

p-Block Elements (Nitrogen and Oxygen Family)

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

Group 15 Elements : The nitrogen family

1. Occurrence :

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

2. Atomic & physical properties :

ATOMIC & PHYSICAL PROPERTIES

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

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

Nitrogen { Non metals **Arsenic** } **Phosphorus** { **Antimony** } **Metalloid** **Bismuth** {Typical metal}

(i) **Electronic Configuration** : The valence shell electronic configuration of these elements is ns^2np^3 . The s orbital in these elements is completely filled and p orbitals are half-filled, making their electronic configuration extra stable.

(ii) **Atomic and Ionic Radii** : Covalent and ionic (in a particular state) radii increase in size down the group. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled d and / or f orbitals in heavier members.

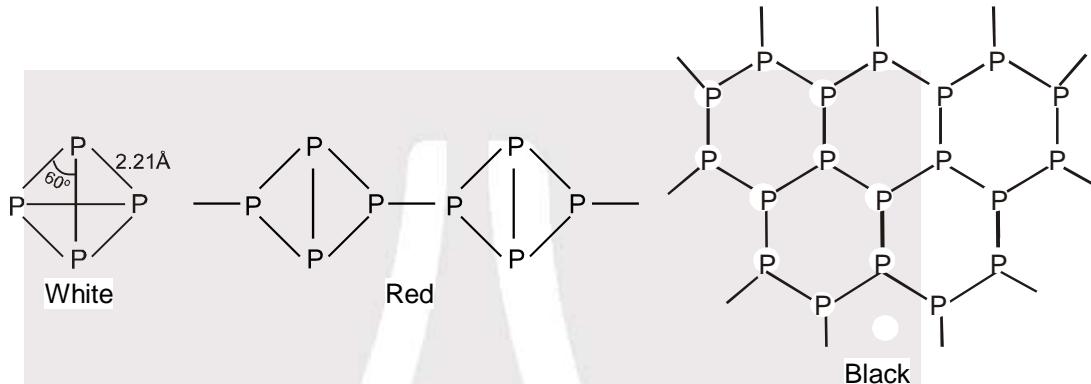
(iii) **Ionisation Enthalpy** :

- Ionisation enthalpy decreases down the group due to gradual increase in atomic size because of the extra stable half-filled p-orbital electronic configuration and smaller size.
- The ionisation enthalpy of the group 15 element is much greater than of group 14 elements in the corresponding periods. The order of successive ionisation enthalpies, as expected is $\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3$

(iv) **Electronegativity** : The electronegativity value, in general, decreases down the group with increasing atomic size. However, amongst the heavier elements, the difference is not that much pronounced.

(v) **Physical Properties :**

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

3. Allotropy3.1. **Nitrogen** : does not show allotropy3.2. **Phosphorus** : 3 types of allotropes: white, red and black.

Properties	White-P	Red-P
Physical state	Soft waxy solid	Brittle powder
Colour	White when pure. Attains yellow colour on standing	Red
Odour	Garlic	Odourless
Melting point	44°C	Sublimes in absence of air at 290°C
Physiological Action	Highly Poisonous	Non-Poisonous
Solubility in water	Insoluble	Insoluble
Solubility in CS_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_4O_{10}	From P_4O_{10}
Reaction with NaOH	Evolves phosphine	No action
Reaction with hot HNO_3	Forms H_3PO_4	Forms H_3PO_4

White Phosphorus :The P_4 molecules is tetrahedral in shape.

It remains in both liquid and gaseous states.

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

It is stored under water.

Above 800°C it dissociates to P_2 .Due to slow oxidation in dark it glows. This phenomenon is known as **phosphorescence**

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

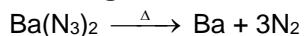
Red Phosphorus :

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

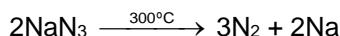
**(b) Industrial preparation :**

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

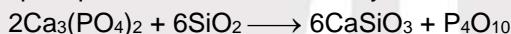
(ii) From producer gas from furnaces: Producer gas is a mixture of CO and N_2 . When the mixture of CO and N_2 is passed over heated CuO , the CO gas is oxidized to CO_2 which is absorbed in alkalies & N_2 remains which is collected in gas cylinders.

(c) Very pure nitrogen :

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

**4.2. Phosphorous :**

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

**Physical Properties of Nitrogen & Phosphorus**

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

Solved Examples

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

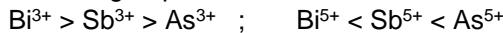
Sol. Thermal decomposition of sodium azide gives dinitrogen gas. $2NaN_3 \longrightarrow 2Na + 3N_2$.

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

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

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

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



- The only well characterised Bi (V) compound is BiF_5 .
- Apart from these oxidation states nitrogen exhibits a large number of oxidation states from -3 to $+5$.

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

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



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

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

- Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and -3 both in alkali and acid medium. However +3 oxidation state in case of arsenic, antimony and bismuth become increasingly stable with respect to disproportionation.
- Nitrogen is restricted to a maximum covalency of 4 since only four (one s and three p) orbitals are available for bonding.
- The heavier elements have vacant d orbitals in the outermost shell which can be used for bonding (covalency) and hence, expand their covalence as in PF_6^- .

(ii) Reactivity towards hydrogen (hydrides) :

All the elements of Group 15 form hydrides of the type EH_3 where E = N, P, As, Sb or Bi.

All these hydrides are colourless poisonous gases. The poisonous nature increases from NH_3 to BiH_3 .

Table : Properties of Hydrides of Group 15 Elements

Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
m.p./K	195.2	139.5	156.7	185	-
b.p./K	238.5	185.5	210.6	254.6	290
H-E distance/pm	101.7	141.9	151.9	170.7	-
HEH angle (°)	107.8	93.6	91.8	91.3	-
$\Delta_f H^\circ/\text{kJ mol}^{-1}$	-46.1	13.4	66.4	145.1	278
$\Delta_{\text{diss}} H (\text{H-E})/\text{kJ mol}^{-1}$	389	322	297	255	-

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

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

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

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

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

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

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

(iii) Reactivity towards oxygen :

- All these elements form two types of oxides : E_2O_3 and E_2O_5 .
- The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state.
- Their acidic character decreases down the group.
- The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and that of bismuth is predominantly basic.
- The oxides in lower oxidation state (i.e. +3) will act as reducing reagents and their reduction power decreases from nitrogen to bismuth
- The oxides in higher oxidation state (i.e. +5) will act as oxidising agents and their oxidation power should increase from nitrogen to bismuth as their stability of +5 oxidation state decreases from nitrogen to bismuth but N (V) and Bi (V) are strong oxidising agents than the intervening three elements.
- The solubility of oxides in water decreases from nitrogen to bismuth.

Table : Oxides of the group 15 elements

Element	Trioxide	Pentoxide
Nitrogen	N_2O_3	N_2O_5
Phosphorus	P_4O_6	P_4O_{10}
Arsenic	As_2O_6	As_2O_{10}
Antimony	Sb_2O_6	Sb_2O_{10}
Bismuth	Bi_2O_3	-

(iv) **Reactivity towards halogens :**

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

Table : Halides of the group 15 elements

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

(v) **Reactivity towards metals :**

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

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

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

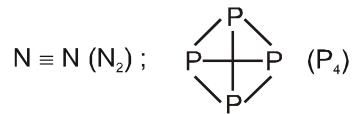


Solved Examples

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

Sol. In the form of elemental nitrogen it exists as a diatomic molecule (N_2).

This is due to the fact that nitrogen can form $p\pi$ - $p\pi$ multiple bond ($N=N$) because of small size of nitrogen atom. Heavier elements of this group do not form $p\pi$ - $p\pi$ bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping. Further P-P single bond is stronger than N-N single bond. Hence phosphorus has tendency to undergo catenation.



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

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

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

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

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

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

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

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

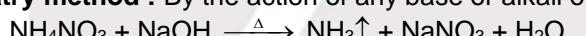
Section (C) : Compounds of Nitrogen (Hydrides, Oxides & Oxyacids)

6. Hydrides :

6.1. Ammonia (NH_3)

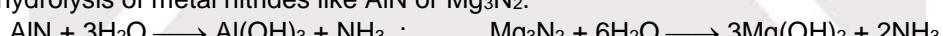
6.1.1 PREPARATION:

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



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

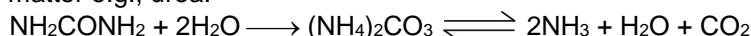
(ii) By the hydrolysis of metal nitrides like AlN or Mg_3N_2 .



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

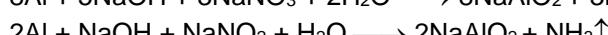
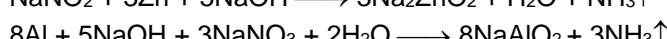
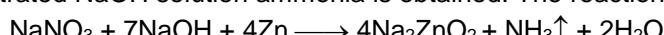


(iv) Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.



(v) Quantitative estimation of nitrogen :

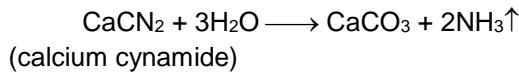
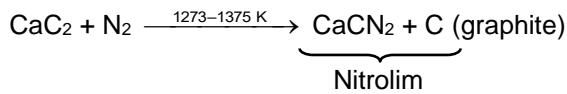
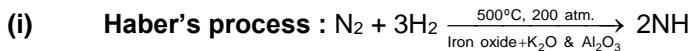
From nitrates and nitrites: When a metal nitrate or nitrite is heated with zinc powder or aluminium and concentrated $NaOH$ solution ammonia is obtained. The reactions are





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

Industrial methods of preparation :



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

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

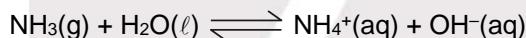
The liquor ammonia is a concentrated solution of ammonia and ammonium salts. When heated it gives out ammonia. When all the free NH_3 is obtained, the residual liquid is heated with $Ca(OH)_2$ when ammonium salts get decomposed to liberate further quantity of ammonia.

6.1.2. Physical properties :

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

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

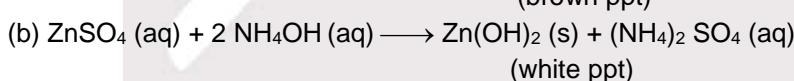
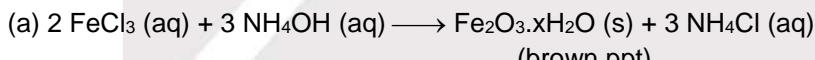
(iii) Ammonia gas is highly soluble in water. Its aqueous solution is weakly basic due to the formation of OH^- ions.



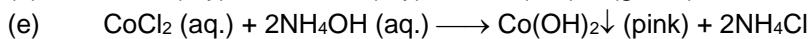
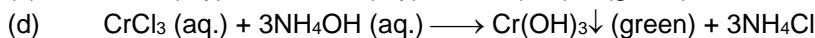
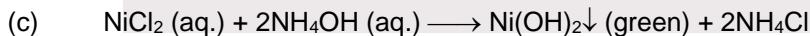
6.1.3. Chemical properties :

(i) **NH_3 as weak base :**

It forms ammonium salts with acids, e.g., NH_4Cl , $(NH_4)_2SO_4$ etc. As a weak base, it precipitates the hydroxides of many metals from their salt solutions. For example ,



White precipitate is soluble in excess of ammonia solution forming $[Zn(NH_3)_4]^{2+}$, soluble complex.

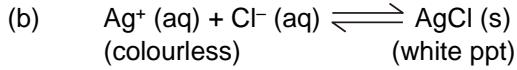
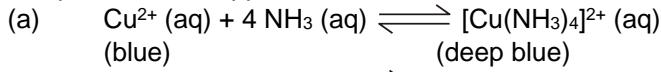


$Cr(OH)_3$ (precipitate) is partially soluble in excess ammonia whereas

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

(ii) **Complex formation by NH_3 :**

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



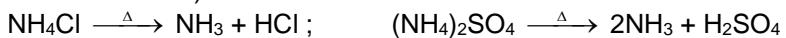


(c) $\text{AgCl}(\text{s}) + 2\text{NH}_3(\text{aq}) \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl}(\text{aq})$
(white ppt) (colourless)

(d) $\text{Cd}^{2+}(\text{aq}) + 4\text{NH}_3(\text{aq}) \longrightarrow [\text{Cd}(\text{NH}_3)_4]^{2+}(\text{aq})$
(colourless)

(iii) Thermal decomposition 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.

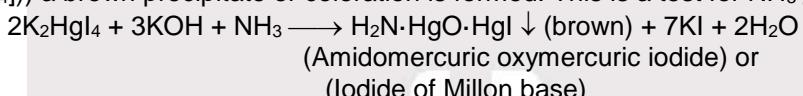


If the anion is more oxidising (e.g. NO_2^- , NO_3^- , ClO_4^- , $\text{Cr}_2\text{O}_7^{2-}$) then NH_4^+ is oxidised to N_2 or N_2O .



(iv) Test of Ammonia and Ammonium salts :

When NH_3 gas is passed into the colourless solution of Nessler's reagent (Alkaline solution of $(\text{K}_2[\text{HgI}_4])$) a brown precipitate or coloration is formed. This is a test for NH_3 gas.



(v) Reaction with Halogens :

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



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



6.1.4. USES OF NH_3 :

- Used as a refrigeration fluid.
- For the production of nitrogenous fertilizers such as ammonium sulphate, ammonium phosphate, ammonium nitrate, urea etc.
- For removing grease because NH_4OH dissolves grease.
- For manufacture of HNO_3 by the Ostwald process.
- As a laboratory reagent.
- In the production of artificial rayon, silk, nylon etc. in the form of tetraamine copper(II) sulphate (Schweitzer's reagent)

Solved Examples

Ex-8. What happens when:

(a) NH_4Cl & NaNO_3 is heated strongly. (b) $(\text{NH}_4)_2\text{CO}_3$ is heated. (c) NH_4NO_2 is heated.

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

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

7.1. Oxides of nitrogen

S.N. / Compounds	Preparation	Properties
1. N_2O (Nitrous Oxide)	$\text{NH}_4\text{NO}_3 \xrightarrow{280^\circ\text{C}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$	Stable, relatively unreactive, colourless gas and a neutral oxide. Used as an anaesthetic and called laughing gas.
2. NO (Nitric)	Laboratory method: (i) $3\text{Cu} + 8\text{HNO}_3 \rightarrow 2\text{NO} + 3\text{Cu}(\text{NO}_3)_2 + 4\text{H}_2\text{O}$	Colourless gas, an important intermediate in manufacturing of nitric acid by Ostwald process. Neutral oxide, not an acid anhydride.



Oxide)	(ii) $2\text{HNO}_2 + 2\text{I}^- + 2\text{H}^+ \rightarrow 2\text{NO} + \text{I}_2 + 2\text{H}_2\text{O}$	Reacts instantly with O_2 to give NO_2 $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ $3\text{NO} \xrightarrow[\text{30 - 50}^\circ\text{C}]{\text{High pressure}} \text{N}_2\text{O} + \text{NO}_2$
3. N_2O_3 [Dinitrogen trioxide]	By condensing equimolar amounts of NO and NO_2 together or by reacting NO with appropriate amount of O_2 . $\text{NO} + \text{NO}_2 \rightarrow \text{N}_2\text{O}_3$ $4\text{NO} + \text{O}_2 \rightarrow 2\text{N}_2\text{O}_3$	Blue solid, acidic oxide and anhydride of HNO_2 . With alkali forms nitrites $\text{N}_2\text{O}_3 + \text{NaOH} \rightarrow 2\text{NaNO}_2 + \text{H}_2\text{O}$ $\text{N}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{HNO}_2$
4. [Nitrogen dioxide] and N_2O_4	Laboratory method: $2\text{Pb}(\text{NO}_3)_2 \rightarrow 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$ $\text{Cu} + 4\text{HNO}_3 \xrightarrow[\text{(conc.)}]{\text{Cu}} \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$ $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ Paramagnetic Brown Diamagnetic colourless	Red-brown poisonous gas, very reactive, dimerizes into colourless N_2O_4 . Mixed anhydride as it reacts with water to give nitric and nitrous acids. $\text{N}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_2$ $\text{NO}_2 - \text{N}_2\text{O}_4$ system is a strong oxidizing agent
5. N_2O_5 (Dinitrogen pentoxide)	Prepared by carefully dehydrating HNO_3 with P_2O_5 at low temperature $4\text{HNO}_3 + \text{P}_4\text{O}_{10} \rightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$	Colourless deliquescent solid, highly reactive, strong oxidizing agent Anhydride of HNO_3 . In gas phase, decomposes into NO_2 , NO and O_2

Table : Structures of Oxides of Nitrogen

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

Formula	Resonance Structures	Bond Parameters
N_2O	$\ddot{\text{N}}=\text{N}=\text{O} \longleftrightarrow \ddot{\text{N}}=\text{N}-\ddot{\text{O}}\ddot{\text{N}}$	$\text{N}-\text{N}-\text{O}$ 113pm 119pm Linear
NO	$\ddot{\text{N}}=\ddot{\text{O}} \longleftrightarrow \ddot{\text{N}}=\ddot{\text{O}}$	$\text{N}-\text{O}$ 115pm
N_2O_3		
NO_2		
N_2O_4		
N_2O_5		



Solved Examples

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

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

Sol. $\text{NH}_4\text{NO}_3 + \text{NaOH} \xrightarrow{\Delta} \text{NH}_3 + \text{NaNO}_3 + \text{H}_2\text{O}$; $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$ (white fumes)
 $\text{NaNO}_3 + 7\text{NaOH} + 4\text{Zn} \rightarrow 4\text{Na}_2\text{ZnO}_2 + \text{NH}_3 \uparrow + 2\text{H}_2\text{O}$
 $\text{NH}_4\text{NO}_3 \xrightarrow{\Delta} \text{N}_2\text{O} + 2\text{H}_2\text{O}$
 So, (A) = NH_4NO_3 , (B) = NH_3 , (C) = NaNO_3 , (D) = N_2O and (E) = H_2O .

Ex-10. NO_2 can not be dried by an alkali, why ?

Sol. NO_2 being acidic in nature is absorbed by alkali.

8.1 OXY ACIDS OF NITROGEN :

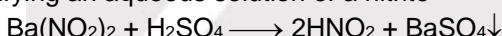
(N atom sp^2 hybridised)

1.	HNO_3	Nitric acid (Colourless)	
2.	HNO_2	Nitrous acid (Pale blue)	
3.	$\text{H}_2\text{N}_2\text{O}_2$	Hyponitrous acid	
4.	HNO_4 or $\text{HNO}_2(\text{O}_2)$	Pernitric acid or Peroxy nitric acid	
5.	$\text{HNO}(\text{O}_2)$	Peroxy nitrous acid	

8.1.1 NITROUS ACID (HNO_2) :

PREPARATION :

By acidifying an aqueous solution of a nitrite



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.

$$3\text{HNO}_2 \rightarrow \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}$$
- (iii) Nitrous acid and nitrites are good oxidizing agents and convert iodides to iodine, ferrous salts to ferric, stannous to stannic and sulphites to sulphates eg.

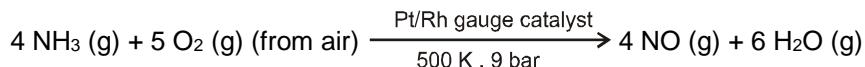
$$2\text{KI} + 2\text{HNO}_2 + 2\text{HCl} \rightarrow 2\text{H}_2\text{O} + 2\text{NO} + 2\text{KCl} + \text{I}_2$$
- (iv) With strong oxidizing agents like KMnO_4 nitrous acid and nitrites function as reducing agents and get oxidized to NO_3^- ions: $2\text{KMnO}_4 + 5\text{KNO}_2 + 6\text{HCl} \rightarrow 2\text{MnCl}_2 + 5\text{KNO}_3 + 3\text{H}_2\text{O} + 2\text{KCl}$

8.1.2 NITRIC ACID (HNO_3) :

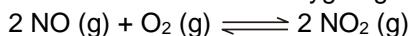
PREPARATION :

- (i) **In the laboratory :**
 Nitric acid is prepared by heating KNO_3 or NaNO_3 and concentrated H_2SO_4 in a glass retort.

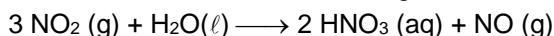
$$\text{NaNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HNO}_3$$
- (ii) On a large scale it is prepared mainly by Ostwald's process.
 This method is based upon catalytic oxidation of NH_3 by atmospheric oxygen.



Nitric oxide thus formed combines with oxygen giving NO_2 .



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



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

Physical properties :

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

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

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



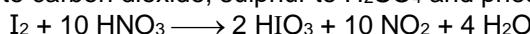
Chemical properties :

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

Table-4 : Reactions of Elements (Metals/Metalloids with HNO_3)

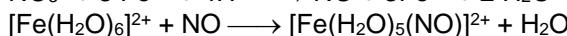
Element	Nature of HNO_3	Changes to	Reactions
(A) Metals placed above H in electrochemical series (ECS)			
1. Mg, Mn	cold and dilute	$\text{M}(\text{NO}_3)_2$	$\text{M} + 2\text{HNO}_3 \rightarrow \text{M}(\text{NO}_3)_2 + \text{H}_2$
2. Zn, Fe	(a) very dilute	NH_4NO_3	$4\text{Zn} + 10\text{HNO}_3 \rightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$
	(b) dilute	N_2O	$4\text{Zn} + 10\text{HNO}_3 \rightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{N}_2\text{O} + 5\text{H}_2\text{O}$
	(c) concentrated	NO_2	$\text{Zn} + 4\text{HNO}_3 \rightarrow \text{Zn}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
3. Sn	(a) dilute	NH_4NO_3	$4\text{Sn} + 10\text{HNO}_3 \rightarrow 4\text{Sn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$
	(b) concentrated	NO_2	$\text{Sn} + 4\text{HNO}_3 \rightarrow \text{H}_2\text{SnO}_3 + 4\text{NO}_2 + \text{H}_2\text{O}$ meta stannic acid
4. Pb	(a) dilute	NO	$3\text{Pb} + 8\text{HNO}_3 \rightarrow 3\text{Pb}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$
	(b) concentrated	NO_2	$\text{Pb} + 4\text{HNO}_3 \rightarrow \text{Pb}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
(B) Metals below H in ECS			
5. Cu, Ag, Hg	(a) dilute	NO	$3\text{Cu} + 8\text{HNO}_3 \rightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$. Hg forms $\text{Hg}_2(\text{NO}_3)_2$
	(b) concentrated	NO_2	$\text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
(C) Metalloids			
Sb, As	concentrated	NO_2	$\text{Sb} + 5\text{HNO}_3 \rightarrow \text{H}_3\text{SbO}_4 + 5\text{NO}_2 + \text{H}_2\text{O}$ antimonic acid

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



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.



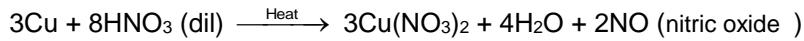
**USES OF HNO₃ :**

- (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 Examples

Ex-11. Illustrate how copper metal can give different products on reaction with HNO₃.

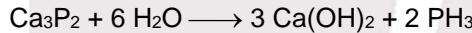
Sol. On heating with dil. HNO₃, copper gives copper nitrate and nitric oxide.



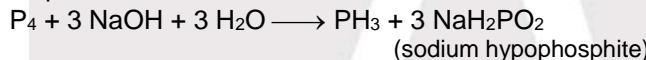
With conc. HNO₃, instead of NO, NO₂ is evolved.

**Section (D) : Compounds of Phosphorous (Hydride, Halides, Oxides & Oxyacids)****9. HYDRIDE****9.1. PHOSPHINE (PH₃) :****9.1.1 PREPARATION :**

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



(ii) In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO₂.

**9.1.2. PROPERTIES :**

(i) It is a colourless gas with a slightly garlic or rotten fish smell.

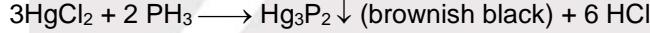
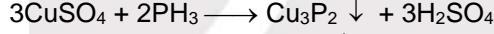
(ii) It is highly poisonous.

(iii) It explodes in contact with traces of oxidising agents like HNO₃, Cl₂ and Br₂ vapours.

(iv) It is slightly soluble in water but soluble in CS₂ and other organic solvents.

(v) The solution of PH₃ in water decomposes in presence of light giving red phosphorus and H₂.

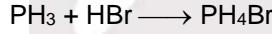
(vi) When absorbed in copper sulphate or mercuric chloride, the corresponding phosphides are obtained.



(vii) On reaction with silver nitrate, decomposes to black Ag.



(viii) Phosphine is weakly basic and like ammonia. Phosphonium compounds are obtained when anhydrous phosphine reacts with anhydrous halogen acids.

**9.1.3. USES OF PH₃ :**

(i) The spontaneous combustion of phosphine is technically used in Holme's signals.

(ii) Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.

(iii) It is also used in the production of smoke screens. Calcium phosphide reacts with water producing phosphine which burns in air to give clouds of phosphorus pentoxide and that acts as smoke screens.

Solved Examples

Ex-12. What happens ?

(a) When phosphine is heated at 150°C.

(b) When phosphine is dissolved in water in presence of light.

Sol. (a) Phosphine on heating at 150°C burns forming H₃PO₄ $\text{PH}_3 + 2\text{O}_2 \longrightarrow \text{H}_3\text{PO}_4$

(b) The solution of PH₃ in water decomposes in presence of light giving red phosphorus and H₂.

9.2. OXIDES OF PHOSPHORUS :

Table : Oxides of phosphorus

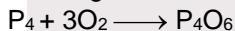
P_4O_6		P–O bond length shows that the bridging bonds on the edges are 1.65 Å and are normal single bonds. There is no P–P bonds.
P_4O_{10}		The P–O bond lengths shows that the bridging bonds on the edges are 1.60 Å but the P=O bonds on the corners are 1.43 Å and this P=O is formed by $p\pi-d\pi$ back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

9.2.1. PHOSPHORUS TRIOXIDE (P_2O_3) :

It is dimeric and has formula P_4O_6

PREPARATION :

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



PROPERTIES :

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

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

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

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

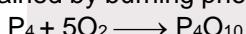
$$P_4O_6 + 5Cl_2 \longrightarrow 2POCl_3 + 2PO_2Cl$$

9.2.2 PHOSPHORUS PENTAOXIDE (P_4O_{10}) :

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

PREPARATION :

It is obtained by burning phosphorus in excess air.



PROPERTIES:

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

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

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

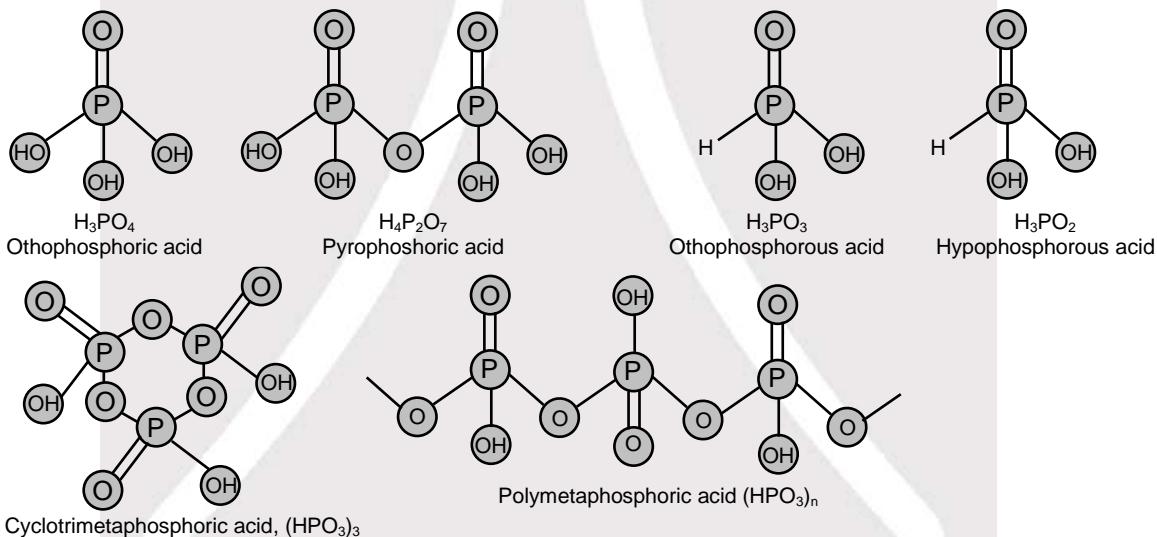
$$P_4O_{10} + 6CaO \longrightarrow 2Ca_3(PO_4)_2$$

USES OF P_4O_{10} :

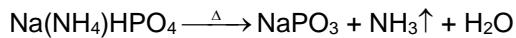
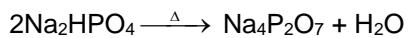
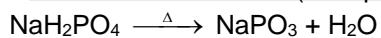
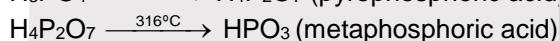
1. For drying acidic gases.	2. As a dehydrating agent
3. For the preparation of SO_3 and N_2O_5 .	4. For the preparation of phosphoric acid.

9.3. Oxy acids of phosphorous:

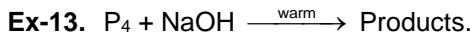
Name	Formula	Oxidation	Characteristic	Preparation
Hypophosphorous (Phosphinic)	H_3PO_2	+1	One P-OH Two P-H One P=O	White P_4 + alkali
Orthophosphorous (Phosphinic)	H_3PO_3	+3	Two P-OH One P-H One P=O	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+3	Two P-OH Two P-H Two P=O	$PCl_3 + H_3PO_3$
Hypophosphoric	$H_4P_2O_6$	+4	Four P-OH Two P=O One P-P	Red P_4 + alkali
Orthophosphoric	H_3PO_4	+5	Three P-OH One P=O	$P_4O_{10} + H_2O$
Pyrophosphoric	$H_4P_2O_7$	+5	Four P-OH Two P=O One P-O-P	Heating phosphoric acid
Metaphosphoric	$(HPO_3)_n$	+5	Three P-OH Three P=O Three P-O-P	Phosphorus acid + Br_2 , heat in a sealed tube



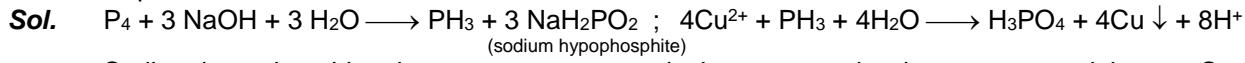
Action of heat on phosphoric acid and its salts :



Solved Examples



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



Sodium hypophosphite also acts as a strong reducing agent and reduces copper sulphate to Cu_2H_2 .



Ex-14. (i) Sodium salt of an acid (A) is formed on boiling white phosphorus with NaOH solution.
(ii) On passing chlorine through phosphorus kept fused under water, another acid (B) is formed.
(iii) Phosphorus on treatment with concentrated HNO_3 gives an acid (C) which is also formed by the action of dilute H_2SO_4 on powdered phosphorite rock.
(iv) (A) on treatment with a solution of HgCl_2 first gives a white precipitate of compound (D) and then a grey precipitate of (E). Identify (A) to (E) and write balanced chemical equations for the reactions at steps (i) to (iv).

Ans. (A) NaH_2PO_2 ; (B) H_3PO_3 ; (C) H_3PO_4 ; (D) Hg_2Cl_2 ; (E) Hg

Sol. The given changes are :

(i) $\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow 3\text{NaH}_2\text{PO}_2$ (sodium hypophosphite) + PH_3
Thus acid (A) is H_3PO_2 , i.e., hypophosphorus acid.

(ii) $2\text{P} + 3\text{Cl}_2 + 6\text{H}_2\text{O} \longrightarrow 2\text{H}_3\text{PO}_3$ (phosphorus acid) + 6HCl
Thus, acid (B) is H_3PO_3

(iii) $\text{P}_4 + 20\text{HNO}_3 \longrightarrow 4\text{H}_3\text{PO}_4$ (C) + $20\text{NO}_2 + 4\text{H}_2\text{O}$
 $\text{P}_4 + 10\text{H}_2\text{SO}_4 \longrightarrow 4\text{H}_3\text{PO}_4$ (C) (phosphoric acid) + $10\text{SO}_2 + 4\text{H}_2\text{O}$
Thus, acid (C) is H_3PO_4

(iv) $\text{H}_3\text{PO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_4 + 4\text{H}$
 $\text{HgCl}_2 + 2\text{H} \longrightarrow \text{Hg}_2\text{Cl}_2$ (D) (white) + 2HCl ; $\text{Hg}_2\text{Cl}_2 + 2\text{H} \longrightarrow 2\text{Hg}$ (E) (grey) + 2HCl

10. HALIDES AND OXYHALIDES

Phosphorus forms two types of halides, PX_3 [X = F, Cl, Br, I] and PX_5 [X = F, Cl, Br]

10.1. Phosphorus Trichloride :

10.1.1 Preparation :

(i) It is obtained by passing dry chlorine over heated white phosphorus.
 $\text{P}_4 + 6\text{Cl}_2 \longrightarrow 4\text{PCl}_3$

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

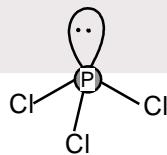
10.1.2 Properties :

(i) It is a colourless oily liquid and hydrolyses in the presence of moisture.
 $\text{PCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_3 + 3\text{HCl}$

(ii) It reacts with organic compounds containing -OH group such as CH_3COOH , $\text{C}_2\text{H}_5\text{OH}$.
 $3\text{CH}_3\text{COOH} + \text{PCl}_3 \longrightarrow 3\text{CH}_3\text{COCl} + \text{H}_3\text{PO}_3$
 $3\text{C}_2\text{H}_5\text{OH} + \text{PCl}_3 \longrightarrow 3\text{C}_2\text{H}_5\text{Cl} + \text{H}_3\text{PO}_3$

(iii) It also acts as a reducing agent when treated with SO_3 , conc. H_2SO_4 and Sulphur chloride
 $\text{PCl}_3 + \text{SO}_3 \longrightarrow \text{POCl}_3 + \text{SO}_2$
 $\text{PCl}_3 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{SO}_3\text{HCl} + \text{SO}_2 + 2\text{HCl} + \text{HPO}_3$
 $3\text{PCl}_3 + \text{S}_2\text{Cl}_2 \longrightarrow \text{PCl}_5 + 2\text{PSCl}_3$

Structure :

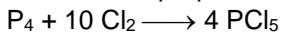


Pyramidal structure of PCl_3

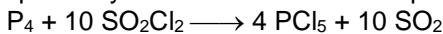
10.2. Phosphorus pentachloride :

10.2.1 Preparation :

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



It can also be prepared by the action of SO_2Cl_2 on phosphorus.





10.2.2 Properties :

(i) PCl_5 is a yellowish white powder and in moist air, it hydrolyses to POCl_3 and finally gets converted to phosphoric acid.

$$\text{PCl}_5 + \text{H}_2\text{O} \longrightarrow \text{POCl}_3 + 2 \text{HCl}$$

$$\text{POCl}_3 + 3 \text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_4 + 3 \text{HCl}$$

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

$$\text{PCl}_5 \xrightarrow{250^\circ\text{C}} \text{PCl}_3 + \text{Cl}_2$$

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

$$\text{C}_2\text{H}_5\text{OH} + \text{PCl}_5 \longrightarrow \text{C}_2\text{H}_5\text{Cl} + \text{POCl}_3 + \text{HCl}$$

$$\text{CH}_3\text{COOH} + \text{PCl}_5 \longrightarrow \text{CH}_3\text{COCl} + \text{POCl}_3 + \text{HCl}$$

(iv) PCl_5 on heating with finely divided metals give corresponding chlorides.

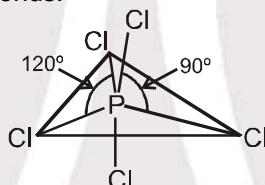
$$2 \text{Ag} + \text{PCl}_5 \longrightarrow 2 \text{AgCl} + \text{PCl}_3$$

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

It is used in the synthesis of some organic compounds, e.g., $\text{C}_2\text{H}_5\text{Cl}$, CH_3COCl .

Structure :

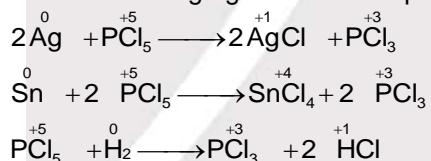
It is covalent in the gaseous state but in solid state exists as ionic solid consisting of $[\text{PCl}_4]^+$ (tetrahedral) and $[\text{PCl}_6]^-$ (octahedral). All P–Cl bonds are not of equal lengths. Here axial bonds are longer and weaker than equatorial bonds.



Solved Examples

Ex-15. Can PCl_5 act as an oxidising as well as a reducing agent? Justify.

Sol. The oxidation state of P in PCl_5 is +5. Since P has five electrons in its valence shell, therefore, it cannot increase its oxidation state beyond +5 by donating electrons, therefore, PCl_5 cannot act as a reducing agent. However, it can decrease its oxidation number from +5 to +3 or some lower value, therefore, PCl_5 acts as an oxidising agent. For example, it oxidises Ag to AgCl , Sn to SnCl_4 and H_2 to HCl .



Ex-16. What happens when

(a) PCl_5 is heated, (b) PCl_5 is reacted with heavy water, (c) H_3PO_3 is heated.

Ans : (a) $\text{PCl}_5 \xrightarrow{\Delta} \text{PCl}_3 + \text{Cl}_2$;
 (b) $\text{PCl}_5 + \text{D}_2\text{O} \xrightarrow{\Delta} \text{POCl}_3 + 2 \text{DCl}$;
 (c) $4 \text{H}_3\text{PO}_3 \xrightarrow{\Delta} 3 \text{H}_3\text{PO}_4 + \text{PH}_3$

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

11. Occurrence :

Element	Occurrence
Oxygen	Most abundant of all elements. Exists in free form as O_2 and makes up 20.9% by volume and 23% by weight of atmosphere. Most of this has been produced by photosynthesis. $6\text{CO}_2 + 6\text{H}_2\text{O} + \text{energy from sun} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$ Also occurs as many metal oxide ore and
Sulphur	Constitutes 0.034% by weight of earth's crust and occurs mainly in combined form as numerous sulphide ores and as sulphates (particularly gypsum).



12. ATOMIC & PHYSICAL PROPERTIES

Element	O	S	Se	Te
Atomic Number	8	16	34	52
Atomic Mass	16	32.06	78.96	127.6
Electronic configuration	[He] 2s 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
Ionic Radius X ⁻² / pm	140	184	198	221
Ionization enthalpy / (kJ mol ⁻¹)	I	1314	1000	941
	II	3388	2251	2045
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

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

Oxygen **Non metals** **Selenium** **Tellurium** **Metalloids** **Polonium {Radio active Metal}**

(i) **Electronic Configuration** : The elements of group 16 have six electrons in the outermost shell and have $ns^2 np^4$ general valence shell electronic configuration.

(ii) **Atomic and Ionic Radii** : Due to increase in the number of shells , atomic and ionic radii increase from top to bottom in the group. The size of oxygen atoms is however, exceptionally small.

(iii) **Ionisation Enthalpy** : Ionisation enthalpy decreases down the group. It is due to increase in size. However, the element of this group have lower ionisation enthalpy values compared to those of group 15 in the corresponding periods. This is due to the fact that group 15 elements have extra stable half-filled p orbitals electronic configurations.

(iv) **Electron Gain Enthalpy** : Because of the compact nature of oxygen atom, it has less negative electron gain enthalpy than sulphur. However from sulphur onwards the value again becomes less negative upto polonium.

(v) **Electronegativity** : Next to fluorine, oxygen has the highest electronegativity value amongst the elements. Within the group, electronegativity decrease with an increase in atomic number. This indicates that the metallic character increases from oxygen to polonium.

(vi) **Physical Properties** :

- Oxygen and sulphur are non-metal, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life 13.8 days).
- The melting and boiling points increase with an increase in atomic number down the group.
- The larger difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity; oxygen exist as diatomic molecules (O_2) whereas sulphur exists as polyatomic molecule (S_8).

(vii) **Catenation** : Tendency for catenation decreases down the group. This property is prominently displayed by sulphur (S_8). The S—S bond is important in biological system and is found in some proteins and enzymes such as cysteine.

○ Selenium has unique property of photo conductivity and is used in photocopying machines and also a decolouriser of glass.

13. Allotropes

13.1 Oxygen : Exists in 2 allotropic forms :

(a) O_2 (b) O_3 (unstable and decomposes to O_2)

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



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

(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 CS_2 .

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

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

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

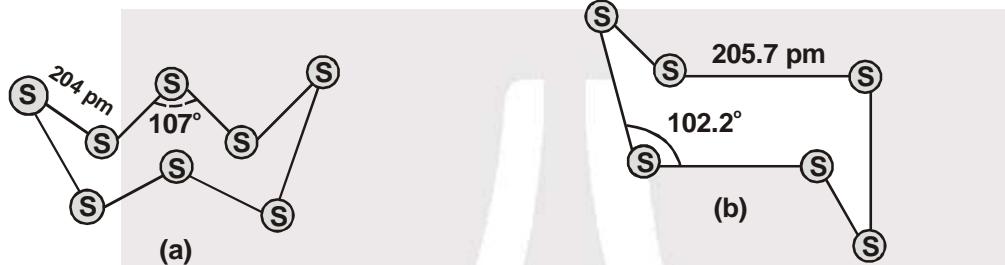


Fig. : The structures of (a) S_8 ring in rhombic sulphur and (b) S_6 form

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

(c) Plastic Sulphur :

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

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

Heating effect on sulphur :

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

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

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

Solved Examples

Ex-17. Write the allotropic forms of oxygen

Ans. Ordinary oxygen and ozone.

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

Ans. Rhombic sulphur

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

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

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

Ans. S_8 (melt) $\xrightleftharpoons[160^\circ C]{160^\circ C}$ S_8 ring break and diradical so formed polymerises to forms long chain polymer and

viscosity starts to increase $\xrightarrow{at 200^\circ C}$ Viscosity further \uparrow $\xrightarrow{at 444^\circ C}$ viscosity \downarrow shorter chains and boiling point

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



14. Preparation & Properties of elements

14.1 Preparation of Elements :

14.1.1 Oxygen :

(a) Dioxygen is produced industrially by fractional distillation of liquid air.
 (b) It is prepared on a small scale in a laboratory by thermal decomposition of KClO_3 (with MnO_2 as catalyst)



(c) It can also be prepared by catalytic decomposition of hypochlorites.
 $2\text{HOCl} \xrightarrow{\text{CO}^{+2}} 2\text{HCl} + \text{O}_2$ or by electrolysis of water with a force of H_2SO_4 or $\text{Ba}(\text{OH})_2$ solution.
 (d) By thermal decomposition of oxides of metals.

$$2\text{HgO} \xrightarrow{450^\circ \text{C}} 2\text{Hg} + \text{O}_2; \quad 2\text{Ag}_2\text{O} \xrightarrow{350^\circ \text{C}} 4\text{Ag} + \text{O}_2$$

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

(e) Thermal decomposition of $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4

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

14.1.2 Sulphur :

(a) Large amounts of sulphur are obtained from natural gas plants, oil refineries. It is obtained from gas and petroleum. After cracking long chain hydrocarbon, H_2S and other sulphur derivatives are removed because of their objectionable smell. About a third of H_2S is oxidized in air to give SO_2 which is subsequently reacted with remaining H_2S .

$$2\text{H}_2\text{S} + 3\text{O}_2 \longrightarrow 2\text{SO}_2 + 2\text{H}_2\text{O}; \quad \text{SO}_2 + 2\text{H}_2\text{S} \longrightarrow 2\text{H}_2\text{O} + 3\text{S}$$

(b) Deposits of sulphur were formed by anaerobic bacteria which metabolize CaSO_4 to form H_2S and S. This was mined by Frash process, now obsolete.

14.2 Physical Properties of Oxygen & Sulphur

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

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

15. Oxidation states and trends in chemical reactivity:

- The elements of group 16 exhibit a number of oxidation states. The stability of -2 oxidation state decreases down the group. Polonium hardly shows -2 oxidation states.
- Electronegativity of oxygen is very high, therefore it shows only negative oxidation states as -2 except in the case of OF_2 where its oxidation states is $+2$.
- Other elements of the group exhibit $+2$, $+4$, $+6$ oxidation states but $+4$ and $+6$ are more common. Sulphur, selenium and tellurium usually show $+4$ oxidation in their compounds with oxygen and $+6$ oxidations state with fluorine.
- The stability of $+6$ oxidation state decreases down the group and stability of $+4$ oxidation state increases (inert pair effect). Bonding in $+4$ and $+6$ oxidation states are primarily covalent.

○ HNO_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.

(ii) Reactivity with hydrogen : All the elements of group 16 form hydrides of the type H_2E ($\text{E} = \text{S, Se, Te, Po}$). Some properties of hydrides are given in Table.

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

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

The order of volatility is : H₂S > H₂Se > H₂Te > H₂O

The order of stability : H₂O > H₂S > H₂Se > H₂Te

The order of boiling points : H₂O > H₂Te > H₂Se > H₂S

The order of K_a values : H₂Te > H₂Se > H₂S > H₂O

(iii) Reactivity towards oxygen :

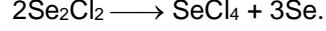
- All these elements form oxides of the EO₂ and EO₃ types where E = S, Se, Te or Po.
- Ozone (O₃) and sulphur dioxide (SO₂) are gases while selenium dioxide (SeO₂) is solid.
- Reducing property of dioxide decreases from SO₂ to TeO₂; while oxidation property increases from SO₂ to TeO₂.
- Both dioxides and trioxides are acidic in nature.
- Trioxides act only as oxidising agents. Oxidation power of trioxides should increase from SO₃ to SeO₃ but SO₃ act as strong oxidising agent in acid medium due to protonation S-O bond becomes weak.

Table : Oxides of Group 16 Elements

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

(iv) Reactivity toward the Halogens :

- Elements of group 16 form a larger number of halides of the type EX₆, EX₄ and EX₂ where E is an element of the group –16 and X is an halogen.
- The order of stability of halides of sulphur with different halogens is : F⁻ > Cl⁻ > Br⁻ > I⁻
- Amongst hexahalides, hexafluorides are the only stable halides.
- All hexafluorides are gaseous in nature. They have octahedral structure. Sulphur hexafluoride SF₆ is exceptionally stable for steric reasons.
- Amongst tetrafluorides, SF₄ is a gas, SeF₄ liquid and TeF₄ a solid.
- The tetrafluorides 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.
- 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 are having open book structure.
- These dimeric halides undergo disproportionation as given below :

**Table : Halides of Group 16 Elements**

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

Tellurium	—	TeCl ₂ TeBr ₂ TeI ₂	TeF ₄ TeCl ₄ TeBr ₄ TeI ₄	TeF ₆	—
Polonium	—	PoCl ₂ PoBr ₂	PoCl ₄ PoBr ₄ PoI ₄	—	—

(v) Anomalous behaviour of oxygen :

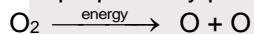
- The anomalous behaviour of oxygen, like other member of p-block present in second period is due to its:
 - (a) Small size and (b) high electronegativity.
- Because of this strong hydrogen bonding is present in H₂O which is not found in H₂S.
- The absence of d orbitals in oxygen restricts its covalency to four and in practice, rarely increases beyond two.
- In case of other elements of the same group, the valence shell can be expanded and covalence exceeds four.

Section (G) : Ozone and Hydrogen peroxide

16. OZONE (O₃)

16.1.1. PREPARATION :

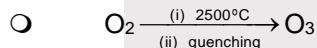
It is prepared by passing silent electric discharge through pure and dry oxygen.



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

Higher concentration or pure O₃ can be obtained by fractional liquefaction of the mixture.

Low concentration of O₃ can be made by UV irradiation of O₂.



16.1.2. PROPERTIES :

(a) PHYSICAL PROPERTIES :

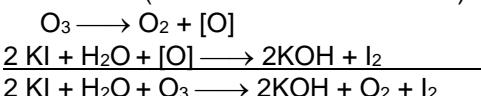
- Dark blue gas which forms a blue liquid on cooling and on solidification forms violet black crystals. The colour is due to intense absorption of red light.
- It also absorbs strongly in the UV region. Thus it protects the people on the earth from the harmful UV radiation from the sun.
- It has sharp smell often associated with sparking electrical equipment. It is toxic and is slightly soluble in water but more in turpentine oil, glacial acetic acid or CCl₄. O₃ molecule is diamagnetic but O₃[—] is paramagnetic.

(b) CHEMICAL PROPERTIES:

- Oxidising agent :** O₃ + 2H⁺ + 2e[—] → O₂ + H₂O ; SRP = + 2.07 V (in acidic medium)
O₃ + H₂O + 2e[—] → O₂ + 2OH[—] ; SRP = + 1.24 V (in alkaline medium)

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

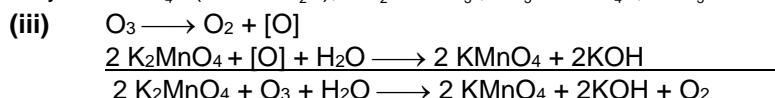
(a) (i) It oxidises I[—] to I₂ (from neutral solution of KI)



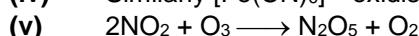
(ii) Alkaline KI is oxidised to potassium iodate & periodate.



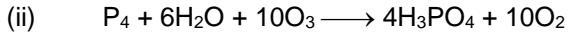
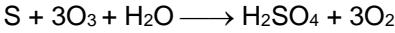
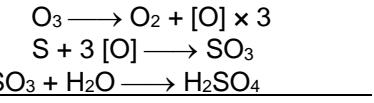
Note: Similarly S^{2—} to SO₄^{2—} (but not H₂S), NO₂[—] to NO₃[—], SO₃^{2—} to SO₄^{2—}, AsO₃^{3—} to AsO₄^{3—}, Sn²⁺ to Sn⁴⁺ (acidic medium).



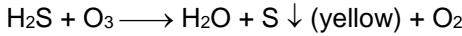
(iv) Similarly [Fe(CN)₆]^{4—} oxidises to [Fe(CN)₆]^{3—} (basic medium).



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



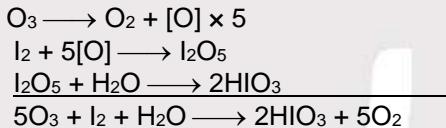
(c) It oxidises H_2S to S.



(d) **Reaction with dry I_2 :** $2 \text{I}_2 + 9[\text{O}_3] \longrightarrow \text{I}_4\text{O}_9 + 9\text{O}_2$

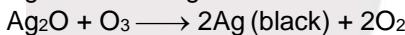
○ I_4O_9 yellow solid has the composition $\text{I}^{+3} (\text{IO}_3^-)_3$. Formation of this compound is a direct evidence in favour of basic nature of I_2 (i.e. its tendency to form cations).

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

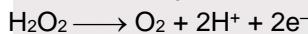
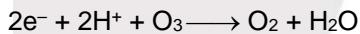


(f) **Reaction with Silver :**

Silver articles become black in contact with ozone.



(g) **Reaction with H_2O_2 :**



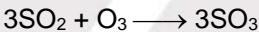
Oxidising agent

Reducing agent

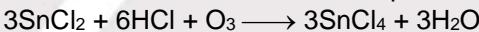
It is supported by the fact that SRP of ozone is higher (+2.07) than SRP of hydrogen peroxide (+1.77). Therefore, ozone is stronger oxidising agent than hydrogen peroxide.

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

(i) SO_2 is oxidised to SO_3

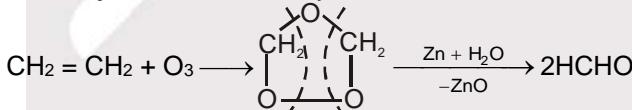


(ii) SnCl_2 is oxidised to SnCl_4 in the presence of HCl .



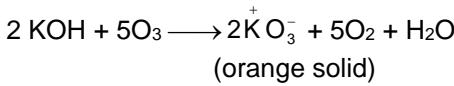
(i) **Bleaching Action :** O_3 also bleaches coloured substances through oxidation.

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



(k) **Reaction with KOH :**

Forms orange coloured compound, potassium ozonide.

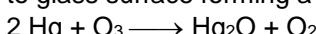


16.1.3. TESTS FOR OZONE

(i) A filter paper soaked in a alcoholic benzidine $\left[\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{NH}_2\right]$ becomes brown when brought in contact with O_3 (this is not shown by H_2O_2).

(ii) **Tailing of mercury**

Pure mercury is a mobile liquid but when brought in contact with O_3 its mobility decreases and it starts sticking to glass surface forming a type of tail due to the dissolution of Hg_2O (mercury sub-oxide) in Hg.



**USES OF OZONE :**

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

Solved Examples

Ex-21. O_3 is a powerful oxidising agent. Write equation to represent oxidation of

- I^- to I_2 in acidic solutions,
- sulphur to sulphuric acid in the presence of moisture,

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

Ex-22. 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, KMnO_4 etc. It is also used for bleaching oil, ivory, flour starch etc.

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

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

Sol. (A) $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$
 (B) $\text{Cl}_2\text{CF}_2 \rightarrow \cdot\text{Cl} + \cdot\text{CClF}_2$; $\cdot\text{Cl} + \text{O}_3 \rightarrow \text{ClO}^\cdot + \text{O}_2$
 $\text{ClO}^\cdot \rightarrow \text{Cl}^\cdot + \text{O}^\cdot$; $\text{ClO}^\cdot + \text{O}^\cdot \rightarrow \cdot\text{Cl} + \text{O}_2$

Ex-24. O_3 is a powerful oxidising agent. Write equation to represent oxidation of

- I^- to I_2 in acidic solutions,
- sulphur to sulphuric acid in the presence of moisture,

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

Ex-25. Give the important applications of O_3 .

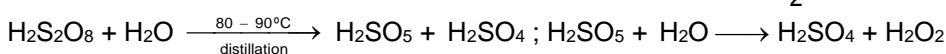
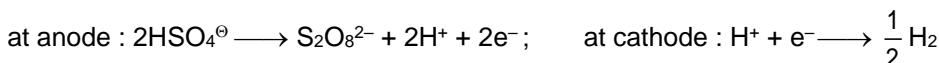
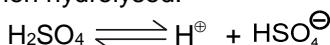
Sol. (A) As a germicide and disinfectant for sterilising water and improving the atmosphere of crowded places.
 (B) For detecting the position of double bond in the unsaturated organic compounds.
 (C) In mfg. of artificial silk, synthetic camphor, KMnO_4 etc. It is also used for bleaching oil, ivory, flour starch etc.

16.2. HYDROGEN PEROXIDE (H_2O_2) :**16.2.1 PREPARATION :****(i) Laboratory Method :**

BaSO_4 is filtered to get aqueous hydrogen peroxide.

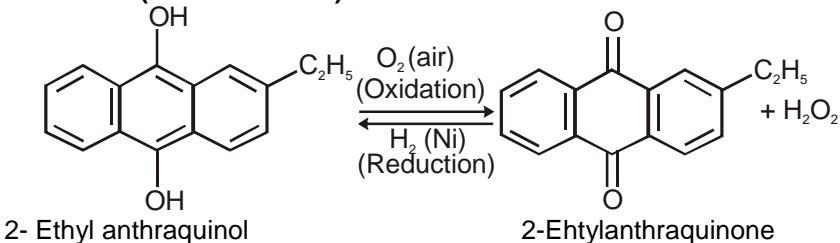
- The reaction between anhydrous BaO_2 and H_2SO_4 is slow and practically ceases after sometimes due to the formation of a protective layer of BaSO_4 on BaO_2 . So hydrated barium peroxide is used.
 $\text{Ba}(\text{OH})_2 + \text{H}_2\text{O}_2 + 6\text{H}_2\text{O} \rightarrow \text{BaO}_2 \cdot 8\text{H}_2\text{O}$
- 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
 $3\text{BaO}_2 + 2\text{H}_3\text{PO}_4 \rightarrow \text{Ba}_3(\text{PO}_4)_2 \downarrow + 3\text{H}_2\text{O}_2$; $\text{Ba}_3(\text{PO}_4)_2 + 3\text{H}_2\text{SO}_4 \rightarrow 3\text{BaSO}_4 \downarrow + 2\text{H}_3\text{PO}_4$
 H_3PO_4 can again be used.

(ii) By electrolysis of concentrated H_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$ at a high current density to form peroxosulphates, which then hydrolysed.





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



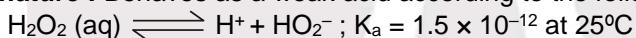
16.2.2 PROPERTIES :

(a) **PHYSICAL PROPERTIES :**

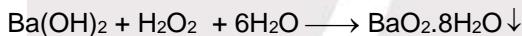
- (i) Colourless viscous liquid which appears blue in the larger quantity and is soluble in water (due to H-bonding) in all proportions and form a hydrate $\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ (melting point 221 K).
- (ii) Its boiling point 423 K is more than water but freezing point (-4°C) is less than water. Density and dielectric constant are also higher than H_2O
- (iii) Its aqueous solution is more stable than the anhydrous liquid where it decomposes into water and O_2 slowly on exposure to light. $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$

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



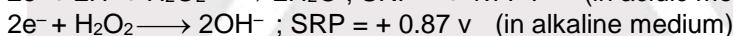
Aqueous solution of H_2O_2 turns blue litmus red which is then bleached by the oxidising property of H_2O_2



- A 30% H_2O_2 solution has pH = 4.0

(b) **CHEMICAL PROPERTIES :**

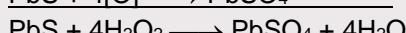
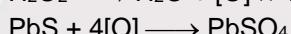
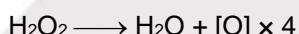
(i) **Oxidising Agent :**



- On the basis of the above potentials, we can say that H_2O_2 is strong oxidising agent in acidic medium but kinetically it is found that reactions are faster in basic medium.

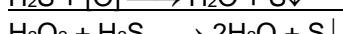
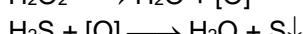
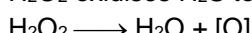
(A) **In acidic medium :**

- (a) It oxidises PbS to PbSO_4 .

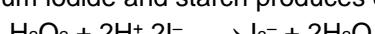


This property is utilised in restoring the white colour in old paintings which turns black due to the formation of PbS by the action of atmospheric H_2S .

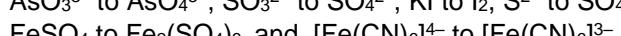
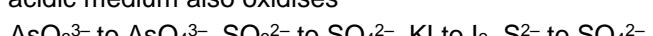
- (b) H_2O_2 oxidises H_2S to sulphur.

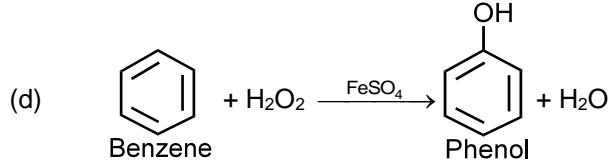


- Potassium iodide and starch produces deeper blue colour with acidified H_2O_2 .

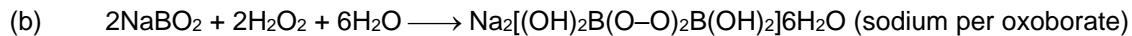
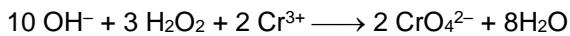
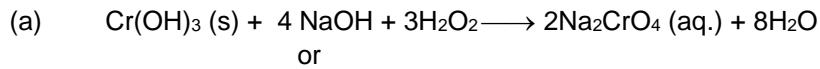


- H_2O_2 in acidic medium also oxidises



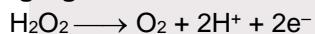


(B) In alkaline medium :



Used as a brightener in washing powder.

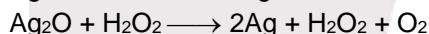
(ii) Reducing Agent : It acts as a reducing agent towards powerful oxidising agent.



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



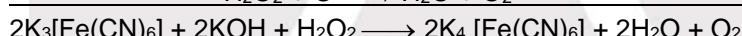
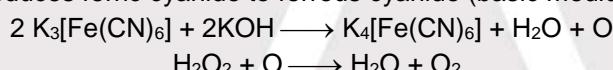
(a) Ag_2O is reduced to Ag .



(b) It reduces O_3 to O_2 ..



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



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

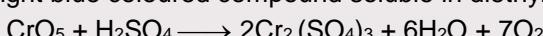


It also reduces MnO_4^- to Mn^{2+} (acidic medium), MnO_4^- to MnO_2 (basic medium), OCl^- to Cl^- , IO_4^- to IO_3^- and Cl_2 to Cl^-

16.2.3 TESTS FOR H_2O_2 :

(i) With $\text{K}_2\text{Cr}_2\text{O}_7$: $\text{Cr}_2\text{O}_7^{2-} + 2\text{H}^+ + 4\text{H}_2\text{O}_2 \xrightarrow{\text{amyl alcohol}} 2\text{CrO}_5 + 5\text{H}_2\text{O}$

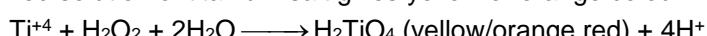
CrO_5 bright blue coloured compound soluble in diethyl ether, amyl alcohol and amyl acetate.



(ii) $2\text{HCHO} + \text{H}_2\text{O}_2 \xrightarrow[\text{pyrogallol}]{\text{OH}^-} 2\text{HCOOH} + \text{H}_2$

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

(iii) An acidified solution of titanium salt gives yellow or orange colour with H_2O_2 .



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

16.2.4 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.

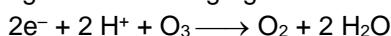


Solved Examples

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



Sol. Ozone is behaving as an oxidising agent and H_2O_2 is behaving as reducing agent.



The above interpretations is further supported on the following grounds.

SRP of H_2O_2 is + 1.77 V while SRP of O_3 is + 2.07 V. Therefore, O_3 is stronger oxidising agent than H_2O_2 .

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

17. HYDRIDE

17.1 HYDROGEN SULPHIDE (H_2S) :

17.1.1. Preparation :

(i) $\text{FeS} + \text{H}_2\text{SO}_4 \longrightarrow \text{FeSO}_4 + \text{H}_2\text{S}$
It is prepared in kipp's apparatus

(ii) Preparation of pure H_2S gas
 Sb_2S_3 (pure) + 6 HCl (pure) $\longrightarrow 2 \text{SbCl}_3 + 3 \text{H}_2\text{S}$

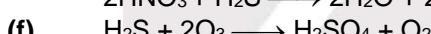
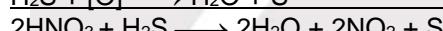
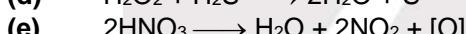
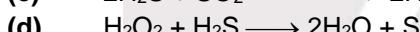
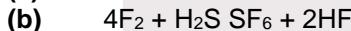
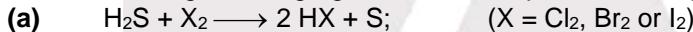
17.1.2 Physical Properties :

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

17.1.3. Chemical Properties :

(i) Reducing Agent :

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

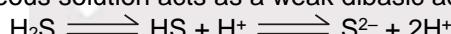


(g) It also reduces MnO_4^- to Mn^{2+} , H_2SO_4 to SO_2 & $\text{K}_2\text{Cr}_2\text{O}_7$ to Cr^{3+} (acidic medium)

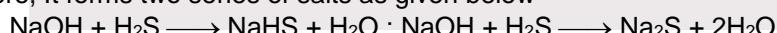
(h) MnO_4^- to MnO_2 (alkaline medium)

(ii) Acidic Nature :

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

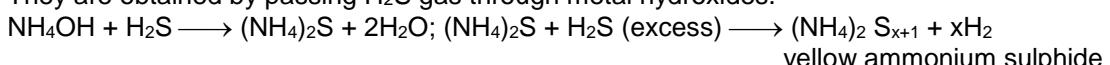


Therefore, It forms two series of salts as given below



(iii) Formation of Polysulphides :

They are obtained by passing H_2S gas through metal hydroxides.



17.1.4. TESTS FOR H_2S :

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

17.1.5. USES OF H_2S :

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

Other hydrides not in syllabus



18. OXIDES OF SULPHUR :

SO_2		Both bonds are equivalent
SO_3		All three S-O bonds are equivalent. Out of 3π bonds. One is $p\pi-p\pi$ other two are $p\pi-d\pi$.

18.1 SULPHUR DIOXIDE :

18.1.1 PREPARATION :

- (i) $\text{S} + \text{O}_2$ or air $\xrightarrow{\text{Burn}}$ SO_2
- (ii) CaSO_4 (gypsum) + C $\xrightarrow[1000^\circ\text{C}]{\Delta}$ $2 \text{CaO} + \text{SO}_2 + \text{CO}_2$

○ By this method SO_2 is obtained in large scale

18.1.2 PROPERTIES :

- (i) Colourless gas with burning sulphur smell.
- (ii) It is heavier than air and is highly soluble in water. SO_2 in solution is almost completely present as $\text{SO}_2 \cdot 6\text{H}_2\text{O}$ 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.

$$3\text{Mg} + \text{SO}_2 \longrightarrow 2 \text{MgO} + \text{MgS} ; 4\text{K} + 3\text{SO}_2 \longrightarrow \text{K}_2\text{SO}_3 + \text{K}_2\text{S}_2\text{O}_3$$
- (iv) **Acidic Nature :** Acidic oxide and thus dissolve in water forming sulphurous acid.

$$\text{SO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_3$$
- (v) **Addition Reaction :**

$$\text{SO}_2 + \text{Cl}_2 \xrightarrow[\text{platinised}]{\text{Sun light}} \text{SO}_2\text{Cl}_2 \text{ (sulphuryl chloride)}$$

$$\text{SO}_2 + \text{O}_2 \xrightleftharpoons[\text{Asbests}]{\quad} \text{SO}_3 ; \text{PbO}_2 + \text{SO}_2 \longrightarrow \text{PbSO}_4$$
- (vi) **Reducing Nature :**

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

$$\text{H}_2\text{O} + \text{SO}_2 \longrightarrow \text{H}_2\text{SO}_3 ; \text{H}_2\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + 2\text{H}$$

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

 - (a) Reduces halogens to corresponding halides.

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

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

$$\text{SO}_2 + 2\text{H}_2\text{O} + \text{Cl}_2 \longrightarrow \text{H}_2\text{SO}_4 + 2\text{HCl}$$
 - (b) Reduces acidified iodates to iodine

$$\text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + 2\text{H} \times 5$$

$$2\text{KIO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{HIO}_3$$

$$\underline{2\text{HIO}_3 + 10\text{H} \longrightarrow \text{I}_2 + 6\text{H}_2\text{O}}$$

$$2\text{KIO}_3 + 5\text{SO}_2 + 4\text{H}_2\text{O} \longrightarrow \text{K}_2\text{SO}_4 + 4\text{H}_2\text{SO}_4 + \text{I}_2$$
 - It also reduces acidified $\text{KMnO}_4 \longrightarrow \text{Mn}^{2+}$ (decolourises),

$$\text{Acidified K}_2\text{Cr}_2\text{O}_7 \longrightarrow \text{Cr}^{3+}$$
 (green coloured solution) & Ferric Sulphate \longrightarrow Ferrous sulphate
- (vii) **Oxidising nature :** Acts as oxidising agent with strong reducing agent
 - (a) $2\text{H}_2\text{S} + \text{SO}_2 \xrightarrow{\text{moisture}} 2\text{H}_2\text{O} + 3\text{S}$
 - (b) $2\text{SnCl}_2 + \text{SO}_2 + 4\text{HCl} \longrightarrow 2\text{SnCl}_4 + 2\text{H}_2\text{O} + \text{S}$
 - (c) $2\text{Hg}_2\text{Cl}_2 + \text{SO}_2 + 4\text{HCl} \longrightarrow 2\text{HgCl}_2 + 2\text{H}_2\text{O} + \text{S}$
 - (d) $2\text{CO} + \text{SO}_2 \longrightarrow 2\text{CO}_2 + \text{S}$
 - (e) $2\text{Fe} + \text{SO}_2 \longrightarrow 2\text{FeO} + \text{FeS}$
- (viii) **Bleaching Action :**

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

This is due to the reducing nature of SO_2

$$\text{Coloured matter} + \text{H} \xrightleftharpoons[\text{Air oxidation}]{\quad} \text{colourless matter.}$$

Therefore, bleaching is temporary.



18.1.3 USES OF SO_2 :

- Used in manufacture of H_2SO_4 & paper from wood pulp.
- As a bleaching agent for delicate articles like wool, silk and straw.
- Used in refining of petroleum and sugar.

18.2 SULPHUR TRIOXIDE (SO_3):

18.2.1 PREPARATION :

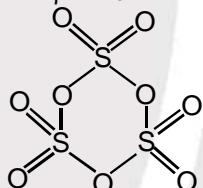
- $6\text{H}_2\text{SO}_4 + \text{P}_4\text{O}_{10} \longrightarrow 6\text{SO}_3 + 4\text{H}_3\text{PO}_4$
○ P_4O_{10} is dehydrating agent
- $\text{Fe}_2(\text{SO}_4)_3 \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + 3\text{SO}_3$
- $2\text{SO}_2 + \text{O}_2 \xrightleftharpoons{\text{pt}} 2\text{SO}_3$

18.2.2 PROPERTIES :

SO_3 exists in three allotropic forms :

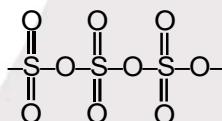
At room temperature SO_3 is solid and exists in three distinct forms.

(a) $\gamma\text{-SO}_3$: It is ice-like and is a cyclic trimer (SO_3)₃, m.p. 16.8°C. If SO_3 is kept for a long time, or if a trace of water is present, either $\beta\text{-SO}_3$ or $\alpha\text{-SO}_3$ is formed.



Cyclic trimer of $\gamma\text{-SO}_3$

(b) $\alpha\text{-SO}_3/\beta\text{-SO}_3$: $\beta\text{-SO}_3$ (m.p. 32.5°C) is made up of infinite helical chains of tetrahedral $[\text{SO}_4]$ unit each sharing two corners. This structure is similar to that of chain phosphates. $\alpha\text{-SO}_3$ (m.p. 62.2°C) is the most stable form, and is made of chains cross-linked into sheets. Both look like asbestos, and comprise bundles of white silky needles.

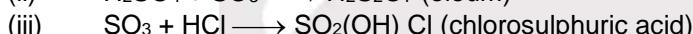
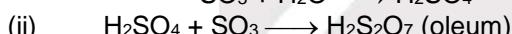


Structure of SO_3 chains ($\alpha\text{-SO}_3$ or $\beta\text{-SO}_3$).

SO_3 is a powerful oxidizing agent, especially when hot. It oxidizes HBr to Br_2 and P to P_4O_{10} .

(i) Acidic Nature :

Dissolves in water forming sulphuric acid



(iv) Oxidising Nature :



18.2.3 USES OF SO_3 :

- Used in manufacture of H_2SO_4 and oleum.
- Used as a drying agent for gases.
- 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.

19. OXY ACIDS OF SULPHUR

Sulphur forms a number of oxoacid such as H_2SO_3 , $\text{H}_2\text{S}_2\text{O}_4$, $\text{H}_2\text{S}_2\text{O}_5$, $\text{H}_2\text{S}_2\text{O}_6$ ($x = 2$ to 5), H_2SO_4 , $\text{H}_2\text{S}_2\text{O}_7$, H_2SO_8 . Some of these acids are unstable and cannot be isolated. They are known in aqueous solution or in the forms of their salts. Structures of some important oxoacids are shown in figure.

Oxyacid	Formula of acid	Oxidation state of S	Structure	Other information
(a) Sulphurous acid series				
Sulphurous acid	H ₂ SO ₃	+4	$\text{HO}-\overset{\text{..}}{\underset{\text{O}}{\text{S}}}-\text{OH}$	Tautomeric structures are possible
Thiosulphurous acid	H ₂ S ₂ O ₂	-2, +4	$\text{HO}-\overset{\text{..}}{\underset{\text{S}}{\text{S}}}-\text{OH}$	pπ-dπ bond between sulphur atoms
Dithionous acid	H ₂ S ₂ O ₄	+3, +3	$\text{HO}-\overset{\text{..}}{\underset{\text{O}}{\text{S}}}-\overset{\text{..}}{\underset{\text{O}}{\text{S}}}-\text{OH}$	Unstable and is known as hyposulphurous form
Pyrosulphurous acid	H ₂ S ₂ O ₅	+5, +3	$\text{HO}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\overset{\text{..}}{\underset{\text{O}}{\text{S}}}-\text{OH}$	Average oxidation state of sulphur is +4
(b) Sulphuric acid series				
Sulphuric acid	H ₂ SO ₄	+6	$\text{HO}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{OH}$	Has 2 pπ-dπ bond
Thiosulphuric acid	H ₂ S ₂ O ₃	-2, +6	$\text{HO}-\overset{\text{S}}{\underset{\text{O}}{\text{S}}}-\text{OH}$	Hydrated thiosulphates are familiar as hypo (Na ₂ S ₂ O ₃ .5H ₂ O).
Pyrosulphuric acid	H ₂ S ₂ O ₇	+6, +6	$\text{HO}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{OH}$	It is called oleum and also as fuming sulphuric acid
(c) Thionic acid series				
Dithionic acid	H ₂ S ₂ O ₆	+5, +5	$\text{HO}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{OH}$	Has 2 pπ-dπ bonds each sulphur atom
Polythionic acid (x = n + 2) (n = 1-12)	H ₂ S _x O ₆	+5, 0, +5	$\text{HO}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}_n}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{OH}$	Middle sulphur atom have zero oxidation state
(d) Peroxy acid series				
Peroxymono-sulphuric acid	H ₂ SO ₅	+6	$\text{HO}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{O}-\text{OH}$	Called Caro's acid. Fairly stable



Peroxydi-sulphuric acid	$\text{H}_2\text{S}_2\text{O}_8$	+6, +6	$\begin{array}{c} \text{O} & \text{O} \\ \parallel & \parallel \\ \text{HO}-\text{S}-\text{O}-\text{O}-\text{S}-\text{OH} \\ \parallel & \parallel \\ \text{O} & \text{O} \end{array}$	Called Marshall's acid. Persulphates are well known
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19.1 SULPHURIC ACID (H_2SO_4) :

19.1.1 Preparation :

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

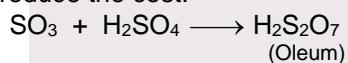
(a) Contact process :

- (i) Burning of sulphur or sulphide ores in air to generate SO_2
- (ii) Conversion of SO_2 to SO_3 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 ($\text{H}_2\text{S}_2\text{O}_7$)
- (iv) The SO_2 produced is purified 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).



(vi) The SO_3 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.



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

(b) Lead chamber process :



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

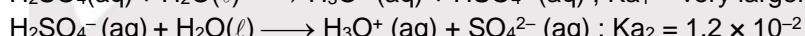
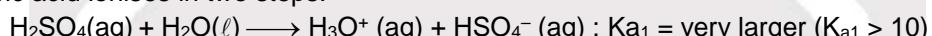
Note : It is outdated process, need not remember.

19.1.2 (a) Physical Properties :

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

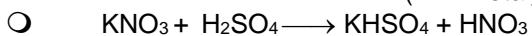
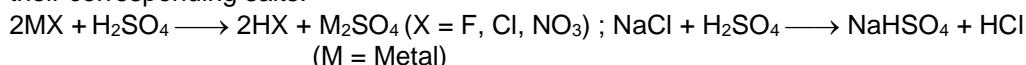
(b) Chemical Properties :

(i) Sulphuric acid ionises in two steps.

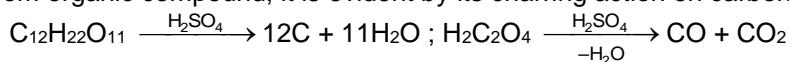


The larger value of $\text{K}_{\text{a}1}$ ($\text{K}_{\text{a}1} > 10$) means that H_2SO_4 is largely dissociated into H^+ and HSO_4^- . Greater the value of dissociation constant (K_a) the stronger is the acid.

- (a) The acid forms two series of salts : normal sulphates (such as sodium sulphate and copper sulphate and acid sulphate (e.g., sodium hydrogen sulphate)
- (b) Decomposes carbonates and bicarbonates into CO_2 .
- (c) Sulphuric acid, because of its low volatility can be used to manufacture more volatile acid from their corresponding salts.

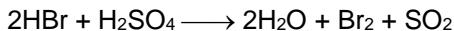
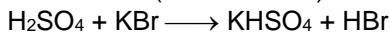
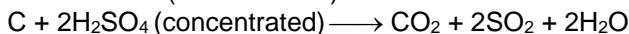


(ii) Concentrated sulphuric acid is a strong dehydrating agent. Many wet gases can be dried by passing them through sulphuric acid, provided the gases do not react with the acid. Sulphuric acid removes water from organic compound; it is evident by its charring action on carbohydrates.





(iii) Hot concentrated sulphuric acid is moderately strong oxidising agent. In this respect it is intermediate between phosphoric and nitric acids. Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to SO_2 .



(iv) With PCl_5 forms mono and di-acid chlorides.



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

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

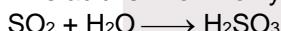
19.1.3 USES OF H_2SO_4 :

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

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

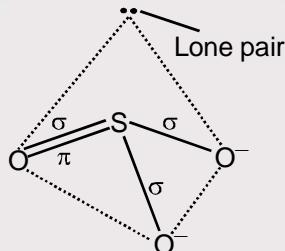
19.2.1 SULPHUROUS ACID (H_2SO_3) :

This acid is known only in solution. The solution is obtained by dissolving SO_2 in water.



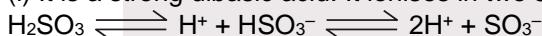
Though SO_2 is very soluble in water, most is present as hydrated $\text{SO}_2(\text{SO}_2 \cdot \text{H}_2\text{O})$. Sulphurous acid. H_2SO_3 may exist in the solution in minute amounts, or not at all, through the solution is acidic. Its salts, the sulphites SO_3^{2-} form stable crystalline solids.

On heating it gives a smell of SO_2 . It is, thus, believed that the acid is present in equilibrium with the free gas.



19.2.2 Properties :

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

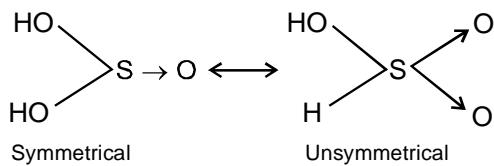


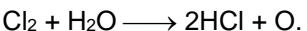
(ii) It thus forms two series of salts. The salts are known as bisulphites (e.g. NaHSO_3) and sulphites (e.g., Na_2SO_3). The salts are fairly stable.

(iii) Like SO_2 , it acts as a reducing agent and shows bleaching properties. These properties have been described under sulphur dioxide.

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

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



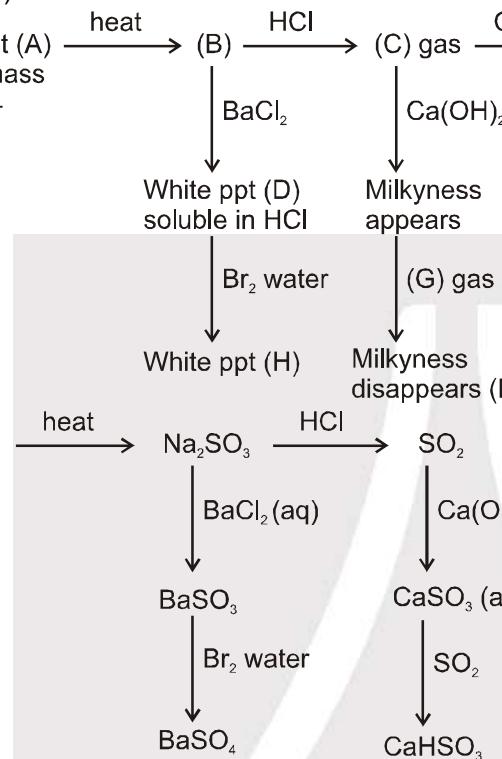
Solved Examples**Ex-27.** SO_2 and Cl_2 both are used as bleaching agent. What factors cause bleaching?

Bleaching action of SO_2 is due to H (that causes reduction) and that of Cl_2 is due to O (that causes oxidation).

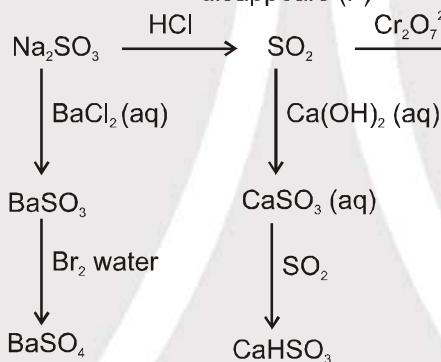
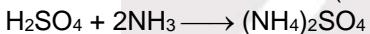
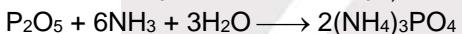
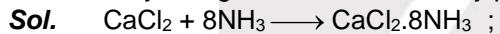
Ex-28. Acid salt (A) $\xrightarrow{\text{heat}}$ (B) $\xrightarrow{\text{HCl}}$ (C) gas $\xrightarrow{\text{Cr}_2\text{O}_7^{2-}/\text{H}^+}$ (G) green

Molar mass

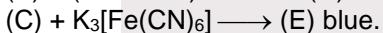
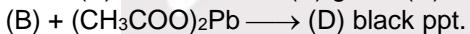
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Sol. $\text{NaHSO}_3 \xrightarrow{\text{heat}} \text{Na}_2\text{SO}_3 \xrightarrow{\text{HCl}} \text{SO}_2 \xrightarrow{\text{Cr}_2\text{O}_7^{2-}/\text{H}^+} \text{Cr}^{3+} \text{ (green solution)}$

**Ex-29.** Why NH_3 gas cannot be dried by passing over P_2O_5 , CaCl_2 and H_2SO_4 ?

So it is dried by passing over quick lime (CaO).

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

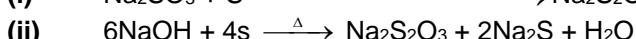
(C) also decolourises acidified KMnO_4 . Identify (A) to (E).

**Ex-31.** Why concentrated H_2SO_4 can not be used for drying H_2 ?

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

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

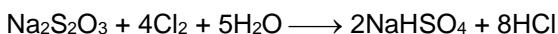
20.1.1 PREPARATION :



**20.1.2 PROPERTIES:**

(i) It is a colourless crystalline substance soluble in water which loses water of crystallisation on strong heating.

(ii) **As antichlor** : It removes the chlorine from the surface of fibres (while dyeing) according to following reaction.



Therefore, it is known as antichlor.

(iii) **Reaction with HCl** : $\text{S}_2\text{O}_3^{2-} + \text{H}^+ \longrightarrow \text{S} \downarrow$ (white) + $\text{SO}_2 + \text{H}_2\text{O}$ (disproportionation reaction)

This test is used for distinction between $\text{S}_2\text{O}_3^{2-}$ and SO_3^{2-} ions as SO_3^{2-} ions give only SO_2 with HCl.

(iv) **Complex formation reactions:**

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

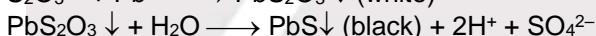
(v) **As reducing agent :**



Reaction (b) finds application in the iodometric and iodimetric methods of titrimetric analysis.

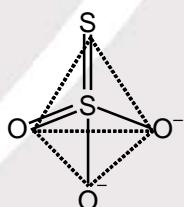
(vi) **Heating effects** : $4\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} \xrightarrow[-\text{H}_2\text{O} \text{ (All)}]{215^\circ\text{C}} 4\text{Na}_2\text{S}_2\text{O}_3 \xrightarrow{220^\circ\text{C}} 3\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_5$

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



○ Ba^{2+} gives white precipitate of BaS_2O_3 but calcium thiosulphate is soluble.

Structure :



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

20.1.3 USES OF HYPO :

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

Solved Examples

Ex-32. Colourless salt (A) decolourises I_2 solution and gives white precipitate (changing to black) with AgNO_3 solution. (A) also produces pink colour with FeCl_3 solution. Identify (A) and explain reactions.

