p-Block Elements (Nitrogen and Oxygen Family)

Section (A) : Physical and Chemical properties of Group 15th elements

Introduction :

(i) Group 13 to 18 of the periodic table of elements constitute the p–block. The p–block contains metals, metalloids as well as non–metals.

(ii) The p–block elements have general valence shell electronic configuration $ns^2 np^{1-6}$.

(iii) **Anomolous behaviour :** The first member of each group from 13–17 of the p–block elements differs in many respects from the other members of their respective groups because of small size, high electronegativity and absence of d–orbitals.

(iv) The first member of a group also has greater ability to form pπ–pπ multiple bonds with itself (e.g. C=C, C≡C, N≡N) and with the elements of second row (e.g C=O, C=N, C≡N, N=O), as compared to the other members of the same group.

(v) The highest oxidation state of p–block elements is equal to (group number –10). Moving down the group, the oxidation state (group number –12) becomes increasingly more stable in groups 13 to 16 due to inert pair effect (reluctance of s-subshell electrons to participate in chemical bonding). Note that inert pair effect predominates only in sixth period of p-block.

(vi) Group 15 includes nitrogen phosphorus, arsenic, antimony and bismuth. 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.

(vii) As we go down the group, there is a shift from non-metallic to metallic through metalloidic character. Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids and bismuth is a typical metal. In group-16, O and S are non-metals, Se and Te are metalloids while Po is metallic and radioacitve.

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 $Ca_3(PO_4)_2$ or $[3(Ca_3(PO_4)_2).CaF_2]$. Nucleic acid such as DNA and RNA are made up of polyester chains of phosphates and sugars with organic bases.
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. $6CO_2 + 6H_2O + \text{energy from sun} \rightarrow C_6H_{12}O_6 + 6O_2$ Oxy salts like carbonate, sulphate and phosphates
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).

Atomic & physical properties:

Group 15 Elements : The Nitrogen family :

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	703
	II	2856	1903	1798	1595	1610
	III	4577	2910	2736	2443	2466
Electronegativity		3.0	2.1	2.0	1.9	1.9

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

Nitrogen, Phosphorus } Non metals

Arsenic, Antimony } Metalloid

Bismuth {Typical metal}

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

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

(iii) **Ionisation Enthalpy :**

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

(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.

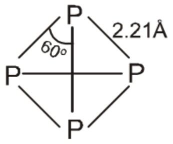
(v) **Physical Properties :**

- 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.

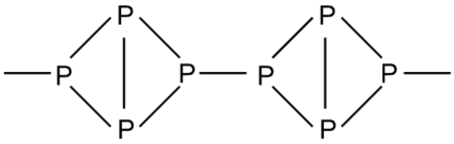
Allotropy

(i). **Nitrogen :** does not show allotropy

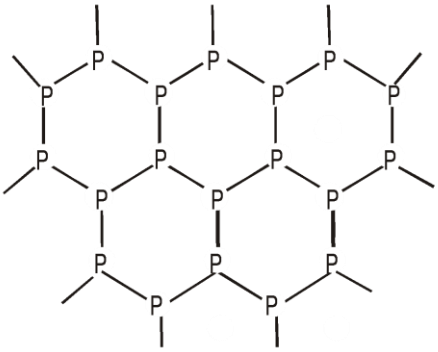
(ii). **Phosphorus :** 3 types of allotropes: white, red and black.



White-P



Red-P



Black-P

Properties	White-Phosphorus	Red-Phosphorus
Physical state	Soft waxy solid	Brittle powder
Colour	White when pure. Attains yellow colour on standing	Red
Odour	Garlic	Odourless
Melting point	44ºC	Sublimes in absence of air at 290ºC
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

(iii) **White :** Exists as tetrahedral P_4 molecule and structure remains in the liquid and gaseous states. If white phosphorous is heated to about 250°C or a low temperature in presence of sunlight, then red P is formed. It is highly toxic.

(iv) **Red :** Polymeric solid which is less reactive than white phosphorous.

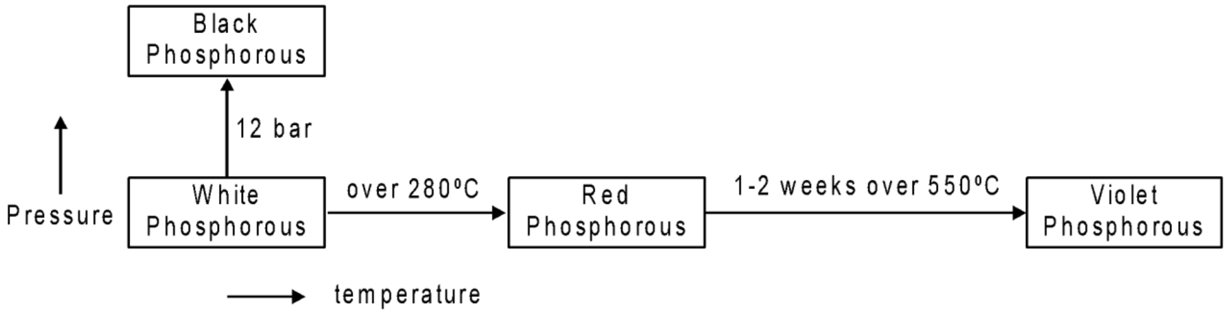
(v) **Black :**

(1) Thermodynamically, the most stable allotrope of phosphorous.

(2) It has two forms α-black phosphorus and β-black phosphorous.

(3) α-black phosphorus is formed when red phosphorus is heated in a sealed tube at 803 K. It can be sublimed in air and has opaque monoclinic or rhombohedral crystal. It does not oxidise in air.

(4) β-black phosphorus is prepared by heating white phosphorus at 473 K under high pressure. It does not burn in air upto 673 K.



General trends and Chemical properties :

(i) Group 15 Elements : The Nitrogen family :

(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 , bismuth hardly forms any compound in –3 oxidation state.

- The stability of +5 oxidation state decreases down the group. The only well characterised Bi (V) compound is BiF_5 .The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group.

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

- Nitrogen exhibits +1, +2, +4 oxidation states also when it reacts with oxygen. Phosphorus also shows +1 and +4 oxidation states in some oxoacids.
- In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution.

For example, $3\,HNO_2 \longrightarrow HNO_3 + H_2O + 2\,NO$

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

(ii) 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 those of bismuth is predominantly basic.

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_4O_6	As_4O_{10}
Antimony	Sb_4O_6	Sb_4O_{10}
Bismuth	Bi_2O_3	–

(a) All these oxides are generally covalent and acidic. Sb_4O_6 is amphoteric and Bi_2O_3 is basic. Acidic nature decreases from the oxide of nitrogen to that of bismuth.

(b) Pentoxides are more acidic than the corresponding trioxides.

(iii) 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. Some of the properties of these hydrides are shown in Table.

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	-
$\Delta_f H°/kJ\ mol^{-1}$	–46.1	13.4	66.4	145.1	278
$\Delta_{diss} H$ (H-E)/kJ mol^{-1}	389	322	297	255	-

The order of volatility is : $PH_3 > AsH_3 > NH_3 > SbH_3$

The order of basic nature : $NH_3 > PH_3 > AsH_3 > SbH_3$

The order of stability : $NH_3 > PH_3 > AsH_3 > SbH_3$

The order of reducing nature : $SbH_3 > AsH_3 > PH_3 > NH_3$

(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.

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

Only BiF_3 is ionic and all other halides are covalent :

(i) PCl_5 is less stable than PCl_3.

(ii) Trihalides are pyramidal and pentahalides are trigonal bipyramidal.

(iii) Reducing nature of trihalides : $PI_3 > PBr_3 > PCl_3 > PF_3$

(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 pπ–pπ 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 pπ–pπ 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 dπ–pπ bonds as the heavier elements can e.g., $R_3P=O$ or $R_3P=CH_2$ (R = alkyl group). Phosphorus and arsenic can form dπ–pπ 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.

Preparation of Elements :

(a). **Nitrogen :**

Lab preparation

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

$$NH_4Cl + NaNO_2 \longrightarrow NH_4NO_2 + NaCl$$

$$NH_4NO_2 \xrightarrow{\Delta} N_2\uparrow + 2H_2O$$

(ii) It is also obtained by oxidizing NH_3 for example with calcuim hypochlorite, bromine water or CuO. Small quantities of very pure N_2 may be obtained by carefully warming sodium azide NaN_3 to about 300°C.

$$8NH_3 + 3Br_2 \longrightarrow N_2 + 6NH_4Br$$

$$2NaN_3 \xrightarrow{\Delta} 3N_2 + 2Na$$

(b). **Industrial preparation :**

(i) From liquified air by fractional distillation : The boiling point of N_2 is -196^oC and that of oxygen is -183^oC 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 :**

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

Sodium azide also gives N_2 on heating.

Phosphorous :

It is obtained by reduction of calcium phosphate with C in an electric furnace at 1400-1500°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.

$$2Ca_3(PO_4)_2 + 6SiO_2 \longrightarrow 6CaSiO_3 + P_4O_{10}$$

$$P_4O_{10} + 10C \longrightarrow P_4 + 10\,CO$$

Section (B) : Compounds of Nitrogen and phosphorus

Hydrides :

(a) Ammonia (NH_3)

PREPARATION :

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

$NH_4NO_3 + NaOH \xrightarrow{\Delta} NH_3\uparrow + NaNO_3 + H_2O$; $(NH_4)_2SO_4 + CaO \xrightarrow{\Delta} 2NH_3\uparrow + CaSO_4 + H_2O$

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.

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

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

$CaCl_2 + 8NH_3 \longrightarrow CaCl_2\cdot 8NH_3$; $P_2O_5 + 6NH_3 + 3H_2O \longrightarrow 2(NH_4)_3PO_4$

$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4$; $CaO + H_2O \longrightarrow Ca(OH)_2$

(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.

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

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

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

$$NaNO_3 + 7NaOH + 4Zn \longrightarrow 4Na_2ZnO_2 + NH_3\uparrow + 2H_2O$$

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

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

(b) Industrial methods of preparation :

(i) **Haber's process :** $N_2 + 3H_2 \xrightarrow[\text{Iron oxide}+K_2O\,\&\,Al_2O_3]{500°C,\,200\,atm.} 2NH_3$

(ii) **Cyanamide process :**

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

(c) Physical properties :

(i) Ammonia is a colourless gas with a pungent odour. Its freezing point and boiling point are 198.4 and 239.7 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.

$$NH_3\,(g) + H_2O\,(\ell) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

(d) Chemical properties :

(i) NH_3 as weak base :

It forms ammonium salts with acids, e.g., NH_4Cl, $(NH_4)_2\,SO_4$ etc. As a weak base, it precipitates the hydroxides of many metals from their salt solutions. For example ,

(a) $2\,FeCl_3\,(aq) + 3\,NH_4OH\,(aq) \longrightarrow \underset{\text{(brown ppt)}}{Fe_2O_3 . xH_2O\,(s)} + 3\,NH_4Cl\,(aq)$

(b) $ZnSO_4\,(aq) + 2\,NH_4OH\,(aq) \longrightarrow \underset{\text{(white ppt)}}{Zn(OH)_2\,(s)} + (NH_4)_2\,SO_4\,(aq)$

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

(c) $NiCl_2\,(aq.) + 2NH_4OH\,(aq.) \longrightarrow Ni(OH)_2\downarrow$ (green) $+ 2NH_4Cl$

(d) $CrCl_3\,(aq.) + 3NH_4OH\,(aq.) \longrightarrow Cr(OH)_3\downarrow$ (green) $+ 3NH_4Cl$

(e) $CoCl_2\,(aq.) + 2NH_4OH\,(aq.) \longrightarrow Co(OH)_2\downarrow$ (pink) $+ 2NH_4Cl$

$Cr(OH)_3$ (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+} :

(a) $\underset{\text{(blue)}}{Cu^{2+}\,(aq)} + 4\,NH_3\,(aq) \rightleftharpoons \underset{\text{(deep blue)}}{[Cu(NH_3)_4]^{2+}\,(aq)}$

(b) $\underset{\text{(colourless)}}{Ag^+\,(aq) + Cl^-\,(aq)} \rightleftharpoons \underset{\text{(white ppt)}}{AgCl\,(s)}$

(c) $\underset{\text{(white ppt)}}{AgCl\,(s)} + 2\,NH_3\,(aq) \longrightarrow \underset{\text{(colourless)}}{[Ag\,(NH_3)_2]Cl\,(aq)}$

(d) $Cd^{2+}\,(aq) + 4NH_3(aq) \longrightarrow \underset{\text{(colourless)}}{[Cd(NH_3)_4]^{2+}\,(aq)}$

(iii) Thermal dicompostion of ammonium salts :

Ammonium salts decompose quite readily on heating. If the anion is not particularly oxidising (e.g. Cl^- CO_3^{2-} or SO_4^{2-}) then ammonia is evolved.

$$NH_4Cl \xrightarrow{\Delta} NH_3 + HCl \; ; \qquad (NH_4)_2SO_4 \xrightarrow{\Delta} 2NH_3 + H_2SO_4$$

If the anion is more oxidising (e.g. NO_2^-, NO_3^-, ClO_4^-, $Cr_2O_7^{2-}$) then NH_4^+ is oxidised to N_2 or N_2O.

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

(iv) Test of Ammonia and Ammonium salts :

When NH_3 gas is passed into the colourless solution of Nessler's reagent a brown precipitate or coloration is

formed. This is a test for NH_3 gas.

$$2K_2HgI_4 + 3KOH + NH_3 \longrightarrow \underset{\text{(Millon base)}}{H_2N{\cdot}HgO{\cdot}HgI} \downarrow \text{(brown)} + 7KI + 2H_2O$$

(v) Reaction with Ammonia :

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

$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$

$NH_3 + HCl \rightarrow NH_4Cl \times 6$

$8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$

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

$NH_3 + 3Cl \rightarrow NCl_3 + 3HCl$.

(e) USES OF NH_3 :

1. Used as a refrigeration fluid.
2. For the production of ammonium fertilizers such as ammonium sulphate, ammonium phosphate, ammonium nitrate, urea etc.
3. For removing grease because NH_4OH dissolves grease.
4. For manufacture of HNO_3 by the Ostwald process.
5. As a laboratory reagent.
6. In the production of artificial rayon, silk, nylon etc.

PHOSPHINE (PH_3) :

(a) PREPARATION :

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

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

(ii) In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO_2.

$$P_4 + 3\,NaOH + 3\,H_2O \longrightarrow PH_3 + 3\,\underset{\text{(sodium hypophosphite)}}{NaH_2PO_2}$$

(b) PROPERTIES :

(i) It is a colourless gas with a slightly garlic or rotten fish smell and is highly poisonous. It explodes in contact with traces of oxidising agents like HNO_3 , Cl_2 and Br_2 vapours.

(ii) It is slightly soluble in water but soluble in CS_2 and other organic solvents. The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2.

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

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

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

Note : With silver nitrate, Later on decomposes to black Ag.

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

$$PH_3 + HBr \longrightarrow PH_4Br$$

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

(c) USES OF PH_3 :

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

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

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

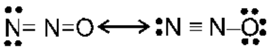
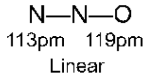
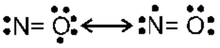
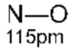
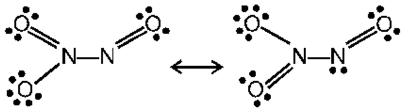
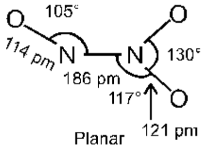
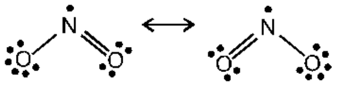
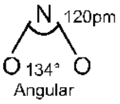
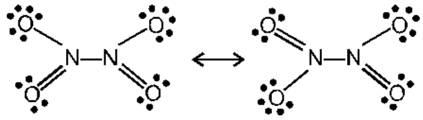
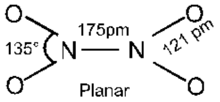
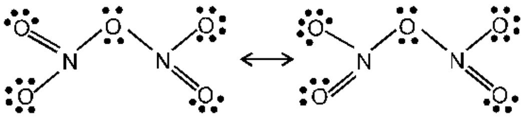
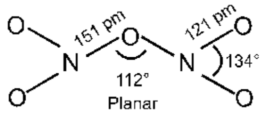
Oxides :

(a) Oxides of nitrogen

S.N. / Compounds	Preparation	Properties
1. N_2O (Nitrous Oxide)	$NH_4NO_3 \xrightarrow{280°C} N_2O + 2H_2O$	• Stable, relatively unreactive, colourless gas and a neutral oxide. • Used as an anaesthetic and called laughing gas.
2. NO (Nitric Oxide)	**Laboratory method:** (i) $3Cu + 8HNO_3 \rightarrow 2NO + 3Cu(NO_3)_2 + 4H_2O$ (ii) $2HNO_2 + 2I^- + 2H^{\oplus} \rightarrow 2NO + I_2 + 2H_2O$	• Colourless gas, an important intermediate in manufacturing of nitric acid by Ostwald process. • Neutral oxide, not an acid anhydride. • Reacts instantly with O_2 to give NO_2 $2NO + O_2 \rightarrow 2NO_2$ • $3NO \xrightarrow[30-50°C]{\text{Highpressure}} N_2O + NO_2$
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. $NO + NO_2 \rightarrow N_2O_3$ $4NO + O_2 \rightarrow 2N_2O_3$	• Blue solid, acidic oxide and anhydride of HNO_2. • With alkali forms nitrites $N_2O_3 + NaOH \rightarrow 2NaNO_3 + H_2O$ $N_2O + H_2O \rightarrow 2HNO_2$
4. [Nitrogendioxide] and N_2O_4	• Laboratory method: $2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$ • $Cu + \underset{\text{(conc.)}}{4HNO_3} \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$ • $\underset{\substack{\text{Paramagnetic}\\\text{Brown}}}{2NO_2} \rightleftharpoons \underset{\substack{\text{Diamagnetic}\\\text{colourless}}}{N_2O_4}$	• 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. $N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2$ • NO_2 –N_2O_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 $4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$	- Colourless deliquescent solid, highly reactive, strong oxidizing agent - Anhydride of HNO_3. - In gas phase, decomposes into NO_2, NO and O_2

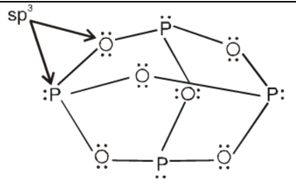
Table : Structures of Oxides of Nitrogen

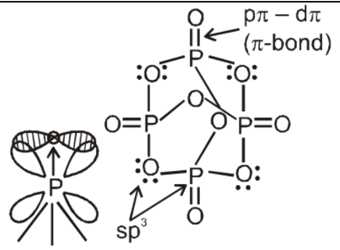
Formula	Resonance Structures	Bond Parameters
N_2O		
NO		
N_2O_3		
NO_2		
N_2O_4		
N_2O_5		

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

(b) 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 pπ-dπ back bonding. A full p-orbital on the oxygen atom overlaps sideway 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 pπ-dπ bonds = 4

(a) 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.

$$P_4 + 3O_2 \longrightarrow P_4O_6$$

PROPERTIES :

(i) It is colourless crystalline solid having melting point 23.8°C and boiling point 178°C.

(ii) It dissolves in cold water to form phosphorus acid. It is thus the anhydride of phosphorus acid.

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$$

(iii) It dissolves in hot water liberating PH_3

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

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

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

(b) PHOSPHORUS PENTAOXIDE (P_4O_{10}) :

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

PREPARATION :

It is obtained by burning phosphorus in excess air.

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

PROPERTIES:

(i) It is a white powder ,acidic in nature and is the anhydride of orthophosphoric acid.

(ii) It sublimes on heating at 250°C.

(iii) It dissolves in water with hissing sound forming metaphosphoric acid and finally orthophosphoric acid.

$$P_4O_{10} + 2H_2O \longrightarrow 4HPO_3\ ; \quad 4HPO_3 + 2H_2O \longrightarrow 2H_4P_2O_7\ ; \quad 2H_4P_2O_7 + 2H_2O \longrightarrow 4H_3PO_4$$

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

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

USES OF P_4O_{10} :

1. For drying acidic gases.

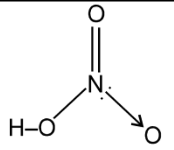
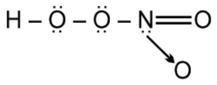
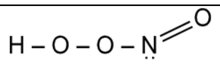
2. As a dehydrating agent
3. For the preparation of SO_3 and N_2O_5.
4. For the preparation of phosphoric acid.

Oxyacids

(a). OXY ACIDS OF NITROGEN :

OXY-ACIDS OF NITROGEN

(N atom sp^2 hybridised)

1.	HNO_3	NITRIC ACID (COLOURLESS)	
2.	HNO_2	NITROUS ACID (PALE BLUE)	$H-\underset{\cdot\cdot}{\ddot{O}}-\ddot{N}=O$
3.	$H_2N_2O_2$	HYPONITROUS ACID	$H-O-\underset{\cdot\cdot}{N}=\underset{\cdot\cdot}{N}-O-H$
4.	HNO_4 or $HNO_2(O_2)$	Pernitric acid or Peroxy nitricacid	
5.	$HNO(O_2)$	PEROXY NITROUS ACID	

(b) NITROUS ACID (HNO_2) :

PREPARATION :

By acidifying an aqueous solution of a nitrite

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

PROPERTIES:

(i) It is an unstable, weak acid which is known only in aqueous solution.

(ii) On trying to concentrate, the acid decomposes as given below.

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

(iii) Nitrous acid and nitrites are good oxidizing agents and convert iodides to iodine, ferrous salts to ferric, stannous to stannic and sulphites to sulphates eg.

$$2KI + 2HNO_2 + 2HCl \longrightarrow 2H_2O + 2NO + 2KCl + I_2$$

(iv) With strong oxidizing agents like $KMnO_4$ nitrous acid and nitrites function as reducing agents and get oxidized to NO_3^- ions : $2KMnO_4 + 5KNO_2 + 6HCl \longrightarrow 2MnCl_2 + 5KNO_3 + 3H_2O + 2KCl$

(c) 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.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

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

This method is based upon catalytic oxidation of NH_3 by atmospheric oxygen.

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

Nitric oxide thus formed combines with oxygen giving NO_2.

$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

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

$$3\,NO_2\,(g) + H_2O\,(\ell) \longrightarrow 2\,HNO_3\,(aq) + NO\,(g)$$

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

Physical properties :

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

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

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

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

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 : 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	$M(NO_3)_2$	$M + 2HNO_3 \rightarrow M(NO_3)_2 + H_2$
2. Zn, Fe	(a) very dilute	NH_4NO_3	$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$
	(b) dilute	N_2O	$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$
	(c) concentrated	NO_2	$Zn + 4HNO_3 \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$
3. Sn	(a) dilute	NH_4NO_3	$4Sn + 10HNO_3 \rightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$
	(b) concentrated	NO_2	$Sn + 4HNO_3 \rightarrow \underset{\text{meta stannic acid}}{H_2SnO_3} + 4NO_2 + H_2O$
4. Pb	(a) dilute	NO	$3Pb + 8HNO_3 \rightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$
	(b) concentrated	NO_2	$Pb + 4HNO_3 \rightarrow Pb(NO_3)_2 + 2NO_2 + 2H_2O$
(B) Metals below H in ECS			

5. Cu, Ag, Hg	(a) dilute Hg forms $Hg_2(NO_3)_2$	NO	$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$.
	(b) concentrated	NO_2	$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

(C) Metalloids

Sb, As	concentrated	NO_2	$Sb + 5HNO_3 \rightarrow \underset{\text{antimonic acid}}{H_3SbO_4} + 5NO_2 + H_2O$

(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.

$$I_2 + 10\ HNO_3 \longrightarrow 2\ HIO_3 + 10\ NO_2 + 4\ H_2O$$

$$C + 4\ HNO_3 \longrightarrow CO_2 + 2\ H_2O + 4\ NO_2$$

$$S_8 + 48\ HNO_3\ \text{(concentrated)} \longrightarrow 8\ H_2SO_4 + 48\ NO_2 + 16\ H_2O$$

$$P_4 + 20\ HNO_3\ \text{(concentrated)} \longrightarrow 4\ H_3PO_4 + 20\ NO_2 + 4\ H_2O$$

(iii) Brown Ring Test :

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

$$NO_3^- + 3\ Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2\ H_2O$$

$$[Fe\ (H_2O)_6]^{2+} + NO \longrightarrow [Fe\ (H_2O)_5\ (NO)]^{2+} + H_2O$$

USES OF HNO_3 :

(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.

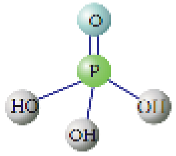
(ii) It is also used for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds.

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

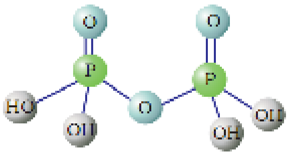
(d) Oxy acids of phosphorous:

Name	Formula	Oxidation	Characteristic	Praparation
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	$PCl_3 + H_3PO_3$

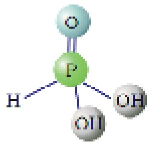
Hypophosphoric	$H_4P_2O_6$	+4	Four P–OH Two P = O One P–P	Red P_4 + alkali
Orthophosphoric	H_3PO_4	+5	Three P–OH One P = O	$P_4O_{10} + H_2O$
Pyrophosphoric	$H_4P_2O_7$	+5	Four P – OH Two P = O One P–O–P	Heating phosphoric acid
Metaphosphoric	$(HPO_3)_n$	+5	Three P–OH Three P = O Three P–O–P	Phosphorus acid + Br_2, heat in a sealed tube



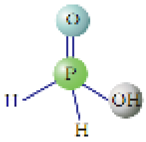
H_3PO_4 Orthophosphoric acid



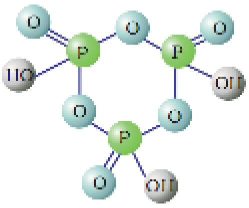
$H_4P_2O_7$ Pyrophosphoric acid



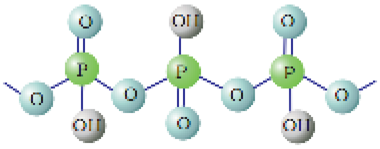
H_3PO_3 Orthophosphorous acid



H_3PO_2 Hypophosphorous acid



Cyclotrimetaphosphoric acid, $(HPO_3)_3$



Polymetaphosphoric acid, $(HPO_3)_n$

Action of heat on phosphoric acid and its salts :

$H_3PO_4 \xrightarrow{220°C} H_4P_2O_7$ (pyrophosphoric acid) ; $H_4P_2O_7 \xrightarrow{316°C} HPO_3$ (metaphosphoric acid)

$$NaH_2PO_4 \xrightarrow{\Delta} NaPO_3 + H_2O$$

$$2Na_2HPO_4 \xrightarrow{\Delta} Na_4P_2O_7 + H_2O$$

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

Halides and Oxyhalides

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

(a) Phosphorus Trichloride :

Preparation :

(i) It is obtained by passing dry chlorine over heated white phosphorus.

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

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

$$P_4 + 8\,SOCl_2 \longrightarrow 4\,PCl_3 + 4\,SO_2 + 2\,S_2Cl_2$$

(b) Properties :

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

$$PCl_3 + 3\ H_2O \longrightarrow H_3PO_3 + 3\ HCl$$

(ii) It reacts with organic compounds containing – OH group such as CH_3COOH, C_2H_5OH.

$$3\ CH_3COOH + PCl_3 \longrightarrow 3\ CH_3COCl + H_3PO_3$$

$$3\ C_2H_5OH + PCl_3 \longrightarrow 3\ C_2H_5Cl + H_3PO_3$$

(c) Phosphorus pentachloride :

(i) Preparation :

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

$$P_4 + 10\ Cl_2 \longrightarrow 4\ PCl_5$$

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

$$P_4 + 10\ SO_2Cl_2 \longrightarrow 4\ PCl_5 + 10\ SO_2$$

(ii) 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.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2\ HCl$$

$$POCl_3 + 3\ H_2O \longrightarrow H_3PO_4 + 3\ HCl$$

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

$$PCl_5 \xrightarrow{250°C} PCl_3 + Cl_2$$

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

$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$$

$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$

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

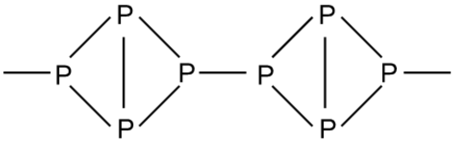
$$2\ Ag + PCl_5 \longrightarrow 2\ AgCl + PCl_3$$

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

It is used in the synthesis of some organic compounds , e.g., C_2H_5Cl , CH_3COCl.

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

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



Ex.2 What happens ?

(a) When phosphine is heated at 150ºC .

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

Sol. (a) Phosphine on heating at 150ºC burns forming H_3PO_4

$$PH_3 + 2O_2 \longrightarrow H_3PO_4$$

(b) The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2.

Ex.3 $P_4 + NaOH \xrightarrow{\text{warm}}$ Products.

Explain the reducing character of one of the products obtained by taking the example of silver nitrate.

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

$3AgNO_3 + PH_3 \longrightarrow Ag_3P \downarrow$ (yellow) + $3HNO_3$. Ag_3P

$Ag_3P + AgNO_3 + 3H_2O \longrightarrow 3Ag \downarrow$ (black) + $3HNO_3 + H_3PO_3$

$4\ AgNO_3 + 2\ H_2O + H_3PO_2 \longrightarrow 4\ Ag + 4\ HNO_3 + H_3PO_4$

Ex.4 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.

$$2\overset{0}{Ag} + \overset{+5}{P}Cl_5 \longrightarrow 2\overset{+1}{Ag}Cl + \overset{+3}{P}Cl_3$$

$$\overset{0}{Sn} + 2\overset{+5}{P}Cl_5 \longrightarrow \overset{+4}{Sn}Cl_4 + 2\overset{+3}{P}Cl_3$$

$$\overset{+5}{P}Cl_5 + \overset{0}{H_2} \longrightarrow \overset{+3}{P}Cl_3 + 2\overset{+1}{H}Cl$$

Ex.5 What happens when

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

Ans : (a) $PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$; (b) $PCl_5 + D_2O \longrightarrow POCl_3 + 2\ DCl$; (c) $4\ H_3PO_3 \xrightarrow{\Delta} 3\ H_3PO_4 + PH_3$

Ex.6 (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) $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2$ (sodium hypophosphite) + PH_3

Thus acid (A) is H_3PO_2, i.e., hypophosphorus acid.

(ii) $2P + 3Cl_2 + 6H_2O \longrightarrow 2H_3PO_3$ (phosphorus acid) + 6HCl

Thus, acid (B) is H_3PO_3

(iii) $P_4 + 20HNO_2 \longrightarrow 4H_3PO_4$ (C) + $20NO_2 + 4H_2O$

$P_4 + 10H_2SO_4 \longrightarrow 4H_3PO_4$ (C) (phosporic acid) + $10SO_2 + 4H_2O$

Thus, acid (C) is H_3PO_4

(iv) $H_3PO_2 + 2H_2O \longrightarrow H_3PO_4 + 4H$

$HgCl_2 + 2H \longrightarrow Hg_2Cl_2$ (D) (white) + 2HCl ; $Hg_2Cl_2 + 2H \longrightarrow 2Hg$ (E) (grey) + 2HCl

Section (C) : Physical and Chemical properties of Group 16th elements :

Atomic & physical properties :

Group 16 Elements : The Oxygen family :

ATOMIC & PHYSICAL PROPERTIES

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.

Polonium {Radio activeMetal}

(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.

Allotropy

(i) **Oxygen :** Exists in 2 allotropic forms :

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

(ii) **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.

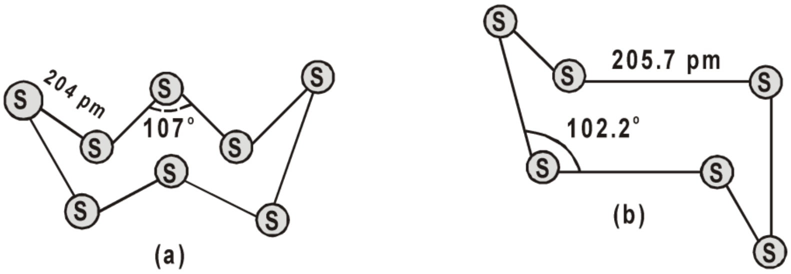


Fig. : The structures of (a) S_8 ring in rhombic sulphur and (b) S_6 form

(vi) 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) $\underset{<160°C}{\overset{\text{at }160°C}{\rightleftharpoons}}$ some S_8 rings break. Diradical so formed polymerises to forms long chain polymer.

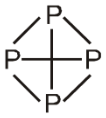
Viscocity starts to increase $\xrightarrow{\text{At } 200^\circ C}$ Viscosity further increases $\xrightarrow[\text{boiling point}]{\text{At } 444^\circ C}$ viscosity decreases, shorter chains and rings are formed $\xrightarrow{\text{At } 600^\circ C}$ in vapour state exist as S_2 molecules (paramagnetic like O_2).

Solved Examples

Ex.7 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 pπ-pπ multiple bond ($N \equiv N$) because of small size of nitrogen atom. Heavier elements of this group do not form pπ-pπ bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping. Further P–P single bond is stronger than N–N single bond. Hence phosphorus has tendency to under go catenation.

$N \equiv N$ (N_2) ;  (P_4)

Ex.8 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.9 Why does nitrogen show catenation properties less than prosphorus?

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

Ex.10 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.

Ex.11 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.

General trends and Chemical properties :

Group 16 Elements : The Oxygen family :

(i) 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 towards oxygen :

All these elements form oxides of the EO_2 and EO_3 types where E = S, Se, Te or Po. Ozone (O_3) and sulphur dioxide (SO_2) are gases while selenium dioxide (SeO_2) is solid. Reducing property of dioxide decreases from SO_2 to TeO_2 ; SO_2 is reducing while TeO_2 is an oxidising agent. Besides EO_2 type sulphur, selenium and tellurium also form EO_3 type oxides (SO_3, SeO_3, TeO_3). Both types of oxides are acidic in nature.

Table : Oxides of Group 16 Elements

Element	Dioxide	Trioxide	Other oxide
Sulphur	SO_2	SO_3	S_2O, S_6O, S_8O
Selenium	SeO_2	SeO_3	–
Tellurium	TeO_2	TeO_3	TeO
Polonium	PoO_2	–	PoO

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

Table : Properties of Hydrides of Group 16 Elements

Property	H_2O	H_2S	H_2Se	H_2Te
m.p./K	273	188	208	222
b.p./K	373	213	232	269
H-E distance/pm	96	134	146	169
HEH angle (°)	104	92	91	90
$\Delta_f H$/kJ mol^{-1}	-286	-20	73	100
$\Delta_{diss} H$ (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 : $H_2S > H_2Se > H_2Te > H_2O$

The order of stability : $H_2O > H_2S > H_2Se > H_2Te$

The order of boiling points : $H_2O > H_2Te > H_2Se > H_2S$

The order of K_a values : $H_2Te > H_2Se > H_2S > H_2O$

(iv) Reactivity toward the Halogens :

(a) Elements of group 16 form a larger number of halides of the type EX_6, EX_4 and EX_2 where E is an element of the group –16 and X is an halogen. The stabilities of the halides decrease in the order F > Cl > Br > I. Amongst hexahalides, hexafluorides are the only stable halides.
(b) All hexafluorides are gaseous in nature. They have octahedral structure. Sulphur hexafluoride SF_6 is exceptionally stable for steric reasons.
(c) Amongst tetrafluorides, SF_4 is a gas , SeF_4 liquid and TeF_4 a solid These fluorides have sp^3d hybridisation and thus, have trigonal bipyramidal structure in which one of the equatorial position is occupied by a lone pair of electrons. This geometry is also regarded as see - saw geometry.
(d) All elements except selenium form dichlorides and dibromides. These dihalides are formed by sp^3 hybridisation and thus have tetrahedral structure. The well known monohalides are dimeric in nature, Examples are S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2 and Se_2Br_2. These dimeric halides undergo disproportionation as given below :

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

(e) The order of stability of halides of sulphur with different halogens is : $F^- > Cl^- > Br^- > I^-$

Table : Halides of Group 16 Elements

Element	M_2X_2 type	MX_2 type	MX_4 type	MX_6 type	Other types of Halides
Sulphur	S_2F_2 S_2Cl_2	SF_2 SCl_2	SF_4 SCl_4	SF_6	S_2F_4 S_2F_{10}
Selenium	Se_2Cl_2 Se_2Br_2	$SeCl_2$	SeF_4 $SeCl_4$	SeF_6	Se_2F_4
Tellurium	Te_2Cl_2	$TeCl_2$ $TeBr_2$ TeI_2	TeF_4 $TeBr_4$ TeI_4	TeF_6 $TeBr_6$	–
Polonium	–	$PoCl_2$ $PoBr_2$	$PoCl_4$ $PoBr_4$		–

(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.

- One typical example of effects of small size and high electronegativity is the presence of strong hydrogen bonding in H_2O which is not found in H_2S.
- The absence of d orbitals in oxygen restricts its covalency to four and in practice, rarely increases beyond two. On the other hand, in case of other elements of the group, the valence shell can be expanded and covalence exceeds four.

Preparation of Elements :

(i) 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)

$$2KClO_3 \xrightarrow[\text{Catalyst}]{150^\circ\ MnO_2} 2KCl + 3O_2 + \text{traces of } Cl_2 \text{ or } ClO_2$$

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

$2HOCl \xrightarrow{Co^{+2}} 2HCl + O_2$ or by electrolysis of water with a force of H_2SO_4 or $Ba(OH)_2$ solution.
(d) By thermal decomposition of oxides of metals.

$2HgO \xrightarrow{450^0 C} 2Hg + O_2$; $2Ag_2O \xrightarrow{350^0 C} 4Ag + O_2$

$3MnO_2 \xrightarrow{\Delta} Mn_3O_4 + O_2$; $2Pb_3O_4 \xrightarrow{\Delta} 6PbO + O_2$

(e) Thermal decomposion of $K_2Cr_2O_7$ and $KMnO_4$

$4\ K_2Cr_2O_7 \xrightarrow{\Delta} 4\ K_2CrO_4 + 2\ Cr_2O_3 + 3O_2$; $2\ KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$

(ii) 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.

$2H_2S + 3O_2 \longrightarrow 2SO_2 + 2H_2O$

$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$

(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.

Physical Properties of Nitrogen, Phosphorus, Oxygen, Sulphur

Element	Physical Properties
Nitrogen	• 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	• Solid at room temperature, soft, waxy and reactive. • Reacts with moist air and give out light (chemiluminescence). • Ignites spontaneously in air at about 35°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°C, P_4 begin to dissociate in to P_2 molecule.
Oxygen	• 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 $^{16}_{8}O$, $^{17}_{8}O$ and $^{18}_{8}O$ • Does not burn but is a strong supporter of combustion.
Sulphur	• Melts to form a mobile liquid. • Dissolves in oleum giving brightly coloured solutions which may be yellow, deep blue or bright red.

Solved Examples

Ex.12 Write the reaction of thermal decomposition of sodium azide.

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

Ex.13 What happens when:

(a) NH_4Cl & $NaNO_3$ is heated strongly. (b) $(NH_4)_2CO_3$ is heated. (c) NH_4NO_2 is heated.

Sol. (a) $NH_4Cl + NaNO_3 \longrightarrow NH_4NO_3 + NaCl$; $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

(b) $(NH_4)_2CO_3 \xrightarrow{\Delta} 2NH_3 + CO_2 + H_2O$ (c) $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

Ex.14 (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. $NH_4NO_3 + NaOH \xrightarrow{\Delta} NH_3 + NaNO_3 + H_2O$; $NH_3 + HCl \xrightarrow{} NH_4Cl$ (white fumes)

$NaNO_3 + 7NaOH + 4Zn \xrightarrow{} 4Na_2ZnO_2 + NH_3\uparrow + 2H_2O$

$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

So, (A) = NH_4NO_3, (B) = NH_3, (C) = $NaNO_3$, (D) = N_2O and (E) = H_2O.

Ex.15 Anhydrous $CaCl_2$, P_4O_{10} or concentrated H_2SO_4 can not be used as drying agent for ammonia. Why ?

Sol. Ammonia cannot be dried using $CaCl_2$, P_2O_5 or concentrated H_2SO_4 because NH_3 reacts with all of these.

$CaCl_2 + 8NH_3 \xrightarrow{} CaCl_2\cdot 8NH_3$; $P_2O_5 + 6NH_3 + 3H_2O \xrightarrow{} 2(NH_4)_3PO_4$

$H_2SO_4 + 2NH_3 \xrightarrow{} (NH_4)_2SO_4$; $CaO + H_2O \xrightarrow{} Ca(OH)_2$

Ex.16 NO_2 can not be dried by an alkali, why ?

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

Ex.17 Illustrate how copper metal can give different products on reaction with HNO_3.

Sol. On heating with dil. HNO_3, copper gives copper nitrate and nitric oxide.

$3Cu + 8HNO_3 \text{ (dil)} \xrightarrow{\text{Heat}} 3Cu(NO_3)_2 + 4H_2O + 2NO$ (nitric oxide)

With conc. HNO_3, instead of NO, NO_2 is evolved.

$Cu + 4HNO_3 \text{ (conc)} \xrightarrow{\text{Heat}} Cu(NO_3)_2 + 2H_2O + 2NO_2$ (nitrogen dioxide)

Section (D) : Compounds of Oxygen and sulphur

Hydrides :

HYDROGEN SULPHIDE (H_2S) :

(a) Preparation :

(i) $FeS + H_2SO_4 \xrightarrow{} FeSO_4 + H_2S$

It is prepared in kipp's apparatus

(ii) Preparation of pure H_2S gas

$Sb_2S_3 \text{ (pure)} + 6\ HCl \text{ (pure)} \xrightarrow{} 2\ SbCl_3 + 3\ H_2S$

(b) Physical Properties :

(i) Colourless gas with rotten egg smell .

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

(c) Chemical Properties :

(i) Reducing Agent :

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

(a) $H_2S + X_2 \xrightarrow{} 2\ HX + S$;

(b) $H_2S + SO_2 \xrightarrow{\text{moisture}} H_2O + S$;

(c) $H_2O_2 + H_2S \xrightarrow{} H_2O + S + O_2$

(d) $2HNO_3 \xrightarrow{} H_2O + 2NO_2 + [O]$

$H_2S + [O] \longrightarrow H_2O + S$

$2HNO_3 \longrightarrow 2H_2O + 2NO_2 + S$

(e) $H_2S + 2O_3 \longrightarrow H_2SO_4 + O_2$

- It also reduces MnO_4^- to Mn^{2+}, H_2SO_4 to SO_2 & $K_2Cr_2O_7$ to Cr^{3+} (acidic medium)
- MnO_4^- to MnO_2 (alkaline medium)

(ii) **Acidic Nature :**

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

$H_2S \rightleftharpoons HS + H^+ \rightleftharpoons S^{2-} + 2H^+$

Therefore, It forms two series of salts as given below

$NaOH + H_2S \longrightarrow NaHS + H_2O$; $NaOH + H_2S \longrightarrow Na_2S + 2H_2O$

(iii) **Formation of Polysulphides :**

They are obtained by passing H_2S gas through metal hydroxides.

$NH_4OH + H_2S \longrightarrow (NH_4)_2S + 2H_2O$; $(NH_4)_2S + H_2S \text{ (excess)} \longrightarrow (NH_4)_2\ S_{x+1} + xH_2$

yellow ammonium sulphide

(d) TESTS FOR H_2S :

(i) Turns acidified lead acetate paper black.

(ii) Gives violet or purple colouration with alkaline sodium nitroprusside solution (containing NaOH).

USES OF H_2S :

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

Other hydrides not in syllabus

Solved Examples

Ex.18 Why NH_3 gas cannot be dried by passing over P_2O_5 , $CaCl_2$ and H_2SO_4 ?

Sol. $CaCl_2 + 8NH_3 \longrightarrow CaCl_2.8NH_3$;

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

$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4$

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

$CaO + H_2O \longrightarrow Ca(OH)_2$

Ex.19 What happens ?

(a) When phosphine is heated at 150ºC.

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

Sol. (a) Phosphine on heating at 150ºC burns forming H_3PO_4 $PH_3 + 2O_2 \longrightarrow H_3PO_4$

(b) The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2.

Ex.20 P_4 + NaOH Products.

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

Sol. $P_4 + 3\,NaOH + 3\,H_2O \longrightarrow PH_3 + \underset{\text{(sodium hypophosphite)}}{3\,NaH_2PO_2}$; $4Cu^{2+} + PH_3 + 4H_2O \longrightarrow H_3PO_4 + 4Cu\downarrow + 8H^+$

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

Ex.21 Black (A) + $H_2SO_4 \longrightarrow$ (B) gas + (C)

(B) + $(CH_3COO)_2Pb \longrightarrow$ (D) black ppt.

(C) + $K_3[Fe(CN)_6] \longrightarrow$ (E) blue.

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

Sol. $FeS + H_2SO_4 \longrightarrow H_2S + FeSO_4$; $H_2S + (CH_3COO)_2Pb \longrightarrow$ PbS (black ppt.) + $2CH_3COOH$.

$Fe^{2+} + K_3[Fe(CN)_6]^{3-} \longrightarrow KFe_{II}[Fe_{III}(CN)_6]$ Turnbull’s blue.

Oxides :

(a) OZONE (O_3)

(i) PREPARATION :

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

$$O_2 \xrightarrow{\text{energy}} O + O$$

$$O_2 + O \longrightarrow O_3 \text{ ; } \Delta H = 2845 \text{ kJ mol}^{-1}$$

$$3O_2 \rightleftharpoons 2O_3$$

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

- Higher concentration or pure O_3 can be obtained by fractional liquefaction of the mixture.
- Low concentration of O_3 can be made by UV irradiation of O_2.
- $O_2 \xrightarrow[\text{(ii) quenching}]{\text{(i) 2500°C}} O_3$

(b) PROPERTIES :

PHYSICAL PROPERTIES :

(i) Dark blue gas which forms a blue liquid on cooling and on solidification forms violet black crystals. The colour is due to intense absorption of red light.

(ii) It also absorbs strongly in the UV region. Thus it protects the people on the earth from the harmful UV radiation from the sun.

(iii) It has sharp smell often associated with sparking electrical equipment. It is toxic and is slightly soluble in water but more in turpentine oil, glacial acetic acid or CCl_4. O_3 molecule is diamagnetic but O_3^- is paramagnetic.

(c) CHEMICAL PROPERTIES :

(i) Oxidising agent : $O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O$; SRP = + 2.07 V (in acidic medium)

$O_3 + H_2O + 2e^- \longrightarrow O_2 + 2OH^-$; SRP = + 1.24 V (in alkaline medium)

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

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

$$\begin{array}{l} O_3 \longrightarrow O_2 + [O] \\ 2\,KI + H_2O + [O] \longrightarrow 2\,KOH + I_2 \\ \hline 2\,KI + H_2O + O_3 \longrightarrow 2\,KOH + O_2 + I_2 \end{array}$$

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

$KI + 3O_3 \longrightarrow KIO_3 + 3O_2$; $KI + 4O_3 \longrightarrow KIO_4 + 4O_2$

Note : Similarly S^{2-} to SO_4^{2-} (but not H_2S), NO_2^- to NO_3^-, SO_3^{2-} to SO_4^{2-}, AsO_3^{3-} to AsO_4^{3-}, Sn^{2+} to Sn^{4+} (acidic medium).

(iii) $O_3 \longrightarrow O_2 + [O]$

$$\begin{array}{l} 2\,K_2MnO_4 + [O] + H_2O \longrightarrow 2\,KMnO_4 + 2KOH \\ \hline 2\,K_2MnO_4 + O_3 + H_2O \longrightarrow 2\,KMnO_4 + 2KOH + O_2 \end{array}$$

(iv) Similarly $[Fe(CN)_6]^{4-}$ oxidises to $[Fe(CN)_6]^{3-}$ (basic medium).

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

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

$$\begin{array}{l} O_3 \longrightarrow O_2 + [O] \times 3 \\ S + 3\,[O] \longrightarrow SO_3 \\ SO_3 + H_2O \longrightarrow H_2SO_4 \\ \hline S + 3O_3 + H_2O \longrightarrow H_2SO_4 + 3O_2 \end{array}$$

(c) It oxidises H_2S to S.

$H_2S + O_3 \longrightarrow H_2O + S \downarrow$ (yellow)

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

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

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

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

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

(f) **Reaction with Silver :**

Silver articles become black in contact with ozone.

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

(g) **Reaction with H_2O_2 :**

$2e^- + 2H^+ + O_3 \longrightarrow O_2 + H_2O$

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

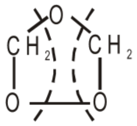
$O_3 + H_2O_2 \longrightarrow 2O_2 + H_2O$

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

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

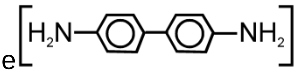
$CH_2 = CH_2 + O_3 \longrightarrow$  $\xrightarrow[-ZnO]{Zn+H_2O}$ 2HCHO

(j) **Reaction with KOH :**

Forms orange coloured compound, potassium ozonide.

$2\ KOH + 5O_3 \longrightarrow 2\overset{+}{K}O_3^{-} + 5O_2 + H_2O$
(orange solid)

(d) TESTS FOR OZONE

(i) A filter paper soaked in a alcoholic benzidine  becomes brown when brought in contact with O_3 (this is not shown by H_2O_2)

(ii) **Tailing of mercury**

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

$2\ Hg + O_3 \longrightarrow Hg_2O + O_2$

USES OF OZONE :

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

Solved Examples

Ex.22 O_3 is a powerful oxidising agent. Write equation to represent oxidation of

(a) I^- to I_2 in acidic solutions,

(b) sulphur to sulphuric acid in the presence of moisture,

Sol. (a) $O_3 + 2I^- + 2H^+ \longrightarrow O_2 + I_2 + H_2O$; (b) $3O_3 + S + H_2O \longrightarrow H_2SO_4 + 3O_2$.

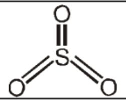
Ex.23 Give the important applications of O_3 .

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.

(e) **Oxides of Sulphur :**

SO_2		Both bonds are equivalent
SO_3		All three S–O bonds are equivalent. out of 3π bonds One is pπ-pπ other two are pπ-dπ.

SULPHUR DIOXIDE :

(f) **PREPARATION :**

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

(ii) $CaSO_4 \text{ (gypsum)} + C \xrightarrow[1000°C]{\Delta} 2\,CaO + SO_2 + CO_2$

○ By this method SO_2 is obtained in large scale

(g) **PROPERTIES :**

(i) Colourless gas with burning sulphur smell.

(ii) It is heavier than air and is highly soluble in water. SO_2 in solution is almost completely present as $SO_2.6H_2O$ and only traces of H_2SO_3.

(iii) Neither burns nor helps in burning but burning magnesium and potassium continue to burn in its atmosphere.

$$3Mg + SO_2 \longrightarrow 2\,MgO + MgS\ ;\ 4K + 3SO_2 \longrightarrow K_2SO_3 + K_2S_2O_3$$

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

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

(v) **Addition Reaction :**

$$SO_2 + Cl_2 \xrightarrow{\text{Sun light}} SO_2Cl_2 \text{ (sulphuryl chloride)}$$

$$SO_2 + O_2 \xrightleftharpoons[\text{Asbests}]{\text{platinised}} SO_3\ ;\ PbO_2 + SO_2 \longrightarrow PbSO_4$$

(vi) **Reducing Nature :**

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

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

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

(a) Reduces halogens to corresponding halides.

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

$$2H + Cl_2 \longrightarrow 2HCl$$

$$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$$

(b) Reduces acidified iodates to iodine

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H] \times 5$$

$$2KIO_3 + H_2SO_4 \longrightarrow K_2SO_4 + 2HIO_3$$

$$2HIO_3 + 10H \longrightarrow I_2 + 6H_2O$$

$$2KIO_3 + 5SO_2 + 4H_2O \longrightarrow K_2SO_4 + 4H_2SO_4 + I_2$$

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

Acidified $K_2Cr_2O_7 \longrightarrow Cr^{3+}$(green coloured solution) & Ferric Sulphate ⟶ Ferrous sulphate

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

(a) $2H_2S + SO_2 \xrightarrow{\text{moisture}} 2H_2O + 3S$

(b) $2SnCl_2 + SO_2 + 4HCl \longrightarrow 2SnCl_4 + 2H_2O + S$

(c) $2Hg_2Cl_2 + SO_2 + 4HCl \longrightarrow 2HgCl_2 + 2H_2O + S$

(d) $2CO + SO_2 \longrightarrow 2CO_2 + S$

(e) $2\,Fe + SO_2 \longrightarrow 2FeO + FeS$

(viii) **Bleaching Action :**

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

This is due to the reducing nature of SO_2

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

Therefore, bleaching is temporary.

USES OF SO_2 :

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

SULPHUR TRIOXIDE (SO_3) :

(h) PREPARATION :

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

○ P_4O_{10} is dehydrating agent

(ii) $Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3$

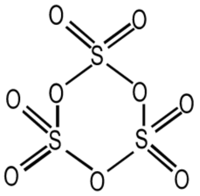
(iii) $2SO_2 + O_2 \overset{pt}{\rightleftharpoons} 2SO_3$

(i) PROPERTIES :

SO_3 exists in three allotropic forms :

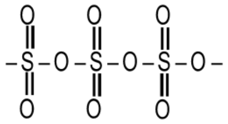
At room temperature SO_3 is solid and exists in three distinct forms.

(a) γ-SO_3 : It is ice-like and is a cyclic trimer $(SO_3)_3$, m.p. 16.8ºC. If SO_3 is kept for a long time, or if a trace of water is present, either β-SO_3 or α-SO_3 is formed.



Cyclic trimer of γ-SO_3

(b) α-SO_3/β-SO_3 : β-SO_3 (m.p. 32.5ºC) is made up of infinite helical chains of tetrahedral $[SO_4]$ unit each sharing two corners. This structure is similar to that of chain phosphates. α-SO_3 (m.P. 62.2ºC) 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 (α-SO_3 or β-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

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

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

(iii) $SO_3 + HCl \longrightarrow SO_2(OH)Cl$ (chlorosulphuric acid)

(iv) **Oxidising Nature :**

(a) $2SO_3 + S \xrightarrow{100^0C} 3SO_2$

(b) $5SO_3 + 2P \longrightarrow 5SO_2 + P_2O_5$

(c) $SO_3 + PCl_5 \longrightarrow POCl_3 + SO_2 + Cl_2$

(d) $SO_3 + 2HBr \longrightarrow H_2O + Br_2 + SO_2$

USES OF SO_3 :

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

Solved Examples

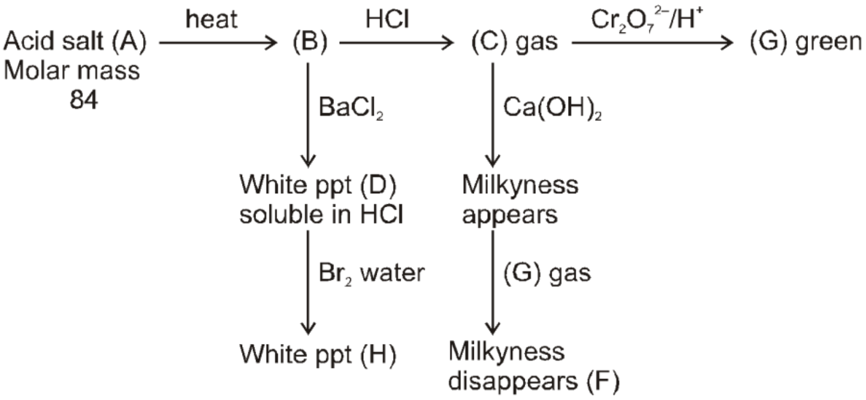
Ex.24 SO_2 and Cl_2 both are used as bleaching agent. What factors cause bleaching ?

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

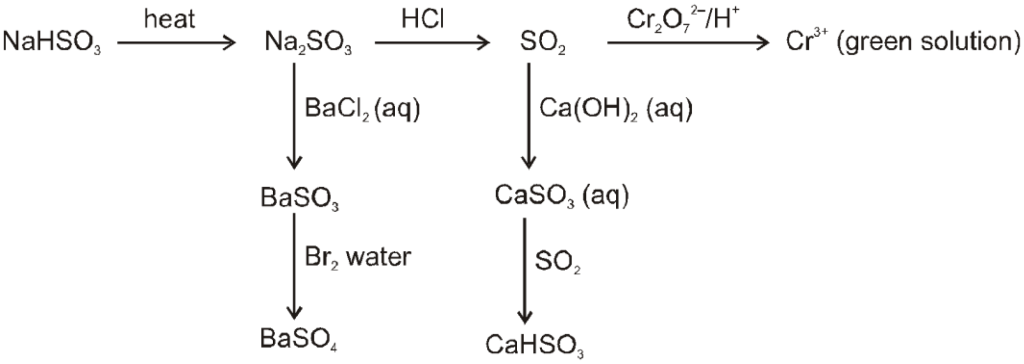
$Cl_2 + H_2O \longrightarrow 2HCl + O$.

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

Ex.25



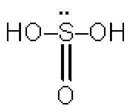
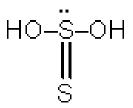
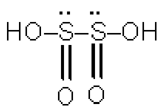
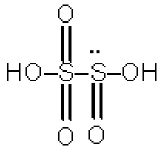
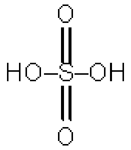
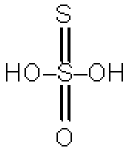
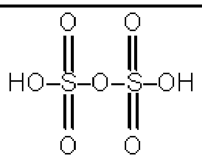
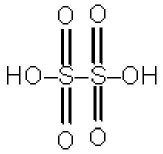
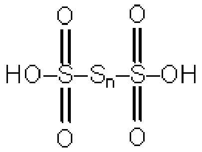
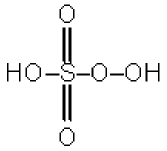
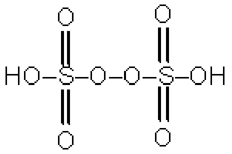
Sol.



Oxyacids

Oxy acids of sulphur

Sulphur forms a number of oxoacid such as H_2SO_3, $H_2S_2O_4$, $H_2S_2O_5$, $H_2S_2O_6$ (x = 2 to 5,) H_2SO_4, $H_2S_2O_7$, H_2SO_8. Some of these acids are unstable and cannot be isolated. They are known in aqueous solution or in the forms of their salts. Structures of some important oxoacids are shown in figure.

Oxyacid	Formula of acid	Oxidation state of S	Structure	Other information
(a) Sulphurous acid series				
Sulphurous acid	H_2SO_3	+4	 $HO-\underset{\underset{O}{\Vert}}{\overset{..}{S}}-OH$	Tautomeric structures are possible
Thiosulphurous acid	$H_2S_2O_2$	-2, +4	 $HO-\underset{\underset{S}{\Vert}}{\overset{..}{S}}-OH$	pπ-dπ bond between sulphur atoms
Dithionous acid	$H_2S_2O_4$	+3, +3	 $HO-\underset{\underset{O}{\Vert}}{\overset{..}{S}}-\underset{\underset{O}{\Vert}}{\overset{..}{S}}-OH$	Unstable and is known as hyposulphurous form
Pyrosulphurous acid	$H_2S_2O_5$	+5, +3	 $HO-\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}-\underset{\underset{O}{\Vert}}{\overset{..}{S}}-OH$	Average oxidation state of sulphur is +4
(b) Sulphuric acid series				
Sulphuric acid	H_2SO_4	+6	 $HO-\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}-OH$	Has 2 pπ-dπ bond
Thiosulphuric acid	$H_2S_2O_3$	-2, +6	 $HO-\overset{\overset{S}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}-OH$	Hydrated thiosulphates are familiar as hypo ($Na_2S_2O_3.5H_2O$).
Pyrosulphuric acid	$H_2S_2O_7$	+6, +6	 $HO-\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}-O-\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}-OH$	It is called oleum and also as fuming sulphuric acid
(c) Thionic acid series				
Dithionic acid	$H_2S_2O_6$	+5, +5	 $HO-\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}-\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}-OH$	Has 2 pπ-dπ bonds each sulphur atom
Polythionic acid (x = n + 2) (n = 1-12)	$H_2S_xO_6$	+5, 0, +5	 $HO-\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}-S_n-\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}-OH$	Middle sulphur atom have zero oxidation state
(d) Peroxy acid series				
Peroxymono-sulphuric acid	H_2SO_5	+6	 $HO-\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}-O-OH$	Called Caro's acid. Fairly stable
Peroxydi-sulphuric acid	$H_2S_2O_8$	+6, +6	 $HO-\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}-O-O-\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}-OH$	Called Marshall's acid. Persulphates are well known

SULPHURIC ACID (H_2SO_4) :

Manufacture :

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

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 ($H_2S_2O_7$)

(iv) The SO_2 produced is profiled by removing dust and other impurities such as arsenic compounds.

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

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

(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.

$$SO_3 + H_2SO_4 \longrightarrow \underset{\text{(Oleum)}}{H_2S_2O_7}$$

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

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

Lead chamber process :

$$2SO_2 + O_2\ \text{(air)} + 2H_2O + [NO]\ \text{(catalyst)} \longrightarrow 2H_2SO_4 + [NO]\ \text{(catalyst)}.$$

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

Note : It is outdated process, need not remember.

Physical Properties :

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

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

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

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

Chemical Properties :

(i) Sulphuric acid ionises in two steps.

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

$$H_2SO_4^-(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq)\ ;\ Ka_2 = 1.2 \times 10^{-2}$$

The larger value of K_{a1} ($K_{a1} > 10$) means that H_2SO_4 is largely dissociated into H^+ and HSO_4^-. Greater the value of dissociation constant (K_a) the stronger is the acid.

(a) The acid forms two series of salts : normal sulphates (such as sodium sulphate and copper sulphate and acid sulphate (e.g., sodium hydrogen sulphate)

(b) Decomposes carbonates and bicarbonates in to CO_2.

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

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

$2MX + H_2SO_4 \rightarrow 2HX + M_2SO_4$ (X = F, Cl, NO_3) ; $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$
(M = Metal)

○ $KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$

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

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

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

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

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

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

$H_2SO_4 + KBr \longrightarrow KHSO_4 + HBr$

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

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

$HO - SO_2 - OH + PCl_5 \longrightarrow Cl - SO_2 - OH + POCl_3 + HCl$

$HO - SO_2 - OH + 2PCl_5 \longrightarrow Cl - SO_2 - Cl + 2POCl_3 + 2HCl$

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

(vi) $3KClO_3 + 3H_2SO_4 \longrightarrow 2KHSO_4 + HClO_4 + 2ClO_2 + H_2O$

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.

SULPHUROUS ACID (H_2SO_3) :

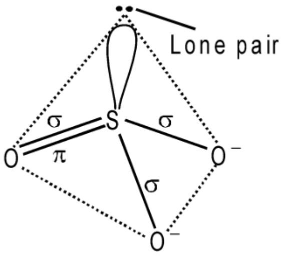
This acid is known only in solution. The solution is obtained by dissolving SO_2 in water.

$SO_2 + H_2O \longrightarrow H_2SO_3$

Though SO_2 is very soluble in water, most is present as hydrated $SO_2(SO_2.H_2O)$. 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.

$H_2SO_3 \rightleftharpoons H_2O + SO_2$



Properties :

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

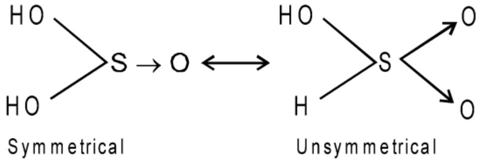
$H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^-$

(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.



Miscellaneous Compounds

HYDROGEN PEROXIDE (H_2O_2) :

PREPARATION :

(i) Laboratory Method :

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

$BaSO_4$ 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.

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

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

$3BaO_2 + 2H_3PO_4 \longrightarrow Ba_3(PO_4)_2\downarrow + 3H_2O_2$; $Ba_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3BaSO_4\downarrow + 2H_3PO_4$

H_3PO_4 can again be used.

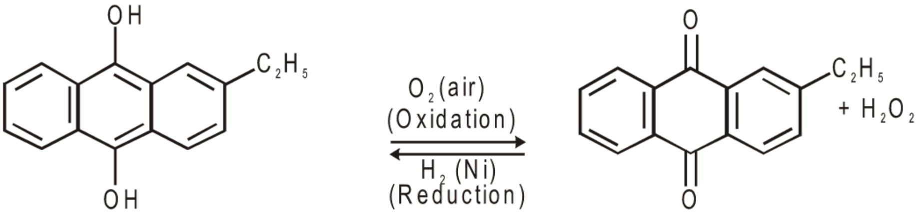
(ii) By electrolysis of concentrated H_2SO_4 or $(NH_4)_2SO_4$ at a high current density to form peroxosulphates, which then hydrolysed.

$$H_2SO_4 \rightleftharpoons H^{\oplus} + HSO_4^{\ominus}$$

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

$$H_2S_2O_8 + H_2O \xrightarrow[\text{distillation}]{80-90°C} H_2SO_5 + H_2SO_4 \text{ ; } H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2$$

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



2- Ethyl anthraquinol 2-Ehtylanthraquinone

PHYSICAL PROPERTIES :

(i) Colourless viscous liquid which appears blue in the larger quantity and is soluble in water (due to H-bonding) in all proportions and form a hydrate $H_2O_2.H_2O$ (melting point 221 K).

(ii) Its boiling point 423 K is more than water but freezing point (–4ºC) 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. $2H_2O_2 \longrightarrow 2H_2O + O_2$

Note : H_2O_2 is not kept in glass containers because traces of alkali metal ions from the glass can catalyse the explosive decomposition of H_2O_2 Therefore, aqueous solution is stored in plastic or wax-lined glass containers and some urea or phosphoric acid or glycerol is added to that solution because these compounds have been found to behave as negative catalyst for the decomposition of H_2O_2

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

$H_2O_2\ (aq) \rightleftharpoons H^+ + HO_2^-$; $K_a = 1.5 \times 10^{-12}$ at 25^0 C

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

$$Na_2CO_3 + H_2O_2 \longrightarrow Na_2O_2 + H_2O + CO_2$$

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

❍ A 30% H_2O_2 solution has pH = 4.0

Chemical Properties :

(i) **Oxidising Agent :**

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

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

❍ 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 $PbSO_4$.

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

$$PbS + 4[O] \longrightarrow PbSO_4$$

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

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

(b) H_2O_2 oxidises H_2S to sulphur.

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

$$H_2S + [O] \longrightarrow H_2O + S\downarrow$$

$$H_2O_2 + H_2S \longrightarrow 2H_2O + S\downarrow$$

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

$$H_2O_2 + 2H^+ 2I^- \longrightarrow I_3^- + 2H_2O$$

- H_2O_2 in acidic medium also oxidises

  AsO_3^{3-} to AsO_4^{3-}, SO_3^{2-} to SO_4^{2-}, KI to I_2, S^{2-} to SO_4^{2-},
  $FeSO_4$ to $Fe_2(SO_4)_3$ and $[Fe(CN)_6]^{4-}$ to$[Fe(CN)_6]^{3-}$

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

(d)

(B) In alkaline medium :

(a) $Cr(OH)_3$ (s) + 4 NaOH + $3H_2O_2 \longrightarrow 2Na_2CrO_4$ (aq.) + $8H_2O$

or

$$10\ OH^- + 3\ H_2O_2 + 2\ Cr^{3+} \longrightarrow 2\ CrO_4^{2-} + 8H_2O$$

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

- Used as a brightener in washing powder.

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

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

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

$$2\ OH^- + H_2O_2 \longrightarrow O_2 + 2H_2O + 2e^-$$

(a) Ag_2O is reduced to Ag.

$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O_2 + O_2$

(b) It reduces O_3 to O_2.

$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$

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

$2\,K_3\,[Fe(CN)_6] + 2KOH \longrightarrow K_4[Fe(CN)_6] + H_2O + O$

$H_2O_2 + O \longrightarrow H_2O + O_2$

$2K_3[Fe(CN)_6] + 2KOH + H_2O_2 \longrightarrow 2K_4\,[Fe(CN)_6] + 2H_2O + O_2$

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

$2\,Au^{3+} + 3H_2O_2 \longrightarrow 2Au\downarrow + 6H^+ + 3O_2$

❍ 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^-

TESTS FOR H_2O_2 :

(i) With $K_2Cr_2O_7$:$Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \xrightarrow{\text{amyl alcohol}} 2CrO_5 + 5H_2O$

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

$CrO_5 + H_2SO_4 \longrightarrow 2Cr_2\,(SO_4)_3 + 6H_2O + 7O_2$

(ii) $2\,HCHO + H_2O_2 \xrightarrow[\text{pyrogallol}]{OH^-} 2\,HCOOH + H_2$

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

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

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

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

USES OF H_2O_2 :

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

Solved Examples

Ex.26 Write the allotropic forms of oxygen

Ans. Ordinary oxygen and ozone.

Ex.27 Ozone layer is being depleted. This is due to :

(A) NO emission from supersonic jets

(B) chloroflurocarbon used as aerosols

(C*) both (A) and (B)

(D) none of the above

Sol. (A) $O_3 + NO \longrightarrow NO_2 + O_2$

(B) $Cl_2CF_2 \longrightarrow .Cl + .CClF_2$; $.Cl + O_3 \longrightarrow ClO. + O_2$

$ClO. \longrightarrow Cl. + O.$; $ClO. + O. \longrightarrow .Cl + O_2$

Ex.28 In the following reaction explain which one is oxidising agent and which one is reducing agent ?

$$H_2O_2 + O_3 \longrightarrow 2\,O_2 + H_2O$$

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

$$2e^- + 2\,H^+ + O_3 \longrightarrow O_2 + 2\,H_2O$$

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

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 .

Ex.29 O_3 is a powerful oxidising agent. Write equation to represent oxidation of

(a) I^- to I_2 in acidic solutions,

(b) sulphur to sulphuric acid in the presence of moisture,

Ans. (a) $O_3 + 2I^- + 2H^+ \longrightarrow O_2 + I_2 + H_2O$

(b) $3O_3 + S + H_2O \longrightarrow H_2SO_4 + 3O_2$.

Ex.30 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.31 Which allotropic form of sulphur is stable at room temperature ?

Ans. Rhombic sulphur

Ex.32 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.33 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.

Ex.34 Describe the changes which occur on heating sulphur .

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