{HCl} \longrightarrow 2\text{HgCl}_2 + 2\text{H}_2\text{O} + \text{S} \end{array}$ (C)
- $\begin{array}{ccc} 2\text{CO} + \text{SO}_2 & \longrightarrow & 2\text{CO}_2 + \text{S} \\ 2 & \text{Fe} + \text{SO}_2 & \longrightarrow & 2\text{FeO} + \text{FeS} \end{array}$ (d)
- (e)

(viii) **Bleaching Action :**

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

This is due to the reducing nature of SO₂

Coloured matter + H ______ colourless matter.

Therefore, bleaching is temporary.

USES OF SO,:

1. Used in manufacture of H₂SO₄ & paper from wood pulp.

2. As a bleaching agent for delicate articles like wool, silk and straw.

3. Used in refining of petroleum and sugar.

SULPHUR TRIOXIDE (SO,) :

PREPARATION:

- (i) $6H_2SO_4 + P_4O_{10} \longrightarrow 6SO_3 + 4H_3PO_4$
- P₄O₁₀ is dehydrating agent О
- $Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3$ (ii)

 $2SO_2 + O_2 \stackrel{\text{pt}}{\longleftrightarrow} 2SO_3$ (iii)

PROPERTIES:

- Acidic Nature : (i) Dissolves in water forming sulphuric acid $SO_3 + H_2O \longrightarrow H_2SO_4$
- (ii)
- $\begin{array}{ll} H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7 \mbox{ (oleum)} \\ SO_3 + HCI \longrightarrow SO_2(OH) \mbox{ Cl (chlorosulphuric acid)} \end{array}$ (iii)
- (iv) **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) $SO_3 + 2HBr \longrightarrow H_2O + Br_2 + SO_2$

Uses of SO₃:

- Used in manufacture of H_2SO_4 and oleum. 1.
- 2. Used as a drying agent for gases.
- 3. Used for the sulphonation of long chain alkyl benzene compounds (like dodeyl benzene). The sodium salt of these alkyl benzene sulphonic acid are anionic surface active agents and are the active ingredient of detergent.

OXYACID 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 , $H_2S_2O_7$, $H_2S_2O_8$. 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.



Fig. Structures of some important oxoacids of sulphur

SULPHURIC ACID (H_2SO_4) :

Manufacture :

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

- (a) Contact process :
 - (i) Burning of sulphur or sulphide ores in air to generate SO₂
 - (ii) Conversion of SO₂ to SO₃ by the reaction with oxygen in the presence of a catalyst (V_2O_5), and
 - (iii) Absorption of SO_2 in H_2SO_4 to give Oleum ($H_2S_2O_7$)
 - (iv) The SO₂ produced is profiled by removing dust and other impurities such as arsenic compounds.
 - (v) 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).
 - $2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g) \Delta_1 H^{\Theta} = -196.6 \text{ kJ mol}^{-1}.$

(vi) The SO₃ 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.

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

$$\begin{array}{ccc} \mathrm{SO}_3 + \ \mathrm{H}_2 \mathrm{SO}_4 \longrightarrow & \mathrm{H}_2 \mathrm{S}_2 \mathrm{O}_7 \\ & & & & & & & \\ \mathrm{(Oleum)} \\ \mathrm{H}_2 \mathrm{S}_2 \mathrm{O}_7 + \mathrm{H}_2 \mathrm{O} \longrightarrow & & & & & \\ \mathrm{2H}_2 \mathrm{SO}_4 \end{array}$$

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

Physical Properties :

(i) Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K.

(ii) The acid freezes at 283 K and boils at 611 K. It dissolves in water with the evolution of a larger quantity of heat.

(iii) The chemical reaction of sulphuric acid are as a result of the following characteristics :

(a) low volatility (b) strong acidic character (c) strong affinity for water and (d) ability to act as an oxidising agent in aqueous solution.

Chemical Properties :

(i) Sulphuric acid ionises in two steps.

 $H_2SO_4(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + HSO_4^-(aq)$; Ka₁ = very larger (K_{a1} > 10)

 $H_2SO_4^{-}(aq) + H_2O(\ell) \rightarrow H_3O^{+}(aq) + SO_4^{-2-}(aq)$; Ka₂ = 1.2 × 10⁻²

The larger value of K_{a1} ($K_{a1} > 10$) means that H_2SO_4 is largely dissociated into H⁺ and HSO₄⁻. 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 .
 - $Na_{2}CO_{3} + H_{2}SO_{4} \longrightarrow Na_{2}SO_{4} + H_{2}O + CO_{2}; NaHCO_{3} + H_{2}SO_{4} \longrightarrow NaHSO_{4} + H_{2}O + CO_{2}$
- (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)

$$O \qquad KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$$

(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 SO₂.

$$Cu + 2H_2SO_4 (concentrated) \longrightarrow CuSO_4 + 2H_2O$$

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

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

$$H_2SO_4 + KBr \longrightarrow KHSO_4 + HBr$$

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

(iv) With PCl₅ forms mono and di-acid chlorides.

 $\begin{array}{l} \mathsf{HO}-\mathsf{SO}_2-\mathsf{OH}+\mathsf{PCI}_5 \longrightarrow \mathsf{CI}-\mathsf{SO}_2-\mathsf{OH}+\mathsf{POCI}_3+\mathsf{HCI} \\ \mathsf{HO}-\mathsf{SO}_2-\mathsf{OH}+\mathsf{2PCI}_5 \longrightarrow \mathsf{CI}-\mathsf{SO}_2-\mathsf{CI}+\mathsf{2POCI}_3+\mathsf{2HCI} \end{array}$

(v) $K_4 [Fe (CN)_6] (s) + 6H_2SO_4 + 6H_2O \xrightarrow{\Delta} 2K_2SO_4 + FeSO_4 + 3(NH_4)SO_4 + 6CO$

Uses of H₂SO₄:

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

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

SOLVED EXAMPLE

Ex.-11 SO_2 and CI_2 both are used as bleaching agent. What factors cause bleaching ?

Sol.
$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H_2$$

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

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

SODIUM THIOSULPHATE (Na,S,O,.5H,O) :

PREPARATION:

- (i) $Na_2SO_3 + S \xrightarrow{\text{boiled}} Na_2S_2O_3$
- (ii) $6NaOH + 4s \xrightarrow{\Delta} Na_2S_2O_3 + 2Na_2S + H_2O$

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. $Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 8HCl$ 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 :

Reactants	Main Products	Special Points
Reaction with silver salts	$Ag_{2}S_{2}O_{3} \downarrow$ (white)	This hydrolytic decomposition can be accelerated by
(AgNO ₃ , AgCl, AgBr or Agl)	-2 2 5	warming.
_		If hypo is in excess, then soluble complex is formed.
		$2S_2O_3^{2-} + Ag^+ \rightarrow [Ag(S_2O_3)_2]^{3-}$ (soluble complex) or
		[Ag(S ₂ O ₃) ₃] ⁵⁻
		This reaction is utilized in photography where hypo is used
		as fixer.
Reaction with FeCl ₃	$[Fe(S_2O_3)_2]$ (Pink or violet)	
Reaction with AuCl ₃	$Na_3 [Au(S_2O_3)_2]$	
	(soluble complex)	
Reaction with CuCl ₂	$Na_{4} [Cu_{6}(S_{2}O_{3})_{5}]$	
	(soluble complex)	

(v) As reducing agent :

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

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

(vi) Heating effects :
$$4Na_2S_2O_3.5H_2O \xrightarrow{215^{\circ}C} 4Na_2S_2O_3 \xrightarrow{220^{\circ}C} 3Na_2SO_4 + Na_2S_5$$

(vii) Reaction with soluble salt of lead :

 $\begin{array}{l} S_2O_3^{\ 2^-} + Pb^{2+} \longrightarrow PbS_2O_3 \downarrow \text{ (white)} \\ PbS_2O_3 \downarrow + H_2O \longrightarrow PbS \downarrow \text{ (black)} + 2H^+ + SO_{4^-}^{\ 2^-} \end{array}$

O Ba²⁺ gives white precipitate of BaS₂O₃ but calcium thiosulphate is soluble.

USES OF HYPO :

- 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.

-Solved Example-

Ex.-12 Colourless salt (A) decolourises I₂ solution and gives white precipitate (changing to black) with AgNO₃ solution. (A) also produces pink colour with FeCl₃ solution. Identify (A) and explain reactions.

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

Exercise #1

> Marked Questions may have for Revision Questions.

PART - I : SUBJECTIVE QUESTIONS

NITROGEN FAMILY

Section (A) : General facts, Physical and chemical properties, periodic trends, chemical bonding

- **A-1.** N_2 , CO, CN⁻ and NO⁺ are isoelectronic but the former is chemically inert and latter three are very reactive, why?
- A-2. Chemiluminescence is a phenomenon in which on element glows in dark when exposed to moisture. Which element of 15th group shows this phenomenon ?
- A-3._ Both PH, and NH, are Lewis bases, but basic strength of PH, is less than that of NH,. Explain

A-4._> Write the oxyacids of the following :

Oxide	Oxyacids
N ₂ O ₃	
NO ₂ /N ₂ O	
N ₂ O ₅	
P ₄ O ₆	
P ₄ O ₁₀	

A-5._ Nitrogen forms a simple diatomic molecule but other elements of same group do not form. Explain.

- A-6._ White phosphorus is very reactive, but not the red one. Why?
- **A-7.** The important source of phosphorus is phosphorite rocks which is mainly phosphates. The same chemical compound is also present in bones. What is the formula of the compound(s).
- A-8. Why is Bi (V) a stronger oxidant than Sb (V)?
- A-9. A. Nitrogen shows different oxidation states in the range _____ to ____. It most stable oxidation state is _____
- A-10. The tendency to exhibit-3 oxidation state by a group VA element decreases down the group. Why?
- A-11. Write the following for a white phosphorus molecule :
 - (a) oxidation state of P (b) valency of P (d) bond order. (e) bond angle
- (c) total number of bonds (f) geometry

- A-12. Why does NO₂ dimerise ?
- A-13. A Write the structures of the oxides : N_2O_3 , N_2O_5 , P_4O_6 and P_4O_{10} .
- A-14. Pentahalides of phosphorus are known, but not pentahydride. Why?

Section (B) : Compounds of Nitrogen family Elements

- B-1._ Ammonium salts generally resemble those of potassium and rubidium in solubility & structure. Give reason
- **B-2.** A Write balanced equation when NH_3 is dissolved in (a) water (b) HCl (c) aq. CO_2
- B-3._ What happens when phosphine is absorbed in mercuric chloride solution?

- **B-4.** On being slowly passed through water, PH₃ forms bubbles but NH₃ dissolves. Why is it so?
- **B-5._** ▶ How is hydrazine prepared ?
- **B-6.** In the preparation of P_4O_6 , a mixture of N_2 and O_2 is used rather than pure O_2 , Why?
- **B-7.** A compound of 15th group element is used as a fast drying agent in the laboratory. It is :
- **B-8.** A compound 'X' which is a yellowish white powder is prepared by the reactions of white phosphours with excess of dry Cl_2 . Identify 'X':
- **B-9.** What happens when (A) PCl₂ is heated.

(B) PCI₅ is reacted with heavy water.

- **B-10.** Why does PCI_3 fume in moist air ?
- **B-11.** Complete and balance the following : (i) $P_4O_{10} + PCI_5 \longrightarrow$ (ii) I

(ii) $NH_3 + NaOCI \longrightarrow$

OXYGEN FAMILY

Section (C) : General facts, Physical and chemical properties, periodic trends, chemical bonding

- C-1. Which allotropic form of sulphur is thermodynamically stable at room temperature and pressure ?
- C-2. Why sulphur in vapour state exhibits paramagnetic behaviour at above 800°C.
- C-3._ Write the structure and oxidation numbers of sulphur in tetrathionate ion.
- C-4. Con moving down the group from H₂O to H₂Te acidic strength increases, why?
- C-5._ Which stable elements of 15th and 16th group do not react with water under normal conditions?
- **C-6._** Sulphur flower on reaction with sulphide ion gets reduce to poly sulphide ion. Write the reaction and upto how many sulphurs atoms the poly sulphide ions are formed significantly.
- C-7._ Tellurium forms oxides of the formula TeO, TeO₂ and TeO₃. What is the nature of these tellurium oxides?
- C-8. Among the hydrides of group 16, water shows unusual boiling point. Why?
- C-9. A Which hydride of the oxygen family shows the lowest boiling point?
- **C-10.** A and B are elements with atomic numbers 16 and 17. Write different combinations of binary compounds known from them.

Section (D) : Compounds of Oxygen family Elements

- **D-1._** How are SO_2CI_2 .SO₃ and SO_2 obtained from sulphuric acid ?
- D-2. Sulphur on oxidation with hot sulphuric acid gives :
- **D-3.** NaHSO₃ + [X] (excess) + H₂O \longrightarrow NaHSO₄ + HI [X] + Na₂S₂O₃ \longrightarrow Nal + [Y] Identify X & Y ?
- D-4._> In the manufacture of sulphuric acid by the contact process, sulphur trioxide is not directly dissolved in water. Why?
- **D-5._** Identify the product of the given reaction :

 $\begin{array}{l} \operatorname{AgBr} + 2\operatorname{Na}_2\operatorname{S}_2\operatorname{O}_3 \longrightarrow \\ \operatorname{H}_2\operatorname{SO}_4(\operatorname{dil}) + \operatorname{Na}_2\operatorname{S}_2\operatorname{O}_3 \longrightarrow \\ \operatorname{H}_2\operatorname{SO}_4(\operatorname{conc.}) + \operatorname{Na}_2\operatorname{S}_2\operatorname{O}_3 \longrightarrow \end{array}$

PART - II : ONLY ONE OPTION CORRECT TYPE

NITROGEN FAMILY

Section (A) : General facts, Physical and chemical properties, periodic trends, chemical bonding

A-1. ➤ Which of the following is least reactive ? (A) White phosphorus (B) Yellow phosphorus (C) Red phosphorus (D) Black phosphorus A-2. A Nitrogen is best obtained by the thermal decomposition of which one of the following : (A) NH₄CI $(B) NH_4NO_3$ (C) AgNO₃ $(D) NH_1NO_2$ In modern process, white phosphorus is manufactured by : A-3. (A) heating a mixture of phosphorite mineral with sand and coke in an electric furnace (B) heating calcium phosphate with lime (C) heating bone ash with coke (D) heating phosphate mineral with sand. A-4. The nitrogen atom may complete its octet in several ways. Which one is incorrect? (A) Electron gain to form the nitride lon, N³⁻ e.g. Li₂N. (B) Formation of electron pair bonds. e.g. NH₃ or NF₃ Azo compounds (–N=N–) (C) Formation of electron - pair bonds with electron gain. e.g. Amide ion NH,- and imide ion NH²⁻. (D) Formation of electron pair bonds with electron gain : NH_4^+ ; $N_2H_5^+$; $(C_2H_5)_4N^+$, NH_3 , NH_2^- , NH^{2-} and N^{3-} are : A-5. NH_{4}^{+} Ammonium Ammonia Amide Imide Nitride (A) Isoelectronic (B) Isostructural (C) Homologous members (D) Nitrogen has different oxidation state A-6. A The hydrides of group 15 elements can act as : (A) lewis acid (B) lewis base (C) both (D) none A-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, and then increases (D) first increases upto AsH, and then decreases A-8. A Red and white phosphorus will differ but not in : (A) smell (B) solubility in CHCl₃ (C) exhibiting phosphorescence (D) reaction with concentrated HNO₃ A-9. A Which of the following oxides of Nitrogen is Neutral $(C) N_2 O_4$ $(A) N_2 O_5$ $(B) N_2 O_3$ (D) N₂O A-10. A Which of the following oxides is amphoteric in nature ? (C) Sb₄O₆ $(A) N_2 O_3$ $(B) P_4 O_6$ $(D) Bi_2O_3$ Which of the following oxides is the most acidic ? A-11. $(C) As_2O_5$ (D) Sb₂O₅ $(B) P_{2}O_{5}$ $(A) N_2 O_5$ A-12. >> 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) $AsH_3 < PH_3 > SbH_3 > BiH_3 > NH_3$ **A-13.** How many P=O bonds are present in (HPO₂)₂? (A) 0 (B)6 (D)9 (C) 3

			F			
A-14. 🖎	The wrong statement at (A) it is nitrous oxide (C) it is not a linear mole	oout N ₂ O is : ecule	(B) it is a neutral oxide (D) it is known as laughi	ing gas		
A-15	Which of the following is (A) Ammonia is prepare (B) All the hydrides of 15 (C) Metal phosphides up (D) Metal phosphides up	Which of the following is incorrect ? (A) Ammonia is prepared in the laboratory by the action of NaOH on Ammonium salt. (B) All the hydrides of 15 th group are colourless, highly volatile and poisonous gases (C) Metal phosphides upon hydrolysis give phosphine. (D) Metal phosphides upon hydrolysis give phosphoric acid.				
Sectio	on (B) : Compounds	s of Nitrogen family	/ Elements			
B-1	P_4 + NaOH $\xrightarrow{\text{warm}}$ Products will be : (A) H_3PO_4 + PH_3	Products (B) PH ₃ + NaH ₂ PO ₂	(C) NaH ₂ PO ₂ + H ₃ PO ₄	(D) H ₃ PO ₄		
B-2≿	Hydrolysis of Nitride of s (A) NH_3 + Metal hydroxid (C) NH_3 + HNO_3	s-Block elements (for e.g de	. Ba_3N_2 , Ca_3N_2 , Li_3N) will (B) only NH_3 (D) NH_4OH	yield		
B-3. Þa	NO_2 can be prepared by (A) NH_4NO_3	heating : (B) NaNO ₃	(C) $Pb(NO_3)_2$	(D) KNO ₃		
B-4. æ	$HNO_3 + P_4O_{10} \longrightarrow HI$ in the above reaction the (A) NO_2	PO ₃ + X e product X is : (B) N ₂ O ₃	(C) N ₂ O ₄	(D) N ₂ O ₅		
B-5	Industrial preparation of (A) oxidation of NH_3 (C) Hydrogenation of NH	nitric acid by ostwald's p I_3	rocess involves : (B) Reduction of NH_3 (D) Hydrolysis of NH_3			
B-6.	One mole of calcium ph (A) one mole of phosphin (C) two moles of phosph	osphide on reaction with ne ine	excess water gives : (B) two moles of phosph (D) one mole of phospho	noric acid prus pentoxide		
B-7. æ	PH_3 (anhydrous) + HBr (A) H_3BrO_3	(anhydrous) $\longrightarrow X.$ (B) PH ₄ Br	Identify X ? (C) Br ₂	(D) P ₄		
B-8.	Calcium phosphide read produces dense white fu (A) $X = PH_3$ and $Y = PH_4$ (C) $X = PH_4^+$ and $Y = PH_4^+$	cts with water or dil. HCl a nes with HI (g) due to fo ا	and gives a compound 'X' rmation of 'Y'. Compound (B) X = NaH ₂ PO ₂ and Y (D) X = PH ₃ and Y = H ₃ F	which fails to react with HCl but X and Y respectively. = H_3PO_2		
B-9.≿	$N_2 \xrightarrow{H_2} H_2 \longrightarrow \Sigma$	$X \xrightarrow{O_2} Y$ Ostwald's Process	$(\xrightarrow{O_2+H_2O} Z)$			
	Identify X, Y, Z (A) NH ₃ , NO ₂ , HNO ₃	$(B)NH_3,NO,HNO_3$	(C) NO ₂ , NH ₃ , HNO ₂	(D) NH ₃ , NO, HNO ₂		
B-10. ≿	Ammonia reacts with ex (A) N_2 and NH_4CI	ccess of chlorine to form : (B) NCl ₃ and HCl	: (C) NH_4CI and NCI_3	(D) N_2 and HCl		
B-11.æ	PCI_{3} reacts with water to (A) PH_{3}	o form : (B) H ₃ PO ₃ and HCI	(C) POCl ₃	(D) H ₃ PO ₄		

B-12. ≽	The final product obtair	ned on hydrolysis of PCl ₅ (B) H ₂ PO ₂	is : (C) POCI	(D) PH ₂
B-13.≽	Which of the following μ (A) PCl ₃	bhosphorus halide is the t (B) PF_3	pest reducing agent? (C) PBr ₃	(D) PI ₃
B-14	Ammonium salts decor	npose quite readily on he	eating:	
	(i) Ammonium salt of we	eak oxidizing anion (e.g.	CI ⁻ , CO ₃ ²⁻ , SO ₄ ²⁻) <u>heat</u>	\rightarrow Gas X
	(ii) Ammonium salt of si Identify X, Y, Z	trong oxidizing anion (e.g	J. NO ₂ ⁻ , NO ₃ ⁻ , CIO ₄ ⁻ , Cr ₂ C	P_7^{2-}) <u>heat</u> Gas Y/Z
	(A) N ₂ , NH ₃ , N ₂ O	(B) NH ₃ , N ₂ , N ₂ O	(C) N_2O , NH_3 , N_2	(D) NO, NH ₃ , N ₂ O
		OXYGE	N FAMILY	
Section	on (C) : General fac bonding	ts, Physical and ch	emical properties,	periodic trends, chemical
C-1≽	Which of the following b (A) Se–Se	oonds has the highest bo (B) Te–Te	nd energy ? (C) S–S	(D) O–O
C-2.	The oxidation state of sulphur in the anions SO_3^{2-} , $S_2O_4^{2-}$ and $S_2O_6^{2-}$ follows the order : (A) $S_2O_6^{2-} < SO_4^{2-} < SO_3^{2-}$ (B) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$ (C) $SO_3^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$ (D) $S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$			
C-3. ൚	 Correct statement about allotropy of sulphur is : (A) Monoclinic sulphur is more stable than Rhombic sulphur at room temperature. (B) Both Monoclinic and Rhombic sulphur have same ring structures and crystalline structure. (C) Rhombic sulphur exists at room temperature. (D) None of these 			
C-4๖	Which of the following $(A) (NH_4)_2 Cr_2 O_7$	does not give oxygen on h (B) KCIO ₃	neating? (C)Zn(ClO ₃) ₂	(D) K ₂ Cr ₂ O ₇
C-5≽	Sulphur and white Phose (A) Conc. H_2SO_4	sphorus react with all exc (B) Dil. H_2SO_4	ept : (C) Conc. HNO ₃	(D) Conc.NaOH

C-7. \geq Following are neutral oxides except :
(A) NO(B) N₂O(C) CO(D) NO₂

C-8._ A The order of stability of halides of sulphur with different halogens is : (A) I⁻ > Br⁻ > CI⁻ > F⁻ (B) F⁻ > CI⁻ > Br⁻ > I⁻ (C) Br⁻ > CI⁻ > F⁻ (D) F⁻ > CI⁻ > Br⁻

C-9. A yellow coloured crystalline substance gave a colourless gas X on reaction with flourine, which is thermally stable and has octahedral geometry. X can be. (A) SF_4 (B) SF_6 (C) SF_2 (D) S_2F_6

Section (D) : Compounds of Oxygen family Elements

D-1._ The correct order of sulphur – oxygen bond length in $S_2O_3^{2-}$, SO_4^{2-} , SO_3 and $S_2O_6^{2-}$ is (A) $S_2O_3^{2-} < SO_4^{2-} < SO_3 < S_2O_6^{2-}$ (B) $S_2O_3^{2-} < S_2O_6^{2-} < SO_3$ (C) $S_2O_3^{2-} < SO_4^{2-} < SO_2^{0-} < SO_3$ (D) $S_2O_6^{2-} < SO_4^{2-} < SO_3 < S_2O_3^{2-}$

	PART - III : MATCH THE COLUMN				
	(A) KOH	(B) O ₂	(C) I ₂	(D) KOD	
- · <u>-</u>	$O_3 + KI + D_2O \longrightarrow$				
D-12.	Which of the following is	s not formed in the below	reaction :		
D-11.	Which of the following g (A) $H_2S_2O_3$	ives H_2O_2 on hydrolysis ? (B) H_2SO_5	$(C) H_2 S_2 O_7$	(D) H ₂ S ₄ O ₆	
D-10.	The term 'thio' is used in (A) $Na_2S_2O_3$	the names of all of the fo (B) Na ₂ S ₂ O ₆	llowing compounds exce (C) NaSCN	pt : (D) Na ₂ SO ₃	
D-9.	The products of the cher (A) HCl + Na_2S	mical reaction between N (B) HCl + NaHSO ₄	$a_2S_2O_3$, Cl ₂ and H ₂ O are : (C) HCl + Na ₂ SO ₃	(D) NaHCIO ₃ + H ₂ O	
D-8.	When sulphur is boiled ((A) sodium sulphide	with Na ₂ SO ₃ solution, the (B) sodium sulphate	compound formed is : (C) sodium persulphate	(D) sodium thiosulphate	
D-7.	Which of the following re (A) $2PCl_5 + H_2SO_4 \longrightarrow$ (C) NaCl + $H_2SO_4 \longrightarrow$	eactions depict the oxidisi $2POCl_3+2HCl+SO_2Cl_2$ $\rightarrow NaHSO_4 + HCl$	ng behaviour of H_2SO_4 ? (B) 2NaOH + H_2SO_4 — (D) 2HI + H_2SO_4 —	$ \longrightarrow \operatorname{Na}_2\operatorname{SO}_4 + 2\operatorname{H}_2\operatorname{O}_2 + \operatorname{SO}_2 + 2\operatorname{H}_2\operatorname{O}_2 $	
D-6.	H_2S burns in O_2 to form (A) $H_2O + S$	(B) H ₂ O + SO ₂	(C) $H_2O + SO_3$	(D) H ₂ SO ₄ + S	
D-5≽	Aqueous solution of SO ₂ (A) weak acid	is a : (B) reducing agent	(C) bleaching agent	(D) All of these	
D-4.	When P_4O_{10} is dissolved (A) H_3PO_2	t in water, the acid formed (B) H_3PO_4	t finally is : (C) H ₃ PO ₃	(D) H ₄ P ₂ O ₇	
D-3ാ	Which of the following is $(A) H_2SO_4$	the most powerful oxidis (B) HPO ₃	ing agent : (C) H ₃ BO ₃	(D) H ₃ PO ₄	
	(C) CaSO ₄ + C $\xrightarrow{\Delta}$		(D) $\operatorname{Fe}_2(\operatorname{SO}_4)_3 \xrightarrow{\Lambda}$		
	$(A) S + H_2 SO_4 \xrightarrow{\Lambda}$		$(B) H_2 SO_4 + PCI_5 \xrightarrow{\Delta}$		
D-2	Sulphur trioxide can be obtained by which of the following reactions :				

Match the reactions listed in column-I with characteristic(s) / type of reactions listed in column-II. 1. 🔈

	Column – I	Column – II
	(A) $PCI_5 \xrightarrow{Moist}_{Air}$	(p) Hydrolysis
	(B) P_4 + NaOH (conc.) + $H_2O \xrightarrow{Warm}$	(q) At least one of the products has tetrahedral hybridisation
	(C) $H_3PO_3 \xrightarrow{200^{\circ}C} \rightarrow$	(r) Disproportionation
	$(D) P_4O_6 + H_2O \xrightarrow{200^\circC} \rightarrow$	(s) At least one of the products has $p\pi$ –d π bonding.
2. 🙇	Match the oxy-acids of phosphorus listed in colu	nn-I with type of bond(s) listed in column-II.
	Column I	Column II
	(Oxy acids of phosphoros)	(Characteristic bonds)
	$(A) H_{A}P_{Q}O_{Z}$	(p) P—P bond (s)
	$(B)H_{A}P_{2}O_{5}$	(q) P—O—P bond (s)
	(C) $H_{3}P_{3}O_{3}$	(r) P—H bond (s)
	(D) $H_{\tilde{s}}P_{3}O_{10}$	(s) Three or four P—OH bonds

Exercise #2

> Marked Questions may have for Revision Questions.

PART - I : ONLY ONE OPTION CORRECT TYPE

1. 🕿	In case of nitrogen, NC possible. It is due to (A) Availability of vacan (B) Lower electronegativ (C) Lower tendency of H (D) Occurrence of P in s	l₃ is possible but not NCl t d-orbital in P but not in N vity of P than N I bond formation in P thar solid while N in gaseous s	s while in case of phospl N τate at room temperature	horous, PCI_3 as well as PCI_5 are	
2. 🙇	The P-P-P bond angle i (A) 120°	n white phosphorus is clo (B) 109°28'	se to : (C) 90°	(D) 60°	
3. 🕿	Red phosphorus can be prepared from white phosphorus by : (A) adding red colour to white phosphorus (B) heating white phosphorus to red heat (C) heating white phosphorus at high pressure, inert atmosphere to 250°C or at low temperature in presence of sun light. (D) heating white phosphorus at low pressure to 250°C or at low temperature in the presence of sun light.				
4. 🕿	As Rhombic sulphur is Process (a) Viscosity increa (b) Viscosity decrea (c) Paramagnetic r (d) Breakage of S_8 (Diradical formation Correct order of temper (A) $T_1 < T_3 < T_4 < T_2$	heated in a test tube : ases eases nolecules rings ation in molten phase) ature is : (B) $T_2 < T_4 < T_3 < T_1$	Temperature T_1 T_2 T_3 T_4 (C) $T_4 < T_1 < T_2 < T_3$	(D) T ₃ < T ₄ < T ₁ < T ₂	
5.	Dinitrogen gas is evolve (A) alone (C) with ammonium hyd	ed when sodium nitrite is h roxide	neated below 500°C : (B) with ammonium chlo (D) with potassium nitrat	ride te	
6.	Which statement is no (A) It is obtained by he (C) It is a typical non-r	t correct for nitrogen ? ating (NH ₄) ₂ Cr ₂ O ₇ netal	(B) It does not readily r (D) d-orbitals are availa	react with O_2 able for bonding	
7.2a	Nitrolim is obtained by p (A) heated mixture of Al (C) calcium carbide	bassing nitrogen over : ${}_{2}O_{3}$ and carbon	(B) oleum (D) heated calcium carb	ide	
8.2	Which of the following h (A) Ozone	nave ∆H⁰ < 0 at 298 K : (B) O (g)	(C) P (red)	(D) S_8 (monoclinic)	
9. 🙇	CS_2 can separate a mix (A) P_4 (white) and S_8 (rho (C) S_8 (rhombic) and S_8	ture of : ombic) (monoclinic)	(B) P_4 (white)and S_8 (mo (D) S_8 (rhombic) and S (p	onoclinic) olastic)	
10.১	Which of the following r (A) $O_3 + KI + H_2O \longrightarrow$ (C) $KO_2(s) + CO_2(g) \longrightarrow$	eactions does not liberate \rightarrow	e oxygen ? (B) $H_2O_2 + CI_2 \longrightarrow$ (D) None of these		

11.24	The gas respectively at (A) O_2, O_3	sorbed by alkaline pyrog (B) SO_2 , O_2	allol and turpentine oil is (C) O_{3} , CH_{4}	: (D) N ₂ O, O ₃	
12.১	Alkaline KI is oxidised I (A) potassium iodate	by ozone to : (B) potassium periodate	e (C) both (A) and (B)	(D) I ₂	
13.๖	NH_3 can't be obtained b (A) heating of NH_4NO_3 o (C) heating of NH_4NO_3 v	y : r NH₄NO₂ ⁄ith NaOH	(B) heating of NH ₄ Cl or ((D) reaction of AIN or M	$(NH_4)_2 CO_3$ g ₃ N ₂ or CaCN ₂ with H ₂ O	
14.	When H_2S is passed the (A) H_2SO_4	ough nitric acid or acidifi (B) colloidal sulphur	ed KMnO ₄ solution, the p (C) SO ₂	roduct first formed is : (D) plastic sulphur	
15.	Ammonia and red hot C (A) Cu_2O , N_2 , H_2	CuO react to produce : (B) Cu, H ₂ O, N ₂	(C) Cu(OH) ₂ , N ₂	(D) [Cu(NH ₃) ₄](OH) ₂	
16.2s	Phosphine is not obtain (A) White P is heated w (C) Ca_3P_2 reacts with wa	ed by the reaction : ith NaOH ater	(B) Red P is heated with (D) Phosphorus trioxide i	n NaOH is boiled with water under pressure.	
17.১	When ammonia is oxid (A) N_2O	sed by oxygen in the pres (B) NO	sence of platinum at 500° (C) NO ₂	PC, the gas obtained is : (D) N ₂ O ₅	
18.	Substances burn more readily in N_2O than in air because N_2O : (A) is reactive at high temperature. (B) dissociates to give more oxygen than in air. (C) the activation energy is increased on increasing temperature. (D) dissociates more readily than O_2 .				
19.১	Which of the following (A) NO	is a mixed acid anhydri (B) NO ₂	de ? (C) N ₂ O ₅	(D) N ₂ O	
20.	When an article is blead (A) exposure to air	ched by SO ₂ it loses its co (B) heating	olour. The colour can be (C) dilution	restored by : (D) none of these	
21.æ	The true statement for the acids of phosphorus H_3PO_2 , H_3PO_3 and H_3PO_4 is. (A) H_3PO_3 on heating does not disproportionate (B) all of them are reducing in nature (C) all of them are tribasic acids (D) H_3PO_2 is obtained by alkaline hydrolysis of P_4 (white				
22.১	Which of the following c (A) $S_2O_8^{2-}$	loes not have S–S linkage (B) $S_2O_6^{2-}$	e but has O—O linkage ? (C) $S_2O_5^{2-}$	(D) S ₂ O ₃ ²⁻	
23.≿	Hydrolysis of one mole of peroxydisulphuric acid produces (A) two moles of sulphuric acid (B) two moles of peroxymonosulphuric acid. (C) one mole of sulphuric acid and one mole of peroxy monosulphuric acid. (D) one mole of sulphuric acid, one mole of hydrogen peroxide.				
24.24	The reaction of SO ₂ with PCl ₅ yield two oxohalides A and B. 'A' can also be prepared industrially by reaction of SO ₃ and SCl ₂ . Which of the following about A and B is incorrect? (A) The structure of B is tetrahedral (B) The structure of A is trigonal pyramidal (C) A reacts vigorously with water and is particularly useful for drying or dehydrating readily hydrolysable inorganic halides (D) A and B contain their respective central atoms in their highest oxidation states.				
25.১	Which of the following c (A) PF ₅	annot dissociate as PX_5 : (B) PCI_5	$ PX_3 + X_2$ (C) PBr ₅	(D) Pl ₅	

26.	Consider the following compou (1) sulphur dioxide (2) hydr Among these compounds, those	nds : drogen peroxide se which can act a	(3) ozone is bleaching agei	nts would inc	lude :
	(A) 1 and 3 (B) 2 a	and 3	(C) 1 and 2	(D)	1, 2 and 3
27.≿	Bleaching of a fabric cloth is do (A) $CaOCl_2$, Na_2SO_3 (B) Na_3	one using A and early $A_2S_2O_3$, CaOCl ₂	ccess of chlorine (C) CaCl ₂ , Na ₂ S	is removed S_2O_3 (D)	using B. A and B are : $CaOCl_2$, $Na_2S_2O_3$
28.	Aqueous hypo solution on reac (A) yellow precipitate changing (C) orange precipitate to blue	tion with aqueous to black	AgNO ₃ gives : (B) white precip (D) no precipita	oitate changir te	ng to black
	PART - II	: NUMERIC	AL TYPE C	UESTIO	NS
1. 🕿	How many of the following is co (a) N > P > As > Sb > Bi (b) N > P > As > Sb (c) N-N < P-P < As-As (d) As ³⁺ > Sb ³⁺ > Bi ³⁺ (e) White > Red > Black (f) H ₃ PO ₂ < H ₃ PO ₃ < H ₃ PO ₄ (g) H ₃ PO ₂ < H ₃ PO ₃ < H ₃ PO ₄	orrect order of spe (First id (Electro (Single (Stabili (React (Protic (Reduc	cified property. onisation enthalp onegativity) bond length) ty of +3 oxidation ivity of allotropes ity of acids) sing power of acid	y) n state) of phosphoru ls)	IS)
2.	How many of the following prop (a) Atomic size (d) Reducing power of hydrides (g) Basic character of hydrides	erties increase do (b) Acidic chara (e) Extent of pπ	wn the group for acter of oxides -pπ overlap.	nitrogen fam (c) (f) l	ily. Boiling point of hydrides Metallic character.
3.24	Given below are some properties. How many of these can hold good for phosphorous.(a) Metal(b) Non-metal(c) Metalloid(d) Exhibits allotropy(e) Catenation property(f) Solid(g) Good conductor of electricity(h) Least dense among nitrogen family elements.				horous. Exhibits allotropy icity
4.22	Below reaction sequence illustrates the various stages of reduction of nitric acid where a, b, c, d are t number of electrons involved in the reduction of 1 mole N-atoms.			acid where a, b, c, d are the	
	$HNO_{3} \xrightarrow[ae^{-}]{ae^{-}} NO_{2} \xrightarrow[be^{-}]{be^{-}}$ Find the value of (2a + b + 3c -	$NO \xrightarrow[ce^-]{ce^-} N_2O$ - d).	$\xrightarrow[de^-]{}$ NH ₃		
5.	A yellow coloured crystalline e undergoes hydrolysis & has oc	lement gives a co ahedral geometry	blourless gas (X) 7. The atomicity o	on reaction f compound	with fluorine which does not (X) would be
6.	Ozone reacts with dry iodine to	form an oxide ha	ving oxygen a	atoms in one	of its molecules.
7.১	Sulphur can form dihalide, tetrahalide and hexahalide with fluorine. One mole of each of these three compounds is mixed with water. The total number of moles of product molecules obtained is If no reaction occurs, count zero.				
8.24	Number of halides undergoing (i) BF ₃ (ii) BCl ₃	complete reactior (iii) NCl ₃	in presence of w (iv)AICI ₃	ater under no (v)CCl ₄	ormal conditions is : (vi) PCl ₃ (vii) AsCl ₃
9.2	In how many of the following re	actions N ₂ gas ma	ay be released		
	(a) $NH_4NO_2 \xrightarrow{\Delta}$ (d) $NH_2CONH_2 + NaOBr \longrightarrow$	(b)(NH ₄) ₂ Cr ₂ O ₇ (e) NH ₃ + Cl ₂ (L	$\xrightarrow{\Delta} R) \longrightarrow$	(c) NH_2CON (f) $NH_3 + Br$	$NH_2 + HNO_2 \xrightarrow{\Delta} HO_2 (LR) \longrightarrow HO_2 $
	(g) NH_3 + NaOCI \longrightarrow	(h) NH ₃ + CaO($Cl_2 \longrightarrow$	(i) Ba(N ₃) ₂ _	$\xrightarrow{\Delta}$

10.2	NH_3 , N_2H_4 , HN_3 , PH_3 , H_2S , AsH_3 , SbH_3 , H_2Se , H_2Te Number of molecules in which lone pair of electrons on the central atom is present in pure s-orbital.					
11.	NH ₃ + NaOCI products					
	The number of n	noles of N—H bond	ls present in one m	nole of the stronges	st nucleophile pre	sent in the product is :
12.১	Number of acid (a) N_2O (g) P_4O_{10}	lic oxides among (b) NO (h) SO ₃	the following is : (c) N_2O_3 (i) B_2O_3	(d) N ₂ O ₄ (j) CO	(e) N_2O_5	(f) P ₄ O ₆
13.	Number of gase (a) N_2O (g) P_4O_{10}	eous oxides amc (b) NO (h) SO ₂	ong the following $(c) N_2O_3$ (i) SO ₃	at room tempera (d) NO ₂	ture is : (e) N ₂ O ₅	(f) P ₄ O ₆
14.১	The number of	O-atoms having	sp ² hybridisation	in P_4O_{10} molecul	e is :	
15.	N_2O_4 , (HPO_3) ₃ , (a) Among the a (b) Among the a Give the answe	H_2CO_3 , SO_2 , SC_3 above compound above compound er as x + y.	D_3 , $P_4O_{10}H_2SO_4$, I is, compounds ha	N ₂ O ₃ , HNO ₃ , H ₃ P aving at least one aving at least one	O_3 . $p\pi$ - $p\pi$ bond are $d\pi$ - $p\pi$ bond are	х. У.
16.১	Number of acid (a) HNO_2 (g) $H_4P_2O_7$	ls having central (b) HNO ₃ (h) H ₂ SO ₃	atom in +3 oxida (c) H_3PO_2 (i) $H_2S_2O_7$	tion state among (d) H ₃ PO ₃ (j) H ₂ S ₂ O ₈	the following is (e) H_3PO_4 (k) H_2SO_4	: (f) H ₄ P ₂ O ₅
17.	How many are	redox reactions -				
	(i) $K_4[Fe(CN)_6]$ (iii) conc. H_2SO (v) conc. H_2SO (vii) conc. H_2SO (ix) conc. H_2SO	+ conc. $H_2SO_4 - D_4 + KBr \longrightarrow$ $H_4 + KNO_3 \longrightarrow$ $D_4 + COCl_2 \longrightarrow$ $D_4 + Cu \longrightarrow$	$\xrightarrow{\Delta}$	(ii) conc. H_2SO (iv) conc. H_2SC (vi) conc. H_2SC (viii) conc. H_2SC	$A_{4} + \text{KCI} \longrightarrow \\ A_{4} + \text{NH}_{3} \longrightarrow \\ A_{4} + \text{PCI}_{5} \longrightarrow \\ O_{4} + \text{Zn} \longrightarrow $	
18.	$x P_4 + y SO_2Cl_2 \longrightarrow$ then y/x ?					
19.24	Complete hydrolysis product of 1 mole each of following will need how many total number of moles of NaOF for complete neutralisation? SOCl ₂ , SO ₂ Cl ₂ , PCl ₃ , PCl ₅ , NCl ₃					number of moles of NaOH
20.	Aqueous solution (i) SF_4 (v) SF_6 (ix) SO_2 (xiii) CCI_4	on of how many (ii) PCI (vi) Sel (x) SO	of the following s F_{6}^{3} $_{2}Cl_{2}$	pecies turn blue (iii) N ₂ O (vii) AsCl ₃ (xi) SOCl ₂	litmus red ? (iv) NC (viii) P (xii) C	D ₂ CI OCI ₃ OCI ₂
21.	The difference in oxidation states of sulphur atoms (in different oxidation states) present in Na $_2$ S $_4$ O $_6$ is :					present in $Na_2S_4O_6$ is :
22.	How many com (i) AsO ₃ ³⁻ (v) H ₂ S	npound(s) or ion((ii) SO (vi) Pb	s) can be oxidise ²⁻ S (vii) O ₃	d by H_2O_2 among (iii) Fe ₂ (SO ₄) ₃	g the following : (iv) NH	H ₂ -NH ₂
23.	S(s) - NaOH(ac)	(A) + (B)				
	$(B) \xrightarrow{CdCl_2} \\ Count total num$	Yellow ppt. (C) nber of sulphur a	; toms in one mole	Solid (A) $\frac{I_2}{2}$	→ (D) + (E)), (B), (C), (D) &	(E) :

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE 1.2 As, Sb and Bi show lesser tendency to form negative ions of the type M³⁻. This is because (A) these elements are less electronegative (B) metallic character increases down the group (C) they are unable to hold the added electrons due to inert pair effect (D) they do not posses half filled np subshells 2.2 The correct statement(s) is/are : (A) The PF_6^{-} ion exists (B) The NF_6^- ion does not exist (C) N can form $p\pi$ - $p\pi$ bonds with itself and with other elements having small size and high E.N. (D) The catenation tendency is weaker in N than P 3. Dinitrogen gas is evolved when sodium nitrite is heated strongly : (A) alone (B) with ammonium chloride (D) with potassium nitrate (C) with ammonium hydroxide Correct statements about allotropy? 4. (A) Plastic sulphur exists as zig-zag chains of sulphur. (B) Monoclinic sulphur is soluble in water and insoluble in CS₂. (C) Milk of sulphur gradually changes to Rhombic sulphur. (D) Milk of sulphur is used in medicines. 5. 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 NH₃ to BiH₃ (D) The reducting power increases in going from NH₃ to BiH₃ 6. Ammonium dichromate on heating liberates a gas. The same gas will be obtained by : (A) heating NaNO₂ and NH₄Cl. (B) treating H_2O_2 with NaNO₂. (C) passing ammonia gas over red hot CuO. (D) treating ammonia with KMnO₄ in neutral medium. Which of the following elements react with metals to form their binary compounds exhibiting -3 oxidation 7.2 state ? (A) N (B) P (C)As (D) Bi White phosphorus may be removed from red phosphorus by : 8.2 (A) sublimation under reduced pressure (B) dissolving in water (D) heating with an alkali solution (C) dissolving in CS₂ The compound(s) which on strong heating gives oxygen is/are : 9. $(C) Pb(NO_3)_2$ (A) AgNO₃ (B) BaO₂ (D) KMnO₄ Which of the following is/are true for oxygen. 10.ര (A) KMnO₄(s) on strong heating gives oxygen gas (B) Oxygen mixed with helium is used for artificial respiration. (C) It has two unpaired electrons in bonding π molecular orbitals. (D) Fractional distillation of liquefied air is used as an industrial method for the preparation of oxygen gas. 11.2 The correct statements(s) regarding hydrides (H_E) of group-16 is/are : (A) The acidic character increases from H_2O to H_2Te . (B) The bond (H-E) dissociation enthalpy decreases down the group. (C) The thermal stability of hydrides decreases down the group (D) The reducing character of hydrides increases down the group

12.为	The correct statements regarding ozone is/are (A) Ozone is thermodynamically less stable with respect to oxygen (B) It acts as powerful oxidising agent (C) It rapidly react with NO(g) and form NO ₂ (g) and O ₂ (g) (D) It is toxic substance			
13.๖	The incorrect statement(s) regarding oxides of g (A) Reducing property of dioxide decreases from (B) All these elements form oxides of the EO ₂ and (C) Selenium and tellurium do not form SeO ₃ and (D) SO ₂ is an oxidising agent while TeO ₂ is a red	roup-16 elements is/are $n SO_2$ to TeO ₂ $nd EO_4$ types $d TeO_3$ ucing agent.		
14.2	Which of the following ions dissolve in excess of $(A) AI^{3+}$ $(B) Cu^{2+}$	f aq. NH_{3} . (C) Ag ⁺ (D) Zn ²⁺		
15.	Which of the following is/are incorrect statement(s) for phosphine ? (A) It is less basic than NH ₃ (B) It is less poisonous than NH ₃ (C) The solution of copper sulphate gives no precipitate with PH ₃ . (D) Phosphine burns in air forming predominantly H ₂ PO			
16.	How is H_2S prepared in laboratory ? (A) FeS + H_2SO_4 (C) FeS + HCl	(B) $FeSO_4 + H_2SO_4$ (D) Elemental H_2 + elemental S_8		
17.	A gas is obtained on heating ammonium nitrate. gas : (A) causes laughter (C) is acidic in nature	Which of the following statements are incorrect about this (B) is anhydride of nitrous acid (D) is basic in nature		
18.	Which of the following represents correct dissociation of nitrate salts on heating.			
	(A) $2\text{LiNO}_3 \longrightarrow \text{Li}_2\text{O} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2$	(B) $Pb(NO_3)_2 \longrightarrow PbO + 2NO_2 + \frac{1}{2}O_2$		
	(C) $NH_4NO_3 \xrightarrow{T < 300^{\circ}C} N_2O + 2H_2O$	$(D) \operatorname{NH}_4\operatorname{NO}_2 \longrightarrow \operatorname{N}_2 + 2\operatorname{H}_2\operatorname{O}$		
19.	SO ₂ can reduce : (A) Cl ₂ to Cl ⁻ (B) Cr ₂ O ₇ ²⁻ / H ⁺ to Cr ³⁺	(C) MnO_4^{-} / H ⁺ to Mn^{2+} (D) IO_3^{-} to I_2		
20.	 A white crystaline oxide (A) having garlic smell reacts with cold water to form a compound (B). On heating, (B) gives compound (C) & gas (D). Which of the following are correct statements : (A) Solution of gas (D) does not turn red litmus blue (B) The gas (D) can also be produced by reaction of NaOH with red phosphorus (C) Gas (D) exists in dimeric form. (D) Compound (B) can act as a reducing agent but (C) cannot. 			
21.	Select the correct statement. (A) Ostwald's method of preparation of HNO_3 is backed (B) HNO_2 can act as both oxidising and reducing (C) NO_2 reacts with O_3 to form N_2O_5 . (D) HNO_3 can be used both as oxidising and reducing the statement of the statement of the statement of the statement.	ased upon catalytic oxidation of NH ₃ by atmospheric oxygen. g agent. ucing agent.		
22.	Which of the following statements is (are) correct (A) Antimony on reaction with conc. HNO, gives	ct?		

- (A) Antimony on reaction with conc. HNO_3 gives antimonic acid. (B) Manganese on reaction with cold and dilute HNO_3 gives NO_2 gas.
- (C) HNO_2 disproportionate to give HNO_3 and NO(D) HNO_3 on reaction with P_4O_{10} gives N_2O_5

23.	Concentrated sulphuric (A) dehydrating agent	acid acts as (B) sulphonating agent	(C) reducing agent	(D) oxidising agent.			
24.2	Which among the follow (A) $H_2S_2O_3$	ving is/are peroxo acid (s) (B) H_2SO_5	? (C) H ₂ S ₂ O ₇	(D) H ₂ S ₂ O ₈			
25.	Which of the following r	eactions are correct.					
	$(A) PCI_5 \xrightarrow{LiF} LiPF_6$		$(B) PCI_5 \xrightarrow{P_4O_{10}} POC$	il ₃			
	$(C) \operatorname{PCl}_{3} + \operatorname{NaH} \longrightarrow F$	PH ₃	(D) $PCl_5 + H_2O \longrightarrow F$ (equimolar amount)	POCI ₃			
26.	Select the correct state (A) It is a redox reaction (B) One of the product i (C) Both the products o (D) Both the products have	ment(s) regarding reactio n. s sulphuryl chloride. n addition of water produc ave same hybridisation of	n of SO ₂ with PCI ₅ . ce strongly acidic solution central atom.	IS.			
27.	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 agents (C) H_2O_2 forms a hydrate, H_2O_2 . H_2O (D) Ozone is used in the manufacture of potassium permangnate from pyrolusite.						
28.	 (D) Ozone is used in the manufacture of potassium permangnate from pyrolusite. Which of the following statement (s) is/are true for sodium thiosulphate ? (A) it acts as an antichlor (B) it is used as a reducing agent in iodometric titration. (C) it reacts with hydrochloric acid to form SO₂ and sulphur. (D) it is used in photography as hypo to dissolve excess of AgBr as a soluble complex. 						
29. 🕿	Which of the following statements are correct for H_2O_2 ? (A) It is neutral towards litmus, but bleaches litmus white. (B) It is more acidic than H_2O . (C) Density and dielectric constant are higher than H_2O . (D) H_2O_2 is produced by auto oxidation of 2-ethyl anthraquinol.						
30.	A solution of ammonia (A) H⁺(aq.)	in water contains which of (B) OH⁻(aq.)	the following species : $(C) \operatorname{NH}_4^+(\operatorname{aq.})$	(D) NH ₃ (aq.)			
			MDDELLENGION				

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension #1

An inorganic iodide (A) on heating gives gases (B) and (C). (B) is neutral towards litmus while (C) is acidic.(B) gives back dense white fumes of (A) when cooled with (C). (A) functions as a strong acid in water. (C) is also obtained by action of (D) on water. (D) can be obtained when (B) reacts with I_2 in presence of anhydrous CaCl₂. (B) is poisonous, has smell of rotten fish and it is sparingly soluble in water. Now answer the following questions :

- **1.** Select the correct statement from the following for the gas (B).
 - (A) It produces dense white fumes with HCI
 - (B) It produces dense violet fumes on combustion
 - (C) It produces dense white fumes with BF_3
 - (D) It can act as oxidising agent.

- **2.** The compound (A) :
 - (A) turns moist red litmus blue
 - (C) is used as a dehydrating agent
- (B) reacts completely with water
- (D) all of these
- **3.** > What is true about compound (D)?
 - (A) The oxidation number of central atom of (D) is + IV
 - (B) Compound (D) produces a yellow precipitate with silver nitrate solution.
 - (C) Compound (D) dissolves in water forming an acid which with sodium hydroxide forms three series of salts.
 - (D) Both (B) and (C)

Comprehension # 2

Oxygen differs from the other elements of the group. Compounds of oxygen with metals are more ionic in nature and hydrogen bonding is more important for oxygen compounds. Oxygen is never more than divalent because when it has formed two covalent bonds, there are no low energy orbitals which can be used to form further bonds. However, the elements S, Se, Te and Po have empty d-orbitals which may be used for bonding, and they can form four or six bonds by unpairing electrons. The higher oxidation states become less stable on descending the group.

The bond between S and O, or Se and O, are much shorter than might be expected for a single bond owing to $p\pi - d\pi$ interaction between the p-orbital of oxygen and d - orbital of S or Se.

4. Which of the following statement is incorrect?

(A) Oxo-anions of sulphur have little tendency to polymerise compared with the phosphates and silicates. (B) In pyrosulphurous acid ($H_2S_2O_5$), the oxidation states of both the sulphur atoms are not same, they are +V and +III

(C) Concentrated HNO_3 oxidises both sulphur and selenium to H_2SO_4 (+VI) and H_2SeO_4 (+VI) respectively. (D) Most metal oxides are ionic and basic in nature while non-metallic oxides are usually covalent and acidic in nature.

5. Which one of the following orders represents the correct order for the properties indicated against them ? (A) $H_2O < H_2S < H_2Se < H_2Te - acidic character$

(B) $H_2O < H_2S < H_2Se < H_2Te$ – thermal stability (C) $H_2S > H_2Se < H_2Te < H_2O$ – reducing character (D) $H_2S < H_2Se < H_2Te < H_2O$ – reducing point

Comprehension # 3

The property of hydrides of p-block elements mostly depends on :

- (i) electronegativity difference between central atom and hydrogen
- (ii) size of central atom

(iii) number of valence electrons in central atom

Some undergo hydrolysis in which central atom is less electronegative, react with OH^- to give hydrogen. While acidic property of hydride in a period depends on electronegativity of central atoms, i.e. more electronegative is the atom, more acidic is hydride. In a group, acidic property is proportional to size of central atom. Some electron deficient hydride behaves as Lewis acid while only one hydride of an element in p-block behaves as Lewis base with lone pair of electrons. Hydrides in which central atom's electronegativity is close to hydrogen has no reaction with water.

6. Which hydride has no reaction with water ?

	(A) NH ₃	(B) CH ₄	(C) BeH ₂	(D) NaH
7.2	Which one is stro	ongest base ?		
	(A) OH⁻	(B) HS [_]	(C) HSe⁻	(D) HTe⁻

Exercise #3

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

* Mark	ed Questions may hav	ve more than one corr	ect option.	
1.	Extra pure N_2 can be ob (A) NH_3 with CuO (C) $(NH_4)_2Cr_2O_7$	tained by heating	(B) NH ₄ NO ₃ (D) Ba(N ₃) ₂	[JEE 2011, 3/160]
2.	Among the following, the H_2SO_4 , P_4O_{10} .	e number of compounds t	hat can react with $\mathrm{PCI}_{\mathrm{s}}$ to ς	give POCl ₃ is O ₂ , CO ₂ , SO ₂ , H ₂ O, [JEE 2011, 3/160]
	O ₂ , CO ₂ , SO ₂ , H ₂ O, H ₂ S	O ₄ , P ₄ O ₁₀ .		
3.	Which ordering of comp	oounds is according to the	decreasing order of the o	xidation state of nitrogen? [JEE 2012, 3/136]
	(A) HNO ₃ , NO, NH ₄ CI, N (C) HNO ₃ , NH ₄ CI, NO, N	2	(B) HNO ₃ , NO, N ₂ , NH ₄ C (D) NO, HNO ₃ , NH ₄ Cl, N	2
4.*	The pair(s) of reagents (A) Na and excess of N (C) Cu and dilute HNO_3	that yield paramagnetic s H ₃	pecies is/are (B) K and excess of O_2 (D) O_2 and 2-ethylanthra	[JEE(Advanced) 2014, 3/120] quinol
5.	The product formed in (A) PCI_3	the reaction of $SOCI_2$ wi (B) SO_2CI_2	th white phosphorous is (C) SCI ₂	: [JEE(Advanced) 2014, 3/120] (D) POCI ₃
6.	Hydrogen peroxide in i (A) reducing agent, oxi (C) oxidising agent, ox	ts reaction with KIO₄ an dising agent idising agent	d NH ₂ OH respectively, is (B) reducing agent, red (D) oxidising agent, red	s acting as a [JEE(Advanced) 2014, 3/120] ucing agent lucing agent
7.*	The nitrogen containing (A) can also be prepare (B) is diamagnetic (C) contains one N-N bc (D) react with Na metal	compound produced in tl d by reaction of P ₄ and Hl ond producing a brown gas	ne reaction of HNO ₃ with F NO ₃	⁰ 4 ^O 10. [JEE(Advanced) 2016, 4/124]
Paragra	aph for Question Nos.	8 to 9		
	Upon heating $KCIO_3$ in W reacts with white pho	the presence of catalytic sphorus to give X. The re	amount of MnO ₂ , a gas W action of X with pure HNO	/ is formed. Excess amount of 9 ₃ gives Y and Z.
8.	Y and Z are, respectivel (A) N_2O_4 and HPO_3 (C) N_2O_3 and H_3PO_4	у	(B) N_2O_4 and H_3PO_3 (D) N_2O_5 and HPO_3	[JEE(Advanced) 2017, 3/122]
9.	W and X are, respective (A) O_2 and P_4O_{10} (C) O_3 and P_4O_6	ly	(B) O_2 and P_4O_6 (D) O_3 and P_4O_{10}	[JEE(Advanced) 2017, 3/122]
10.*	The compound(s) which	generate(s) N ₂ gas upon	thermal decomposition b	elow 300°C is (are)
	(A) NH_4NO_3	$(B)(NH_4)_2Cr_2O_7$	(C) $Ba(N_3)_2$	[J = C(Advanced) 2018, 4/120] (D) Mg ₃ N ₂

11.* Based on the compounds of group 15 elements, the correct statement(s) is (are) [JEE(Advanced) 2018, 4/120] (A) Bi_2O_5 is more basic than N_2O_5 (B) NF₃ is more covalent than BiF₃ (C) PH_3 boils at lower temperature than NH_3 (D) The N-N single bond is stronger than the P-P single bond 12.* With reference to aqua regia, choose the correct option(s). [JEE(Advanced) 2019] (A) Reaction of gold with aqua regia produces NO₂ in the absence of air (B) Aqua regia is prepared by mixing conc. HCl and conc. HNO₃ in 3 : 1 (v/v) ratio (C) Reaction of gold with aqua regia produces an anion having Au in +3 oxidation state (D) The yellow colour of aqua regia is due to the presence of NOCI and Cl. 13. The amount of water produced (in g) in the oxidation of 1 mole of rhombic sulphur by conc.HNO₂ to a compound with the highest oxidation state of sulphur is (Given data : Molar mass of water = 18 g mol^{-1}) [JEE(Advanced) 2019] PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS) 1.* Which of the following statement is wrong? [AIEEE 2011, 4/120] (1) The stability of hydrides increase from NH_3 to BiH_3 in group 15 of the periodic table : (2) Nitrogen cannot form $d\pi$ -p π bond. (3) Single N – N bond is weaker than the single P – P bond. (4) N₂O₄ has two resonance structure 2. Which of the following statements regarding sulphur is **incorrect**? [AIEEE 2011, 4/120] (1) S_2 molecule is paramagnetic. (2) The vapour at 200°C consists mostly of S₈ rings. (3) At 600°C the gas mainly consists of S₂ molecules. (4) The oxidation state of sulphur is never less than +4 in its compounds. 3. Which of the following is the wrong statement? [JEE(Main) 2013, 4/120] (1) ONCI and ONO⁻ are not isoelectronic. (2) O_3 molecule is bent (3) Ozone is violet-black in solid state (4) Ozone is diamagnetic gas. 4. Which of the following properties is not shown by NO? [JEE(Main) 2014, 4/120] (1) It is dimagnetic in gaseous state (2) It is a neutral oxide (3) It combines with oxygen to form nitrogen dioxide (4) It's bond order is 2.5 5. Which of the following is not formed when H₂S reacts with acidic K₂Cr₂O₇ solution ? [JEE(Main) 2014 Online (09-04-14), 4/120] (1) CrSO₄ $(2) Cr_2(SO_4)_3$ (3) K₂SO₄ (4) S Hydrogen peroxide acts both as an oxidizing and as a reducing agent depending upon the nature of the 6. reacting species. In which of the following cases H₂O₂ acts as a reducing agent in acid medium ? [JEE(Main) 2014 Online (12-04-14), 4/120] $(3) SO_3^{2-}$ $(2) Cr_2 O_7^{2-}$ (1) MnO₄[−] (4) KI [JEE(Main) 2014 Online (19-04-14), 4/120] 7. Which of these statements is not true ? (1) NO⁺ is not isoelectronic with O_2 (2) B is always covalent in its compounds (3) In aqueous solution, the TI⁺ ion is much more stable than TI(III) (4) LiAlH₄ is a versatile reducing agent in organic synthesis.

From the following statements regarding H₂O₂, choose the incorrect statement: [JEE(Main) 2015, 4/120] 8. (1) It can act only as an oxidizing agent (2) It decomposed on exposure to light (3) It has to be stored in plastic or wax lined glass bottles in dark (4) It has to be kept away from dust 9. Assertion: Nitrogen and Oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen. [JEE(Main) 2015, 4/120] Reason : The reaction between nitrogen and oxygen requires high temperature. (1) Both assertion and reason are correct, and the reason is the correct explanation for the assertion (2) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion (3) The assertion is incorrect, but the reason is correct (4) Both are assertion and reason are incorrect 10. The pair in which phosphorous atoms have a formal oxidation state of +3 is: [JEE(Main) 2016, 4/120] (1) Pyrophosphorous and hypophosphoric acids (2) Orthophosphorous and hypophosphoric acids (3) Pyrophosphorous and pyrophosphoric acids (4) Orthophosphorous and pyrophosphorous acids 11. The reaction of zinc with dilute and concentrated nitric acid, respectively, produces: [JEE(Main) 2016, 4/120] $(1) NO_2$ and NO (2) NO and N₂O $(3) NO_2 and N_2O$ $(4) N_2O and NO_2$ 12. The non-metal that does not exhibit positive oxidation state is: [JEE(Main) 2016 Online (09-04-16), 4/120] (1) Fluorine (2) Oxygen (3) Chlorine (4) lodine 13. [JEE(Main) 2016 Online (10-04-16), 4/120] Identify the incorrect statement: (1) Rhombic and monoclinic sulphur have S₈ molecules. (2) S_{R} ring has a crown shape. (3) S_2 is paramagnetic like oxygen. (4) The S–S–S bond angles in the S_8 and S_6 rings are the same. 14. Identify the pollutant gases largely responsible for the discoloured and lustreless nature of marble of the Taj Mahal. [JEE(Main) 2017 Online (08-04-17), 4/120] (1) SO₂ and NO₂ (2) SO₂ and O₃ $(3) O_3$ and CO_2 $(4) CO_2$ and NO₂ 15. In which of the following reactions, hydrogen peroxide acts as an oxidizing agent ? [JEE(Main) 2017 Online (08-04-17), 4/120] (1) PbS + $4H_2O_2 \rightarrow PbSO_4 + 4H_2O_2$ $(2) 2MnO_{4}^{-} + 3H_{2}O_{2} \rightarrow 2MnO_{2} + 3O_{2} + 2H_{2}O + 2OH^{-}$ $(3) I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O_2 + O_2$ (4) HOCI + $H_2O_2 \rightarrow H_3O^+ + CI^- + O_2$ Hydrogen peroxide oxidises [Fe(CN),]⁴⁻ to [Fe(CN),]³⁻in acidic medium but reduces [Fe(CN),]³⁻to [Fe(CN),]⁴⁻ 16. in alkaline medium. The other products formed are, respectively. [JEE(Main) 2018, 4/120] (1) $H_{2}O$ and $(H_{2}O + O_{2})$ (2) H_2O and $(H_2O + OH^-)$ (4) $(H_2O + O_2)$ and $(H_2O + OH^-)$ $(3) (H_2O + O_2) and H_2O$ 17. The compound that does not produce nitrogen gas by the thermal decomposition is : [JEE(Main) 2018, 4/120] $(1) NH_1 NO_2$ $(2) (NH_{4})_{2}SO_{4}$ $(3) Ba(N_3)_2$ $(4) (NH_{1})_{2}Cr_{2}O_{7}$

ANSWER KEY

EXERCISE # 1

PART - I

- **A-1._** Although each of the above has same electronic distribution in bonding orbitals, nitrogen is inert because of non-polar nature of bond and high N≡N dissociation energy. Rest all (CO, CN⁻, NO⁺) are polar.
- **A-2.** White phosphorus (P_4) .
- A-3._ (N' atom of NH₃ or 'P' atom of PH₃ has a lone pair of electrons available for donation. Hence NH₃ and PH₃ are Lewis bases. The electron pair density on a larger 'P' atom is less than that of smaller 'N' atom. Hence PH₃ is a weaker base.

Δ-4. 🛪	Oxide	Oxyacids		
~	N_2O_3	HNO ₂		
	NO ₂ /N ₂ O	HNO ₂ + HNO ₃		
	N ₂ O ₅	HNO ₃		
	P ₄ O ₆	H ₃ PO ₃		
	P ₄ O ₁₀	H ₃ PO ₄		

- A-5. Atomic size of nitrogen is very less. Hence 'N' atom can approach close to another 'N' atom. This facilitates the lateral overlap of the p-orbitals forming π -bonds.
 - Due to large size, other atoms of the same group form only single bonds, but not multiple bonds.
- **A-6._** White phosphorus is very reactive, due to the P-P-P bond angle strain at 60°. Red phosphorus is very stable, due to chain like polymeric structure.
- A-7. Phosphorite $Ca_3(PO_4)_2$ and fluoroapatite $Ca_5(PO_4)_3F$
- A-8. Bismuth and antimony both belong to the nitrogen family and exhibit the +5 oxidation state. However, on moving down the group, i.e., from antimony to bismuth, the stability of the +5 oxidation state decreases. This is due to the inert pair effect. Thus, Bi (V) is a stronger oxidant than Sb (V).

A-9. ≥ − 3 to + 5, 0

- A-10. Nitrogen exhibits -3 state in nitride and phosphorus exhibits –3 state in phosphide. Going down the group, the atomic size increases and metallic character also increases. Hence, the tendency to exhibit negative oxidation state decreases down the group VA.
- **A-11.** (a) Oxidation state of phosphorus in P_4 molecule is zero.
 - (b) Valency of P in P_4 molecule is three. Each P atom forms 3 bond pairs and possesses on lone pair.
 - (c) Total number of P-P sigma bonds in a molecule of phosphorus is six.
 - (d) Phosphorus-Phosphorus bond order in P_4 molecule is one.
 - (e) Bond angle 60°.
 - (f) Tetrahedral.
- A-12. NO₂ being odd molecule, on dimerisation is converted to stable N_2O_4 molecule with even number of electrons.

A-13. > P₄O₆







- **A-14.** Phosphorus exhibits pentavalency in excited state. Fluorine, chlorine or bromine is more electronegative and influences excitation to form PX₅. However, hydrogen is not that much electronegative to incluence the excitation in phosphorus. Hence PH₅ is not formed.
- **B-1._** They resemble since the three ions are of comparable radii and same charge : $NH_4^+ = 1.48 \text{ Å}, \text{ K}^+ = 1.33 \text{ Å}, \text{ Rb}^+ = 1.48 \text{ Å}.$
- **B-2.** (a) $NH_3 + H_2O \implies NH_3 \cdot H_2O$ (Ammonium hydroxide) $\implies NH_4^+(aq) + OH^-(aq)$ This reaction occurs to small extent only (1-2 %). Rest of NH_3 remains unreacted. (b) $NH_3(aq.) + HCI(aq.) \implies NH_4CI(aq.)$ (c) $NH_3(aq.) + H_2O + CO_2(aq.) \longrightarrow NH_4HCO_3$ (solvay ammonia process)
- **B-3._** Mercuric phosphide is formed by the reaction between phosphine and mercuric salt, $2PH_3 + 3HgCI_2 \longrightarrow Hg_3P_2 \downarrow + 6HCI$
- **B-4.** N–H bond is more polar than P–H bond. Hence, NH₃ forms hydrogen bonds with H₂O molecules and hence dissolves in it whereas PH₃ does not dissolve and forms bubbles. Also same electronegativity of P and H.
- $\begin{array}{l} \textbf{B-5.} \geqq \ \textbf{NH}_3 + \textbf{NaOCI} \longrightarrow \textbf{NH}_2\textbf{CI} + \textbf{NaOH} \ (fast) \\ \\ \qquad \textbf{NH}_3 + \textbf{NH}_2\textbf{CI} \longrightarrow \textbf{NH}_2\textbf{NH}_2 + \textbf{NH}_4\textbf{CI} \ (slow) \end{array}$
- **B-6.** Pure oxygen will oxidise P_4O_6 to P_4O_{10} despite an excess of P_4 is kept at the start of the reaction. Hence, nitrogen gas is used as a diluent.
- **B-7.** P₄O₁₀
- **B-8._** PCl₅
- **B-9.** (A) $PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$ (B) $PCl_5 + D_2O \longrightarrow POCl_3 + 2 DCl$ $POCl_3 + 3D_2O \longrightarrow D_3PO_4 + 3DCl$
- **B-10.** PCI_3 hydrolyses in the presence of moisture giving fumes of HCl $PCI_3 + H_2O \longrightarrow H_3PO_3 + 3$ HCl
- **B-11.** (i) $P_4O_{10} + 6PCI_5 \longrightarrow 10POCI_3$ (ii) $NH_3 + NaO$

(ii)
$$NH_3 + NaOCI \longrightarrow NH_2CI + NaOH$$
 (fast)
 $NH_3 + NH_2CI \longrightarrow NH_2NH_2 + NH_2CI$ (slow)

- C-1. A Rhombic sulphur
- **C-2.** In vapour state, sulphur exists as S_2 molecule. S_2 molecule, like O_2 molecule, has two unpaired electrons in the anti-bonding n* orbitals. Hence, like O_2 , it exhibits paramagnetism.

Tetrathionate has S–S linkage. The oxidation states of sulphur are : +5, 0, 0 and +5. The average oxidation state of S is +2.5.

C-4. Due to the decrease in bond (E – H) dissociation enthalpy down the group acidic character increases.

- C-5._ All the elements show no reaction with water.
- **C-6.** $S^{2-} + S \Longrightarrow S_2^{2-}$; $S_2^{2-} + S \Longrightarrow S_3^{2-}$ $S_{11}^{2-} + S \Longrightarrow S_{12}^{2-}$ Upto 12 sulphur atoms poly sulphide ions are observed in significant amounts.
- **C-7.** TeO (oxidation number of Te is +2) is basic. TeO₂ (oxidation number of Te is +4) is amphoteric. TeO₃ (oxidation number of Te is +6) is acidic. As the oxidation number of the element forming oxide increases, the acidic nature also increases.
- **C-8.** ➤ Due to high electronegativity of O, the O–H in H₂O forms strong intermolecular H-Bonds. As a result water exists as an associated molecule while other hydrides of group 16 do not form H–Bonds and hence exist as discrete molecules. As a result, water shows unusual physical properties, i.e. high b.p., high thermal stability and weaker acidic character as compared to other hydrides of group 16.

C-10. Atomic number of A = 16. It is sulphur. Atomic number of B = 17. It is chlorine.

Excess sulphur reacts with chlorine to give dimeric monochloride. Sulphur reacts with excess chlorine to give tetrachloride. Molten dimeric monochloride on saturation with chlorine gives dichloride.

 $2S + Cl_2 \longrightarrow S_2Cl_2$; $S_2Cl_2 + Cl_2 \longrightarrow 2SCl_2$

D-1. SO_2CI_2 is formed from H_2SO_4 by treating with excess of phosphorus pentachloride.

 $H_2SO_4 + 2PCI_5 \longrightarrow SO_2CI_2 + 2HCI + 2POCI_3$

SO₃ is obtained from sulphuric acid by dehydration with phosphorus pentachloride.

 $2H_2SO_4 + P_4O_{10} \longrightarrow 4HPO_3 + 2SO_3$

 SO_2 is obtained from conc. H_2SO_4 , when heated with copper metal.

$$2H_2SO_4$$
 (conc.) + Cu \longrightarrow CuSO₄ + $2H_2O$ + $2SO_2$

- **D-2.** SO₂
- **D-3.** $X = I_2$

$$Y = \overline{N}a_2S_4O$$

- **D-4.** \ge SO₃ reacts with water to form H₂SO₄ which forms a mist that is difficult to condense. It escapes in the atmosphere. It is, therefore, absorbed in conc. H₂SO₄ to form oleum which may be diluted to form H₂SO₄.
- **D-5.** AgBr + $2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$ H_2SO_4 (dil) + $Na_2S_2O_3 \longrightarrow Na_2SO_4 + S$ (white turbidity) + $H_2O + SO_2$ $3H_2SO_4$ (conc.) + $Na_2S_2O_3 \longrightarrow Na_2SO_4 + 4SO_2 + 3H_2O$

	PART - II								
A-1.	(D)	A-2	(D)	A-3.	(A)	A-4.	(D)	A-5.	(A)
A-6.	(B)	A-7.	(A)	A-8.	(D)	A-9.	(D)	A-10.	(C)
A-11.	(A)	A-12.	(B)	A-13	(C)	A-14.	(C)	A-15	(D)
B-1	(B)	B-2	(A)	B-3.	(C)	B-4.	(D)	B-5	(A)
B-6.	(C)	B-7.	(B)	B-8.	(A)	B-9.	(B)	B-10.	(B)
B-11.	(B)	B-12.	(A)	B-13.	(D)	B-14	(B)	C-1	(C)
C-2.	(B)	C-3.	(C)	C-4	(A)	C-5	(B)	C-6	(C)
C-7.	(D)	C-8	(B)	C-9	(B)	D-1	(C)	D-2	(D)
D-3	(A)	D-4.	(B)	D-5 (D))	D-6.	(B)	D-7.	(D)
D-8.	(D)	D-9.	(B)	D-10.	(D)	D-11.	(B)	D-12	(A)

				PAI	RT - III				
1.2a	(A - p, q, s) ; (I	3 - p, q,	r, s) ; (C - q, r,	s) ; (D - p	o, q, r, s)				
2. 🔉	(A - q, s) ; (B -	q, r) ; (C - q, s) ; (D - q)					
				EXER	CISE - 2				
				PA	RT - I				
1.	(A)	2.	(D)	3.	(C)	4.	(C)	5.	(B)
6.	(D)	7.	(D)	8.	(C)	9.	(D)	10.	(D)
11.	(A)	12.	(C)	13.	(A)	14.	(B)	15.	(B)
16.	(B)	17.	(B)	18.	(D)	19.	(B)	20.	(A)
21.	(D)	22.	(A)	23.	(C)	24.	(D)	25.	(A)
26.	(D)	27.	(D)	28.	(B)				
				PA	RT - II				
1.	5 (a, b, c, e, f)		2.	3 (a,o	d,f)	3.	05(b,d,e,f,g)		
4.	3		5.	7		6.	9		
1.	8 6 (avecant NUL		8.	5 (1,11,	III,VI & VII)	9.	9 (a,b,c,d,e,f,	g,n,ı)	
10.	$6 (except NH_3, 4 (a, b, d, b))$	N ₂ H ₄ &	HN_{3}) 11.	4		12.	/ 10		
13. 16	4 (a, b, u, li) 3 (a d & f)		14.	10 3 (iii -	viii iv)	15.	12		
19	24		20	10 (e)	xcentiii v&xiii)	21	5		
22.	4 (i,iv,v & vi)		23.	8			Ū		
				PAI	RT - III				
1.	(AB)	2.	(ABCD)	3.	(AB)	4.	(ACD)	5.	(BD)
6.	(ACD)	7.	(ABCD)	8.	(ACD)	9.	(ABC)	10.	(ABD)
11.	(ABCD)	12.	(ABCD)	13.	(BCD)	14.	(BCD)	15.	(BCD)
16.	(AC)	17.	(BCD)	18.	(ABCD)	19.	(ABCD)	20.	(AD)
21.	(ABC)	22.	(ACD)	23.	(ABD)	24.	(BD)	25.	(ABCD)
26.	(CD)	27.	(ABCD)	28.	(ABCD)	29.	(ABCD)	30.	(ABCD)
				PAF	RT - IV				
1.	(C)	2.	(B)	3.	(B)	4.	(C)	5.	(A)
6.	(B)	7.	(A)						
				EXER	RCISE - 3				
				PA	RT - I				
1.	(D)	2.	4	3.	(B)	4.*	(ABC)	5.	(A)
6.	(A)	7.*	(BD)	8.	(D)	9.	(A)	10.*	(BC)
11.*	(ABC)	12.*	(BCD)	13.	(288.00 to 288	.30)			
				ΡΑ	RT - II				
1.*	(1, 4)				2.	(4)			
3.	(All statement	are cori	rect there is no a	answer).	4.	(1)			
5.	(1)	6.	(1)	7.	(1)	8.	(1)	9.	(1)
10.	(4)	11.	(4)	12.	(1)	13.	(4)	14.	(1)
15.	(1)	16.	(1)	17.	(2)				

> Marked Questions may have for Revision Questions.

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Reliable students.

Self Assessment Test

PART-1: PAPER JEE (MAIN) PATTERN

	173		== (
		SECTION-I : (Ma	ximum Marks : 80)					
•	This section contains TWENTY questions.							
•	Each question has FC	DUR options (A), (B), (C) and (D). ONLY ONE o	of these four options is correct.				
•	For each question, da	arken the bubble corresp	onding to the correct op	tion in the ORS.				
•	For each question, ma	arks will be awarded in g	one of the following cate	egories :				
	Full Marks : +4If only	the bubble correspondi	ng to the correct option	is darkened.				
	Zero Marks : 0 If non	e of the bubbles is dark	ened.					
	Negalive Marks1							
1.	There is considerable i	increase in covalent radiu	is from N to P. However, ⁻	from Sb to Bi only small increase				
	(A) poor shielding by co	ompletely filled d- and f-or	rbitals in Bi.					
	(B) similar eletronegati	vity of Sb and Bi.						
	(C) the Bi being last ele	ement of the group.						
	(D) similar densities of	Sb and Bi.						
2.	Which of the following	elements shows highest r	number of allotropes :					
	(A) N	(B) P	(C) S	(D) O				
3.	Ozone is obtained from	noxygen						
	(A) By oxidation at high	n temperature	(B) By oxidation using	a catalyst				
	(C) By silent electric di	scharge	(D) By conversion at hig	gh pressure				
4.	Crown shape of S ₈ mo	lecule is present in :						
	(A) Rhombic sulphur		(B) Monoclinic sulphur					
	(C) BUILL $(A) \propto (D)$		(D) None of these					
5.	Presence of ozone in a	a gas sample may be dete	ected by :					
	$(A) H_2 O_2$	$(B)SO_2$	(C) Hg	(D) KI				
6.	Amongst H ₂ O, H ₂ S, H ₂	$_{2}$ Se and H $_{2}$ Te the one with	the highest boiling point	is				
	(A) H_2O because of hyd	drogen bonding	(B) H_2 Te because of hig	her molecular weight				
	$(C) \Pi_2 S$ because of flyc	logen bonding	(D) Π_2 Se because of iov					
7.	When ammonia is pass	sed over heated copper ox	ide, the metallic copper is	obtained. The reaction shows that				
	ammonia is (A) A dehydrating agen	t	(B) An oxidising agent					
	(C) A reducing agent		(D) A nitrating agent					

8.	 Phosphine is generally prepared in the laboratory (A) By heating phosphorus in a current of hydrogen (B) By heating white phosphorus with aqueous solution of caustic potash (C) By decomposition of P₂H₄ at 110°C (D) By heating red phosphorus with an aqueous solution of caustic soda. 						
9.	Cyanamide process is (A) N_2	used in the formation of (B) HNO ₃	(C) NH ₃	(D) PH ₃	3		
10.	Ammonium nitrate dec (A) Ammonia and nitric (C) Nitrogen, hydrogen	omposes on warming into acid and ozone	(B) Nitrous oxic (D) Nitric oxide	de and wa , nitroger	ater n dioxide and hydrogen		
11.	In the reaction, conc. H (A) PH_3	$H_2SO_4 + P_2O_5 \xrightarrow{\Delta} (X)$ (B) H_3PO_4) + SO ₃ ; the ma (C) HPO ₃	ajor produ	uct (X) is : (D) H ₄ P ₂ O ₇		
12.	Bleaching action of SC (A) its reducing nature (C) its acidic nature	9 ₂ is due to :	(B) its oxidising (D) its both oxid) nature dising as	well as reducing nature		
13.	Which of the following can convert acidified $Cr_2O_7^{2-}$ to green ? (A) $SO_2 / H_2SO_3 / H_2SO_4$ (B) $SO_3 / H_2SO_3 / H_2S$ (C) $SO_3^{2-} / H_2S / Fe^{2+}$ (D) $S_2O_3^{2-} / SO_3 / Fe^{3+}$						
14.	Which of the following statements is true for HNO_2 ? (A) It can be prepared by acidifying an aqueous solution of nitrite. (B) It is unstable weak acid which is known only in aqueous solution. (C) N_2O_3 is an anhydride of HNO_2 . (D) All of these						
15.	The compound which h (A) PCl ₅	nas ionic nature in solid sf (B) POCl ₃	tate is : (C) P ₄ O ₁₀		(D) PCl ₃		
16.	Phosphorus trichloride formula : (A) HPO ₃	, PCl ₃ undergoes, hydroly (B) H ₃ PO ₃	/sis at room temp (C) H ₃ PO ₄	perature 1	to produce an oxoacid. It has the (D) H ₃ PO ₂		
17.	Which of the following $(A) SO_2$	dissolves in water but doe (B) OF ₂	es not give any ox (C) SCI ₄	vyacid so	lution ? (D) SO ₃		
18.	Hypo is used in photography to: (A) Reduce AgBr grains to metallic silver (B) Convert the metallic silver to silver salt (C) Remove undecomposed silver bromide as a soluble complex (D) Remove reduced silver						
19.	Sulphur on boiling with (A) $Na_2S_2O_3 + NaHSO_2$ (C) $Na_2SO_3 + H_2S$	NaOH solution gives	(B) Na ₂ S ₂ O ₃ + (D) Na ₂ SO ₃ + S	Na ₂ S SO ₂			
20.	Sodium thiosulphate is (A) reducing $Na_2 SO_3 s$ (B) Boiling $Na_2 SO_3$ with (C) Neutralising $H_2 S_2 O$ (D) Boiling $Na_2 SO_3$ with	prepared by olution with H_2S n S in alkaline medium. ₃ solution with NaOH th S in an acidic medium					

SECTION-II : (Maximum Marks: 20)

- This section contains **FIVE** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places; e.g. 6.25, 7.00, -0.33, -.30, 30.27, -127.30, if answer is 11.36777.... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.

For Example : If answer is -77.25, 5.2 then fill the bubbles as follows.

Answer to each question will be evaluated according to the following marking scheme:

Full Marks : +4 If ONLY the correct numerical value is entered as answer.

- 21. What is the number of oxygen atoms bonded to each phosphorus atom in P_4O_{10} :
- **22.** 1 mol each of H_3PO_2 , H_3PO_3 and H_3PO_4 will neutralise x mole of POH, y mol of $Q(OH)_2$ and z mol of $R(OH)_3$ (assuming all as strong electrolytes) respectively. x + y + z is
- **23.** How many of the following compounds are possible products when chlorine is passed through hypo solution. S, HCl, Na₂S, Na₂SO₄, Na₂S₄O₆, HClO₄
- **24.** A gas is pale blue in colour on liquifaction, the colour arises from electronic transitions. This transition is forbidden in gaseous state. The gas does not burn but is a strong supporter of combustion. Give the molar mass of this gas.
- **25.** Cold conc. HNO₃ will completely dissolve : Pb, Pb₃O₄, Fe, Sn, Mg, MgO, Hg, Au, Ag, Pt.

PART 2 : PAPER JEE (ADVANCED) PATTERN

SECTION-I : (Maximum Marks : 12)

- This section contains **FOUR** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :

Full Marks	:	+3	If only the bubble corresponding to the correct option is darkened.
Zero Marks	:	0	If none of the bubbles is darkened.
Negative Mark	s:	–1	In all other cases

1.	An unknown subst	ance (P) functions as wea	ak base in water. It produc	es silver mirror test. It reacts with	dilute				
	HCI to produce (Q	HCI to produce (Q) which turns blue litmus red. (P) may be :							
	(A) NH ₃	(B) PH ₃	(C) NH ₂ OH	(D) HPO ₃					
2.	Which of the follow	Which of the following compounds does give N_2 on heating ?							
	$(A) NH_4 NO_2$	$(B) NH_4 NO_3$	(C) NaN ₃	(D) Both (A) and (C)					

- Which of the following cannot result in the formation of NO ?
 (A) N₂ + O₂ (Electric arc)
 (B) NH₃ + O₂; (Pt / Rh catalyst / 1200 K)
 (C) NaNO₃ / HCI
 (D) None of these
- 4. Which of the following will not decolourise acidified $KMnO_4$? (A) $S_2O_4^{2-}$ (B) $S_2O_5^{2-}$ (C) $S_2O_3^{2-}$ (D) $S_2O_7^{2-}$

SECTION-II : (Maximum Marks: 32)

- This section contains **EIGHT** questions.
- Each question has FOUR options for correct answer(s). ONE OR MORE THAN ONE of these four option(s) is (are) correct option(s).
- For each question, choose the correct option(s) to answer the question.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks	:	+4	If only (all) the correct option(s) is (are) chosen.
Partial Marks	:	+3	If all the four options are correct but ONLY three options are chosen.
Partial Marks	:	+2	If three or more options are correct but ONLY two options are chosen, both of which are correct options.
Partial Marks	:	+1	If two or more options are correct but ONLY one option is chosen and it is a correct option.
Zero Marks	:	0	If none of the options is chosen (i.e. the question is unanswered).
Negative Marks	s :	-1	In all other cases.

- For Example : If first, third and fourth are the ONLY three correct options for a question with second option being an incorrect option; selecting only all the three correct options will result in +4 marks. Selecting only two of the three correct options (e.g. the first and fourth options), without selecting any incorrect option (second option in this case), will result in +2 marks. Selecting only one of the three correct options (either first or third or fourth option), without selecting any incorrect option (second option in this case), will result in +1 marks. Selecting any incorrect option(s) (second option in this case), will result in +1 marks. Selecting any incorrect option(s) (second option in this case), will result in −1 marks.
- 5. Which is greater for P_4 (white) than P_4 (red) -(C) Solubility in CS₂ (A) Molar entropy (B) Melting point (D) Ignition temperature 6. What is/are not true about phosphine (PH₂)? (A) It turns red litmus blue. (B) It reacts with HCI (aq.) to give PH,CI. (C) Phosphonium compounds are obtained when anhydrous phosphine reacts with anhydrous HBr or HI. (D) It is prepared by hydrolysis of metal phosphides with acids. 7. Which of the following is/are correct regarding nitrogen family. (A) Nitrogen is restricted to a maximum covalency of 4 as only four orbitals are available for bonding. (B) The single N–N bond is weaker than the single P–P bond. (C) The catenation tendency is weaker in nitrogen as compared to phosphorous. (D) Nitrogen forms $p\pi$ - $p\pi$ bond as well as $p\pi$ - $d\pi$ bonds. 8. P_2O_5 can dehydrate. $(A) H_2 SO_4$ (B) HNO₃ (C) HClO₄ (D) HPO₃ The products formed when H_3PO_2 is heated at 415 K and at 435 K are : 9. $(A) H_3 PO_3$ (B) H₃PO₄ (D) PH₂ (C) HPO₃ $4AgNO_3 + 2H_2O + H_3PO_2 \xrightarrow{\text{boil}} 4Ag + 'X' + 'Y'$ 10. If X is oxyacid of nitrogen and Y is oxyacid of phosphorous then correct statement(s) is/are : (A) X is HNO₂ (B) Y is H₃PO₄ (C) H₃PO₂ act as good reducing agent (D) The oxidation number of 'P' changed from +1 to +5 (P) $\xrightarrow{\text{NaH}}$ (Q) $\uparrow \xrightarrow{\text{CuSO}_4}$ (R) \downarrow black precipitate 11.
- (P) may be : (A) SCl_2 (B) PCl_3 (C) NCl_3 (D) HCl

- 12. Which of the following statements are true about ozone? (A) It is a pale blue gas at room temperature. (B) It oxidises sulphur and phosphorus evolving oxygen gas. (C) It is odourless. (D) It turns dry KOH red. SECTION-III : (Maximum Marks: 18) This section contains SIX questions. The answer to each question is a **NUMERICAL VALUE**. For each question, enter the correct numerical value (in decimal notation, truncated/rounded-off to the second decimal place; e.g. 6.25, 7.00, -0.33, -.30, 30.27, -127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS. For Example : If answer is -77.25, 5.2 then fill the bubbles as follows. Answer to each question will be evaluated according to the following marking scheme: Full Marks : +3 If ONLY the correct numerical value is entered as answer. Zero Marks : 0 In all other cases. Cold dilute nitric acid would dissolve how many of the following without significant evolution of any gas : 13. Pb, Mg, Sb, Au, Ag, Fe, Mn, Sn, P₄ Which of the following on heating will produce an oxide of nitrogen. 14. (NH₄)₂ SO₄, (NH₄)₂Cr₂O₇, NH₄NO₃, KNO₃, Pb(NO₃)₂, (NH₄)₂HPO₄, NH₄CI, NH₄NO₂ 15. NaPO₃ can significantly react with how many of the following ? CaCl₂, MgSO₄, CaO, Na₂CO₃, dry HCl, Ca(HCO₃)₂, Na₃PO₄ One mole of PCl₃ is dissolved in excess of water. No. of moles of NaOH required to neutralise this solution 16. completely is : When hypo solution react with CuCl₂ and produce soluble complex, then how many no. of moles of atoms 17. present in one mole of soluble complex in co-ordination sphere. How many of the following reactions yield POCl₃? 18. (ii) $PCl_5 + CO_2 \longrightarrow$ (i) $PCl_3 + O_2 \longrightarrow$ (iii) $PCl_5 + CH_3COOH \longrightarrow$ (iv) $PCl_5 + H_3BO_3 \longrightarrow$ $(vi) P_4O_{10} + NaCl \longrightarrow$ (v) $PCl_3 + SO_2Cl_2 \longrightarrow$ (vii) $PCl_5 + H_2O \longrightarrow$ (viii) $PCl_5 + SO_2 \longrightarrow$ (ix) $PCI_3 + SO_3 \longrightarrow$ PART - 3 : OLYMPIAD (PREVIOUS YEARS) 1. In the following reaction, $SO_2 + 2H_2S \rightarrow 3S + 2H_2O$ [NSEC-2000] (B) sulphur is oxidised and hydrogen is reduced (A) sulphur is oxidised and reduced (C) sulphur is reduced and there is no oxidation (D) hydrogen is oxidised and sulphur is reduced One gas bleaches the colour of flowers by reduction while the other by oxidation. The gases are 2. [NSEC-2002] $(A) SO_2, CI_2$ (C) H₂S, Br₂ (D) NH₂, SO₂. (B) CO, Cl₂ 3. In nature, ammonia is synthesisd by nitrifying bacteria using enzymes while in industry it is manufactured
 - In nature, ammonia is synthesisd by nitrifying bacteria using enzymes while in industry it is manufactured from N₂ and H₂ using iron oxide catalyst at 550°C. Under the same industrial conditions, enzymes cannot be used because [NSEC-2003]
 - (A) enzymes get deactivated at high temperature
 - (B) enzymes catalyze reactions only in living systems
 - (C) the reaction becomes vigorous and uncontrollable
 - (D) the enzymes use nitrates in place of N_{2} .

4.	The anhydride of nitric a (A) nitric oxide	icid is (B) nitrous oxide	(C) dinitrogen trioxide	(D) dinitrogen pe	[NSEC-2003] entoxide.	
5.	Bones glow in the dark. (A) the presence of red p (C) the presence of calc	This is due to phosphorus. ium carbonate	(B) conversion of white p (D) the presence of calci	phosphorus into re ium phosphate.	[NSEC-2005] ed phosphorus.	
6.	Which of the following cases $(A) H_3PO_2$	ompounds of phosphorus (B) H ₃ PO ₃	does not have resonating $(C) H_3PO_4$	g structures ? (D) (CH ₃) ₂ HPO ₃ .	[NSEC-2006]	
7.	In thiosulphuric acid H_2S (A) + II ,+ II	S_2O_3 , the oxidation states (B) 0, + IV	of sulphur atoms are (C) + I , + III	(D)–II , + VI.	[NSEC-2006]	
8.	The ozone hole in the u reaction is catalyzed by (A) chlorofluorocarbons (B) oxygen generated du (C) carbon dioxide prese (D) chlorine formed by th	upper atmosphere of the uring the reaction ent in the atmosphere he decomposition of chlore	earth is due to the brea	kdown of ozone	to oxygen. The [NSEC-2009]	
9.	$P_4(s) + 3OH^-(aq) + 3H_2$ In the above equation, the (A) P_4 and OH ⁻	$P_{2}O(I) \longrightarrow PH_{3}(g) + 3H$ the species getting oxidize (B) OH ⁻ and P ₄	$H_2PO_2^-$ (aq) and reduced respective (C) P ₄ and H ₂ O	ely are : (D) P_4 and P_4	[NSEC-2009]	
10.	The bond having the hig (A) $C = C$	hest bond energy is (B) C = S	(C) C = O	(D) P = N	[NSEC-2010]	
11.	The nitrogen compound $(A) N_2 O$	formed when Ca(CN) ₂ re (B) NO	eacts with steam or hot wa $(C) NO_2$	ter is (D) NH ₃	[NSEC-2011]	
12.	The most abundant eler (A) aluminium	nent in the earth's crust is (B) oxygen	s : (C) silicon	(D) iron	[NSEC-2011]	
13.	The element that has th (A) silicon	e highest tendency to cat (B) germanium	tenate is : (C) sulphur	(D) boron	[NSEC-2011]	
14.	The chemical formula of (A) NO	'laughing gas' is (B) N ₂ O	(C) N ₂ O ₄	(D) N ₂ O ₅	[NSEC-2012]	
15.	Phosphine is prepared b (A) P and HNO_3	by the reaction of $(B) P$ and H_2SO_4	(C) P and NaOH (D) P ar	nd H_2S	[NSEC-2012]	
16.	The oxidation of SO_2 by O_2 is an exothermic reaction. The yield of SO_3 can be maximized i (A) temperature is increased and pressure is kept constant (B) temperature is decreased and pressure is increased (C) both temperature and pressure are increased (D) both temperature and pressure are decreased					
17.	Which of the following s (I) NaH_2PO_3 (A) I and II only	alt/s of H ₃ PO ₃ exists ? (II) Na ₂ HPO ₃ (B) I, II and III	(III) Na ₃ PO ₃ (C) II and III only	(D) III only	[NSEC-2013]	
18.	The order of acidity in ac (A) $H_2S < H_2Se < H_2Te$ (C) $H_2Te < H_2S < H_2Se$	queous solution for the fo	llowing acids is (B) $H_2Se < H_2S < H_2Te$ (D) $H_2Se < H_2Te < H_2S$		[NSEC-2014]	
19.	Upon long standing cond (A) remains colourless, I (B) turns yellow brown d (C) turns yellow brown d (D) remains colourless, I	centrated HNO ₃ but gives out NO ue to formation NO ₂ ue to the formation of N ₂ O but gives N ₂ O	D_4		[NSEC-2014]	

	-		•		-		
20.	The reaction that does n (A) heating $(NH_4)_2Cr_2O_7$ (C) heating of NaN ₃	ot produce nitrogen is	(B) NH ₃ + excess of Cl ₂ (D) heating of NH ₄ NO ₃	[NSEC-2015]			
21.	White phosphorous on r (A) Na ₂ HPO ₃	eaction with NaOH gives (B) NaH $_2$ PO $_2$	PH_3 and (C) NaH ₂ PO ₃	(D) Na ₃ PO ₄	[NSEC-2016]		
22.	P, Q, R and S are four m	netals whose typical reac	tions are given below :		[NSEC-2016]		
	(I) Only Q and R react w (II) When Q is added to formed.	metallic P, R and	I S are				
	(III) P reacts with concer The correct order of thei (A) $S < P < R < Q$	ir reducing character is : (B) S < R < P < Q	not (C) R < Q < P < S	(D) Q < P < S <	R		
23.	The following compound following statement/s is/	ds are heated (i) KNO_3 , (ii) /are correct ?	$Cu(NO_3)_2$ (iii) Pb(NO ₃) ₂ , (iv) NH₄NO₃. Whic	ch of the [NSEC-2016]		
	(A) (ii) and (iii) liberate N (C) (i), (ii) and (iii) liberat	IO ₂ te O ₂	(B) (iv) liberates N ₂ O (D) All statements are co				
24.	At 25°C, nitrogen exists as N ₂ and phosphorous exists as P ₄ because [NSEC-2017] (A) N ₂ has valence electrons only in bonding and nonbonding orbitals, while P has valence electrons in both bonding and antibonding orbitals (B) higher electronegativity of N favours formation of multiple bonds (C) bigger size of P does not favour multiple bonds (D) P has preference to adapt structures with small bond angles						
25.	Which of the following c (A) S^{2-}	annot act as an oxidising (B) Br ₂	agent ? (C) HSO4 ⁻	(D) SO ₃ ²⁻	[NSEC-2017]		
26.	The anhydride of HNO_3 i (A) NO	s (B) NO ₂	(C) N ₂ O	(D) N ₂ O ₅	[NSEC-2019]		
27.	Among the halides NCI_3 is formed with	(I), $PCI_3(II)$ and $AsCI_3(III)$,	more than one type of ac	id in aqueous sol	ution [NSEC-2019]		
	(A) I, II and III	(B) II only	(C) I and II	(D) II and III			
	PA	ART - 4 : ADDITI	ONAL PROBLEM	/IS			
	O	NLY ONE OPTIO	N CORRECT TY	PE			
1.	The compound which giv (A) Cupric oxide	ves off oxygen on modera (B) Mercuric oxide	ate heating is : (C) Zinc oxide	(D) Aluminium c	oxide		
2.	A substance dissolves in acidic medium :	n water giving a pale blue	solution which decolouris	ses KMnO ₄ and of (D) HNO	xidises KI to I ₂ in		
3.	(A) IN_2O_5 (B) INH_3 Sulphuric acid reacts with PCI_5 to give (A) Thionyl chloride (C) Sulphuryl chloride		(B) Sulphur monochlorid (D) Sulphur tetrachloride				
4.	Of the different allotrope (A) Violet phosphorus (C) Red phosphorus	es of phosphorus, the one	which is most reactive (B) Scarlet phosphorus (D) White phosphorus				
5.	Nitrogen gas is prepared (A) by heating ammoniu (C) by passing HNO_3 va	d : m nitrate. pours on red hot copper.	(B) by reacting excess chlorine with liquor ammonia. (D) by heating lead nitrate.				

6.	With respect to protonic acids, which of the following statement is correct?					
	(A) PH_{3} is more basic th	an NH ₃	(B) PH_3 is less basic than NH_3			
	(C) $PH_{_3}$ is equally basic	as NH_3	(D) PH_3 is amphoteric while NH_3 is basic.			
7.	Phosphorus is manufac (A) Bone ash and coke (C) Bone ash, silica and	tured by heating in an ele I coke	ctric furnance a mixture o (B) Bone ash and silica (D) None of these	of		
8.	Which of the following n (A) White phosphorus (C) Black phosphorus	nay ignite spontaneously	in air ? (B) Red phosphorus (D) Nitrogen			
9.	Which one of the follow	ving combines with Fe(II	I) ions to form a brown c	omplex ?		
	(A) N ₂ O	(B) NO	(C) CO	(D) SO ₂		
10.	Formula for tear gas is : (A) COCl_2	(B) CCl ₃ NO ₂	(C) N ₂ O	(D) None of these		
11.	Ortho phosphoric acid o	n heating above 300°C gi	ves:			
	(A) hypophosphorus aci	d	(B) hypophosphoric acid	t		
	(C) metaphosphoric acid	t	(D) phosphorous acid			

NUMERICAL TYPE QUESTIONS

- **12.** SOCl₂ can react with how many of the following species to liberate SO₂? H₂O, HCl, C₂H₅OH, CH₃COOH, H₂SO₄, H₃PO₄, D₂O
- Cold dil. H₂SO₄ will completely dissolve : Pb, Fe₃O₄, Fe, Cu, Mg, MgO, CoCO₃, CuCO₃, SrCO₃

COMPREHENSION

Paragraph For Questions 14 to 15

An orange solid (A) on heating gives a green residue (B), a colourless gas (C) and water vapours. The dry gas (C) on passing over heated Mg gave a white solid (D). (D) on reaction with water gave a gas (E) which formed black precipitate with mercurous nitrate solution.

- **14.** Select the incorrect statement.
 - (A) The central atom (s) of the anion of solid (A) has sp^3 hybridisation.
 - (B) The orange solid (A) is diamagnetic in nature.
 - (C) The anion of orange solid (A) is oxidising in nature.
 - (D) All metal oxygen bond lengths are equal in anion of solid (A).
- **15.** Which of the following is false for the gas (E)?
 - (A) It gives a deep blue colouration with $CuSO_4$ solution.
 - (B) It is oxidised to a colourless gas (neutral oxide) at 1200 K in presence of a catalyst Pt/Rh in air.
 - (C) It gives the same gas (C) with potassium permanganate solution.
 - (D) It gives black precipitate with HgCl₂.

MATCH THE COLUMN

Column II

16. Match the reactions listed in column-I with characteristic(s) listed in column-II.

Colum	nn I	
(A) 2NO ₂	Cool	\rightarrow

- (B) $\text{ClO}_2 + \text{O}_3 \xrightarrow{H^+}$
- (C) K_4 [Fe(CN)₆] + H_2SO_4 (conc.) + $H_2O \xrightarrow{\Delta}$
- (D) KOH + $O_3 \longrightarrow$
- (A) 1 p, q ; 2 p, q, s ; 3 r ; 4 s
- (C) 1 p ; 2 p, q, r, s ; 3 r ; 4 s

(p) One of the products is a mixed anhydride.

- (q) One of the products is an acidic oxide.
- (r) The oxidation state of the central atom of one of the products is + 6.
- (s) One of the products is a colourless paramagnetic gas.
- (B) 1 p, q ; 2 p, q, r, s ; 3 r ; 4 s
- (D) 1 p, q ; 2 q, r, s ; 3 s ; 4 r

RRP ANSWER KEY

				PA	RT- 1				
				SEC	TION-I				
1.	(A)	2.	(C)	3.	(C)	4.	(C)	5.	(C)
6.	(A)	7.	(C)	8.	(B)	9.	(C)	10.	(B)
11.	(C)	12.	(A)	13.	(C)	14.	(D)	15.	(A)
16.	(B)	17.	(B)	18.	(C)	19.	(B)	20.	(B)
				SEC	TION-II				
21.	4	22.	3	23.	3	24.2	32, O ₂	25.2	6
				PA	RT 2				
				SEC	CTION-I				
1.	(C)	2.	(D)	3.	(C)	4.	(D)		
				SEC	TION-II				
5.	(AC)	6.	(AB)	7.	(ABC)	8.	(ABC)	9.	(ABD)
10.	(BCD)	11.	(AB)	12.	(ABD)				
				SEC	TION-III				
13.	4	14.	2	15.	6	16.	5	17.	31
18.	7								

	PART - 3								
1.	(A)	2.	(A)	3.	(A)	4.	(D)	5.	(D)
6.	(C)	7.	(D)	8.	(D)	9.	(D)	10.	(C)
11.	(D)	12.	(B)	13.	(C)	14.	(B)	15.	(C)
16.	(B)	17.	(A)	18.	(A)	19.	(B)	20.	(B)
21.	(B)	22.	(A)	23.	(D)	24.	(C)	25.	(A)
26.	(D)	27.	(D)						
				PA	RT - 4				
1.	(B)	2.	(C)	3.	(C)	4.	(D)	5.	(C)
6.	(B)	7.	(C)	8.	(A)	9.	(B)	10.	(B)
11.	(C)	12.	6	13.	6	14.	(D)	15.	(D)
16.	(B)								

RRP SOLUTIONS

PART- 1

SECTION-I

1. Poor shielding by f-and d- electrons enhences the effective nuclear charge in Bi. This causes contraction in size.

3.
$$3O_2 \xrightarrow{\text{electric}} 2O_3$$

- 4. Both rhombic & monoclinic sulphur has crown shape.
- 5. Tailing of mercury.
- **6.** The order of boiling point of hydride of oxygen family is $H_2O > H_2Te > H_2Se > H_2S$.
- 7. The oxidation state of copper changes from +2 to 0 i.e. it gets reduced. So, NH₃ works as a reducing agent.

8.
$$P_4 + 3NaOH + 3H_2O \xrightarrow{\Delta} PH_3 + 3NaH_2PO_2$$

- 9. $CaO + 2C + N_2 \xrightarrow{2000^{\circ}C} CaCN_2 + CO^{\uparrow}; CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3^{\uparrow}$ (calcium cynamide)
- **10.** $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$
- **11.** $2H_2SO_4 + P_2O_5$ (dehydrating agent) $\longrightarrow 2SO_3 + 2HPO_3 + H_2O_3$
- 12. $SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$ coloured matter $\xrightarrow{\text{Reduction}}_{\text{Oxidation}}$ colourless matter.
- **13.** (C) Reducing agents can reduce $Cr_2O_7^{2-}$ to Cr^{3+} (green solution).

- 14. (A) $Ba(NO_3)_2 + H_2SO_4 \longrightarrow 2HNO_2 + BaSO_4 \downarrow$ (B) It is an unstable, weak acid which is known only in aqueous solution. (C) $2HNO_2 \longrightarrow N_2O_3 + H_2O$
- **15.** PCI_5 remains covalent in gas as well as in liquid phase but in solid exists as $[PCI_4]^+$ and $[PCI_6]^-$.
- **17.** $H_2O + OF_2 \xrightarrow{\text{very slowly}} 2HF + O_2$ (OF₂ is neutral towards litmus)
- 18. Factual
- **19.** $3S + 6NaOH \longrightarrow 3H_2O + 2Na_2S + Na_2SO_3$

20.
$$\operatorname{Na_2SO_3} + S \xrightarrow[OH]{\text{Boiling}} \operatorname{Na_2S_2O_3}$$

SECTION-II



 H_3PO_2 = monobasic

one ionisable H⁺



 $H \xrightarrow{P} OH$ OH $H_3 PO_3 = dibasic$

two ionisable H⁺



 H_3PO_4 = tribasic. three ionisable H⁺

- **23.** $Cl_2 + Na_2S_2O_3 + H_2O \rightarrow 2HCl + S + Na_2SO_4$
- **25.** Pb, Sn, Mg, MgO, Hg, Ag dissolve in cold conc. HNO_3 . Pb₃O₄ (dissolves partially, PbO₂ remains undissolved), Fe (passivated), Au (insufficient oxidising power of HNO_3), Pt (insufficient oxidising power of HNO_3).

PART 2

SECTION-I

2. (A)
$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O_1$$
 (B) $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O_1$ (C) $2NaN_3 \xrightarrow{\Delta} 3N_2 + 2Na_2$

3. The reaction of $NaNO_3$ and HCl do not give NO.

 $NaNO_3 + HCI \longrightarrow NaCI + HNO_3; \quad 4HNO_3 \longrightarrow H_2O + NO_2 + O_2$

4. (A), (B) and (C) are reducing agents while (D) is not.

SECTION-II

- 5. Factual
- (A) PH₃ is a lewis base but is neutral towards red litmus.
 (B) It does not react with HCl(aq) or HI(aq). This is because water decomposes PH₄X formed to give back PH₄.

(C) It reacts only with anhydrous HI or HBr.

(D) $2Na_3P + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 2PH_3\uparrow$; $Ca_3P_2 + 6HCI \longrightarrow 3CaCl_2 + 2PH_3$

- 7. Nitrogen can not form $p\pi$ -d π bond because nitrogen has no d-orbitals.
- 8. P_2O_5 reacts with H_2SO_4 , HNO_3 , $HCIO_4$.
- **9.** At 415 K ; $3H_3PO_2 \longrightarrow 2H_3PO_3 + PH_3 \uparrow$
- **10.** $4AgNO_3 + 2H_2O + H_3PO_2 \longrightarrow 4Ag + 4HNO_3(X) + H_3PO_4(Y)$
- **11.** $SCI_2 \xrightarrow{NaH} H_2S \uparrow \underline{CuSO_4} CuS \downarrow black precipitate$

SECTION-III

- 13. NO is evolved with Pb, Sb, Ag, P_4 . NH₄NO₃ is formed and no gas is evolved with Mg, Fe, Mn, Sn. No reaction with Au.
- **14.** $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$; $Pb(NO_3)_2 \xrightarrow{\Delta} PbO + NO_2 + O_2$

15. $CaCl_2 + NaPO_3 \longrightarrow$ Forms chelate complex with Ca^{2+} , $[Ca(P_3O_9)_2]^{4-}$, used in softening of hard water. $MgSO_4 + NaPO_3 \longrightarrow$ Forms chelate complex with Mg^{2+} , $[Mg(P_3O_9)_2]^{4-}$, used in softening of hard water. $CaO + NaPO_3 \longrightarrow NaCaPO_4$ $Na_2CO_3 + NaPO_3 \longrightarrow Na_3PO_4 + CO_2$ $dry HCl + NaPO_3 \longrightarrow No reaction$ $Ca(HCO_3)_2 + NaPO_3 \longrightarrow$ Forms chelate complex with Ca^{2+} , $[Ca(P_3O_9)_2]^{4-}$ used in softening of hard water. $Na_3PO_4 + NaPO_3 \longrightarrow Na_4P_2O_7$

- **16.** $PCI_3 + 3H_2O \longrightarrow \underbrace{H_3PO_3}_{(dibasic)} + 3HCI \therefore$ Total 5 moles of NaOH required.
- **17.** $Na_2S_2O_3.5H_2O + CuCl_2 \longrightarrow Na_4[Cu_6(S_2O_3)_5]$

soluable complex

Number of atom in Co-ordination sphere = $6 + 2 \times 5 + 3 \times 5 = 6 + 10 + 15 = 6 + 25 = 31$ Ans.

18. (i) $PCI_3 + O_2 \longrightarrow POCI_3$ (iii) $PCI_5 + CH_3COOH \longrightarrow CH_3COCI + POCI_3 + HCI$ (v) $PCI_3 + SO_2CI_2 \longrightarrow PCI_5 + SO_2$ (vii) $PCI_5 + H_2O \longrightarrow POCI_3 + 2HCI$ (ix) $PCI_3 + SO_3 \longrightarrow POCI_3 + SO_2$

(ii) $PCl_5 + CO_2 \longrightarrow No \text{ reaction.}$ (iv) $PCl_5 + H_3BO_3 \longrightarrow POCl_3 + B_2O_3$ (vi) $P_4O_{10} + NaCl \longrightarrow POCl_3 + NaPO_3$ (viii) $PCl_5 + SO_2 \longrightarrow SOCl_2 + POCl_3$

PART - 3

- 5. Red phosphorus do not show phosphorescence.
- 8. In stratosphere chlorofluorocarbons get broken down by UV radiations, releasing chlorine free radical. Which react with ozone to form chlorine monooxide radical and O₂.

$$\begin{array}{ccc} \mathsf{CF}_2\mathsf{CI}_{2(g)} & \underbrace{\mathsf{UV}} & \mathsf{CI}^{\bullet}_{(g)} + & \mathsf{C}^{\bullet}\mathsf{F}_2\mathsf{CI}_{(g)} \\ \\ \mathsf{CI}^{\bullet}_{(g)} + & \mathsf{O}_{3(g)} & \longrightarrow & \mathsf{CIO}^{\bullet}_{(g)} + & \mathsf{O}_{2(g)} \end{array}$$

- **9.** Disproportionation reaction.
- 11. In our opinionCa(CN)₂ is not likely to react significantly with hot water. The only possible reaction would be. Ca(CN)₂ + 2H–OH \implies Ca(OH)₂ + 2HCN[↑]

HCN might have been hydrolysed to HCOOH + NH_4^+ in acidic medium. But the given reaction proceeds basic medium, hence this is unlikely.

It seems that the examiner might have intended the hydrolysis of CaNCN (Calcium cyanamide), also written as $CaCN_2$. The bracket { $Ca(CN)_2$ } was placed by mistake since oxides of nitrogen are simply impossible to obtain by such a hydrolysis reaction.

formation of nitrogen oxides would involve oxidation of nitrogen (-3 in CN⁻ to +1 in N₂O) H₂O is no oxidant. Hence D is only possible answer but official answer given A.

- 12. Most abundant element is earth crust is oxygen
- **13.** However B and Si also exist as covalent network solid which demonstrates their excellent tedency to catenate (compare B_{12} with S_8 ; or diamond -like Si)
- **14.** Nitrous oxide (N_2O) is a laughing gas.
- **15.** $P_4 + P_4$ $3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$ (White) ($\overline{(Wbc)}$)
- **16.** $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + heat, exothermic therefore low temperature and as molecules are decreasing from L <math>\rightarrow$ R therefore high pressure are suitable conditions.
- **17.** H_3PO_3 is dibasic so $NaH_2PO_3 \& Na_2HPO_3$ both exist.

PART - 4

- 1. 2HgO $\xrightarrow{450^{\circ}\text{C}}$ 2Hg + O₂
- 2. $N_2O_3 + H_2O \longrightarrow HNO_2$; $2KMnO_4 + 5 KNO_2 + 6HCI \longrightarrow 2MnCl_2 + 5KNO_3 + 3H_2O + 2KCI$ $2KI + 2HNO_2 + 2HCI \longrightarrow 2H_2O + 2NO + 3KCI + I_2$
- **3.** $2PCl_5 + H_2SO_4 \longrightarrow SO_2Cl_2 + 2POCl_3 + 2HCl$
- 5. (A) $(NH_4)NO_3$ gives N_2O_2 , (B) chlorine (excess) with liquor NH_3 forms NCI_3 and (D) $Pb(NO_3)_2$ gives NO_2 not N_2 on heating.

(C) 5Cu (red hot) + 2HNO₃ \longrightarrow 5CuO + N₂ \uparrow + H₂O

- **6.** PH₃ is less basic than NH₃ due to lesser availability of lone pair of electrons. The lone pair of electron is present in spherical s-orbital as compared to directional sp³ hybrid orbital in NH₃.
- 7. $2Ca_3(PO_4)_2$ (from bone-ash) + 10C + $6SiO_2 \xrightarrow{\Delta} 6CaSiO_3 + 10CO + P_4(s)$ white phosphorus

8. Factual

- 9. $Fe^{2+} + NO + 5H_2O \longrightarrow [Fe(H_2O)_5NO]^{2+}$ (brown complex).
- **10.** $CHCl_3$ (chloroform) react with conc. HNO_3 on heating to form chloropicrin (CCl_3NO_2) $CHCl_3 + HONO_2 \longrightarrow CCl_3$. $NO_2 + H_2O$

Chloropicrin

Chloropicrin is used as an insecticide and also war gas. It is also known as nitrochloroform or tear gas.

11.
$$H_3PO_4 \xrightarrow{220^{\circ}C} H_4P_2O_7 \xrightarrow{320^{\circ}C} (HPO_3)_n$$

- 12. Except HCl, it will react with all other compounds, replacing OH–group by Cl–group.
- **13.** Pb, Cu, SrCO₃ (fail to dissolve). Remaining can dissolve Fe_3O_4 , Fe, Mg, MgO, CoCO₃, CuCO₃.

14.
$$A = (NH_4)_2 Cr_2 O_7$$



 $Cr_2O_7^{2-}$ acts as strong oxidising agent in acidic medium.

(A) $Cu^{2+} + 4NH_{3} \longrightarrow [Cu(NH_{3})_{4}]^{2+}$ (deep blue colouration).

(D) $HgCl_2 + NH_3 + H_2O \longrightarrow HgO.Hg(NH_2)Cl \downarrow (white)$

16. (A) $2NO_2 \xrightarrow{Cool} N_2O_4$ colourless solid / liquid, acidic, mixed anhydride of HNO_2 and HNO_3

(B)
$$2CIO_2 + 2O_3 \xrightarrow{H^+} CI_2O_6$$
 (yellow solid) + $2O_2$; acidic, mixed anhydride of HCIO₃ and HCIO₄.

(C)
$$K_4 [Fe(CN)_6] + 6H_2O + 6H_2SO_4 \xrightarrow{\Delta} 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO^{\uparrow}$$

(D)
$$2KOH + 5O_3 \longrightarrow 2KO_3$$
 (orange solid) $+ 5O_2 + H_2O_3$