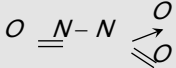
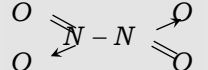
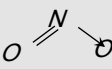
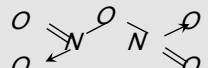
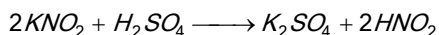
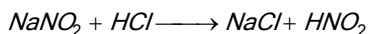


Table : 18.4 Oxides of Nitrogen

Oxide	Structure	Physical appearance	Preparation
Nitrous oxide ( $N_2O$ ) +1	$N \equiv N \rightarrow O$	Colourless gas	By heating ammonium nitrate upto $240^\circ\text{C}$ $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$ , It is Collected over hot water
Nitric oxide ( $NO$ ) +2	$N = O$	Colourless	(a) By the action of cold dil. $HNO_3$ on copper turnings (Laboratory method) $3Cu + 8 \text{ dil. } HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$ (b) By the action of $H_2SO_4$ on a mixture of $FeSO_4$ and $KNO_3$ (4:1) $2KNO_3 + 5H_2SO_4 + 6FeSO_4 \rightarrow 2KHSO_4 + 3Fe_2(SO_4)_3 + 4H_2O + 2NO$ (c) By catalytic oxidation of ammonia. $4NH_3 + 5O_2 \xrightarrow[850^\circ C]{Pt} 4NO + 6H_2O$
Dinitrogen trioxide ( $N_2O_3$ ) +3		Blue solid	(a) By the action of 50% $HNO_3$ on arsenious oxide. $2HNO_3 + As_2O_3 + 2H_2O \rightarrow NO + NO_2 + 2H_3AsO_4$ $\downarrow 250 K$ $N_2O_3$
Dinitrogen tetraoxide ( $N_2O_4$ ) +4		Colourless liquid	(a) By heating nitrates of heavy metals, e.g., lead nitrate. $2Pb(NO_3)_2 \xrightarrow{673 K} 4NO_2 + 2PbO + 2O$
Nitrogen dioxide ( $NO_2$ ) +4		Brown gas	(b) By heating copper turnings with conc. $HNO_3$ . $Cu + 4 HNO_3 (\text{conc.}) \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$
Dinitrogen pentoxide ( $N_2O_5$ ) +5		Colourless gas	(a) By dehydrating $HNO_3$ with phosphorus pentoxide $4HNO_3 + P_4O_{10} \rightarrow 2N_2O_5 + 4HPO_3$

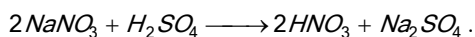
(3) **Oxyacids of nitrogen** : Oxyacids of nitrogen are  $HNO_2, HNO_3, H_4N_2O_4$  and  $HNO_4$ , which are explosive.  
(Nitroxylic acid) (Pernitric acid)

(i) **Nitrous acid ( $HNO_2$ )** : It is prepared by adding ice cold dil,  $HCl$  or dil,  $H_2SO_4$  to a well cooled solution of any nitrite ( $NaNO_2, Ba(NO_2)_2$  etc.).

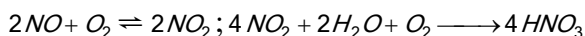
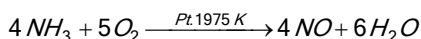


It oxidises  $H_2S$  to  $S$ ,  $KI$  to  $I_2$  and acts as a reducing agent in presence of strong oxidising agent, i.e., it reduces acidified  $KMnO_4, K_2Cr_2O_7, H_2O_2$  etc. to  $Mn^{2+}, Cr^{3+}$  and  $H_2O$  respectively.

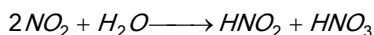
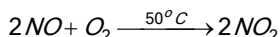
(ii) **Nitric acid ( $HNO_3$ )** :  $HNO_3$  is called aqua fortis. It is prepared in the laboratory by distillation of nitre with conc.  $H_2SO_4$ .



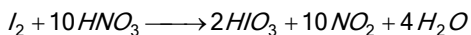
Commercially, it is obtained by Ostwald's process. In this process,  $NH_3$  is first catalytically oxidised to  $NO$  which is cooled to about  $300K$  and then oxidised by air to  $NO_2$ . Absorption of  $NO_2$  in water in presence of oxygen gives  $HNO_3$



From air (Birkeland Eyde electric arc process)



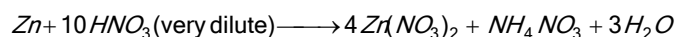
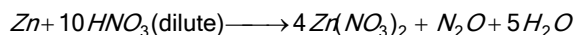
**Properties** : It is a very strong acid and decomposes on boiling or in presence of sunlight. It acts as a strong oxidising agent. It oxidises nonmetals and metalloids to their respective oxy-acids, i.e.,  $C$  to  $H_2CO_3$ ,  $S$  to  $H_2SO_4$ ,  $P$  to  $H_3PO_4$ ,  $I_2$  to  $HIO_3$ ,  $As$  to  $H_3AsO_4$  (arsenic acid) and  $Sb$  to  $H_3SbO_4$  (antimonic acid), while nitric acid itself is reduced to  $NO_2$ .



Nitric acid reacts with metals to form nitrates and is itself reduced to  $NO, N_2O, NO_2$  or  $NH_3$  (which further reacts with  $HNO_3$  to give  $NH_4NO_3$ ) depending upon the concentration of the acid, activity of the metal and the temperature of the reaction.

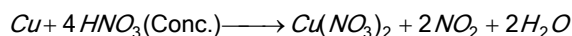
(i) Very active metals such as  $Mn, Mg, Ca$ , etc. give  $H_2$  on treatment with very dilute  $HNO_3$  (2%).

(ii) Less active metals like  $Cu, Hg, Ag, Pb$  etc. give  $NO$  with dil.  $HNO_3$ . Zinc, however, gives  $N_2O$  with dil  $HNO_3$  and  $NH_4NO_3$  with very dilute  $HNO_3$ .

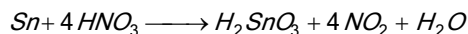


Similarly,  $Fe$  and  $Sn$  react with dilute nitric acid to give  $NH_4NO_3$ .

(iii) Conc.  $HNO_3$  gives  $NO_2$  both with active metals ( $Zn, Pb$  etc.) and less active metals ( $Cu, Hg, Ag$  etc.)

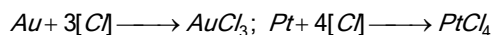
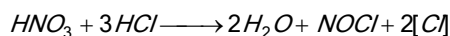


Tin is, however, oxidized by conc.  $HNO_3$  to metastannic acid ( $H_2SnO_3$ ).

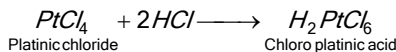
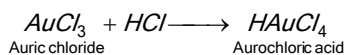


**Passivity** :  $Fe, Cr, Ni$  and  $Al$  become passive in conc.

$HNO_3$  (i.e., lose their normal reactivity) due to the formation of a thin protective layer of the oxide on the surface of the metal which prevents further action. Nitric acid has no action on noble metals ( $Au, Pt$ ) but these metals dissolve in aqua regia (3 vol.  $HCl$  + 1 vol.  $HNO_3$ ) forming their respective chlorides.



These chlorides subsequently dissolve in excess of  $HCl$  forming their corresponding soluble complexes. Thus,



Sugar on oxidation with nitric acid gives oxalic acid. Nitric acid reacts with glycerine to give glycerol trinitrate or nitro glycerine, with toluene it gives 2, 4, 6-trinitrotoluene (T.N.T.) and with cellulose (cotton) it gives cellulose trinitrate (gun cotton). All these are used as explosives.

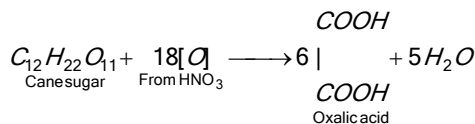


Table : 18.5 Oxyacids of nitrogen

Name of oxoacid	M. F.	Structure	Oxidation State of N	Basicity	pK <sub>a</sub>	Nature
Hyponitrous acid	$H_2N_2O_2$	$\begin{array}{c} \cdot\cdot \\ N-OH \\    \\ HO-N \\ \cdot\cdot \end{array}$	+1	2(dibasic)	Very weak	Highly explosive
Nitrous acid	$HNO_2$	$\begin{array}{c} H-N=O \\   \\ O \end{array}$	+3	1 (monobasic)	3.3	Unstable, Weak acid
Nitric acid	$HNO_3$	$\begin{array}{c} H-O-N=O \\   \\ O \end{array}$	+5	1 (monobasic)	-3.0	Stable, Strong acid
Pernitric acid	$HNO_4$	$\begin{array}{c} O=N-O-O-H \\   \\ O \end{array}$	+5	1 (monobasic)		Unstable and explosive

### Phosphorus and its compounds

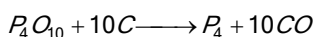
It is the second member of group 15 (VA) of the Periodic table.

Due to larger size of  $P$ , it can not form stable  $P\pi - P\pi$  bonds with other phosphorous atoms where as nitrogen can form  $P\pi - P\pi$  bonds .

(1) **Occurrence** : Phosphorous occurs mainly in the form of phosphate minerals in the crust of earth. Some of these are :

(i) Phosphorite  $Ca_3(PO_4)_2$ , (ii) Fluorapatite  $Ca_5(PO_4)_3F$ , (iii) Chlorapatite  $3Ca_3(PO_4)_2 \cdot CaCl_2$ , (iv) Hydroxyapatite;  $Ca_5(PO_4)_3OH$ . Phosphates are essential constituents of plants and animals. It is mainly present in bones, which contains about 58% calcium phosphate.

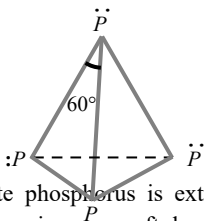
(2) **Isolation** : Elemental phosphorus is isolated by heating the phosphorite rock with coke and sand in an electric furnace at about 1770K,



(3) **Allotropic forms of phosphorus** : Phosphorus exists in three main allotropic forms,

(i) White phosphorus, (ii) Red phosphorus, (iii) Black phosphorus

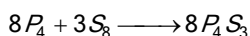
(i) **White or yellow phosphorus** : It is obtained from phosphate rock or phosphorite as explained above. It exists as  $P_4$  units where four  $P$  atoms lie at the corners of a regular tetrahedron with  $\angle PPP = 60^\circ$ . Each  $P$  atom is linked to three other  $P$  atoms by covalent bonds. there are total six bonds and four lone pairs of electrons present in a  $P_4$  molecule of white phosphorus.



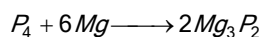
**Properties** : White phosphorus is extremely reactive due to strain in the  $P_4$  molecule, poisonous, soft, low melting (317K) solid, soluble in  $CS_2$ , alcohols and ether. It has a garlic odour. Persons working with white  $P$  develop a disease known as Phossy jaw in which jaw bones decay. It turns yellow on exposure to light. Hence, it is also called yellow phosphorus.

It spontaneously catches fire in air with a greenish glow which is visible in the dark ( $P_4 + 3O_2 \rightarrow P_4O_6$ ). This phenomenon is called phosphorescence. Because of its very low ignition temperature (303K), it is always kept under water.

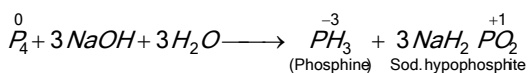
With sulphur it gives tetraphosphorus trisulphide with explosive violence which is used in "strike anywhere matches".



With metals phosphorus forms phosphides. For example,

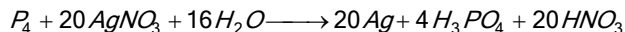
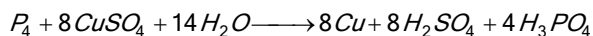


With aqueous alkalis, on heating, white phosphorus gives phosphine

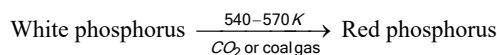


It is an example of a disproportionation reaction where the oxidation state of  $P$  decreases from 0 to  $-3$  (in  $PH_3$ ) and increases to  $+1$  (in  $NaH_2PO_2$ )

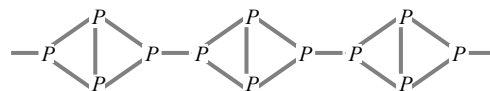
White phosphorus acts as a strong reducing agent. It reduces  $HNO_3$  to  $NO_2$  and  $H_2SO_4$  to  $SO_2$ . It also reduces solutions of  $Cu, Ag$  and  $Au$  salts to their corresponding metals. For examples,



(ii) **Red phosphorus** : It is obtained by heating white phosphorus at 540–570K out of contact with air in an inert atmosphere ( $CO_2$  or coal gas) for several hours.



Red phosphorus exists as chains of  $P_4$  tetrahedra linked together through covalent bonds to give a polymeric structure as shown.



Due to its polymeric structure, red phosphorus is much less reactive and has m.p. much higher than that of white phosphorus.

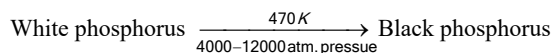
**Properties** : Red phosphorus is a hard, odourless, non poisonous solid, insoluble in organic solvents such as  $CS_2$ , alcohol and ether. Its ignition temperature is much higher than that of white phosphorus and thus does not catch fire easily. It does not show phosphorescence.

It sublimes on heating giving vapours which condense to give white phosphorus. It is denser than white phosphorus and is a bad conductor of electricity.

It burns in oxygen at 565K to give phosphorus pentoxide, reacts with halogens, sulphur and alkali metals only when heated forming their corresponding salts.

It does not react with caustic alkalies and this property is made use in separating red phosphorus from white phosphorus.

(iii) **Black phosphorus** : It is obtained by heating white phosphorus at 470K under high pressure (4000–12000atm) in an inert atmosphere.

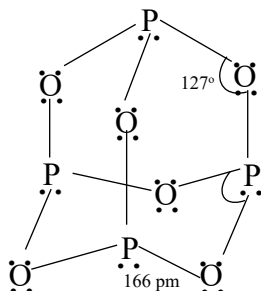


It has a double layered structure. Each layer is made up of zig-zag chains with  $P-P-P$  bond angle of  $99^\circ$ . Since it is highly polymeric, it has high density. It is the most stable (inactive) form of phosphorus and has a black metallic luster. It is a good conductor of heat and electricity.

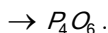
### (4) Compounds of phosphorus

(i) **Oxides and oxyacids of phosphorus** : Phosphorus is quite reactive and forms number of compounds in oxidation states of  $-3$ ,  $+3$  and  $+5$ . Phosphorus forms two common oxides namely, (a) phosphorus trioxide ( $P_4O_6$ ) and (b) phosphorus penta oxide ( $P_4O_{10}$ ).

(a) Phosphorus (III) oxide ( $P_4O_6$ ):



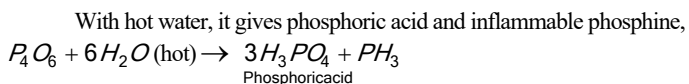
It is formed when P is burnt in a limited supply of air,  $P_4 + 3O_2$  (limited)



It is a crystalline solid with garlic odour. It dissolves in cold water to give phosphorous acid,



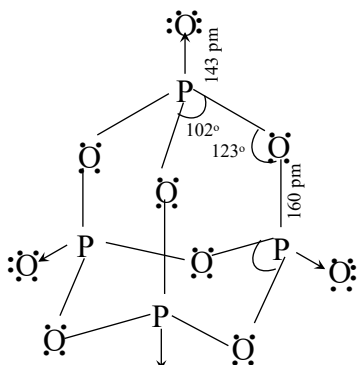
With hot water, it gives phosphoric acid and inflammable phosphine,



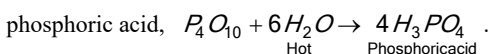
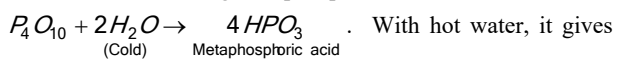
It reacts vigorously with  $Cl_2$  to form a mixture of phosphoryl chloride and meta phosphoryl chloride.



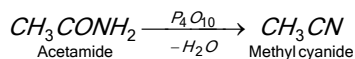
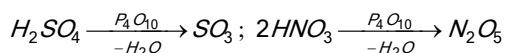
(b) Phosphorus (V) oxide ( $P_4O_{10}$ ):



It is prepared by heating white phosphorus in excess of air,  $P_4 + 5O_2 \xrightarrow{\text{excess}} P_4O_{10}$ . It is a powdery white solid. It readily dissolves in cold water forming metaphosphoric acid.



$P_4O_{10}$  is a very strong dehydrating agent. It extracts water from many compounds including  $H_2SO_4$  and  $HNO_3$ ,



(ii) Oxyacids of phosphorus : Phosphorus forms a number of oxyacids which differs in their structure and oxidation state of phosphorus. These are  $H_3PO_2$ ,  $H_3PO_3$ ,  $H_4P_2O_6$ ,  $H_3PO_4$ ,

$(HPO_3)_n$ ,  $H_4P_2O_5$ ,  $H_4P_2O_7$ . From these  $H_3PO_2$ ,  $H_3PO_3$  are reducing agents.  $H_4P_2O_5$  (pyrophosphoric acid) is dibasic acid.

$(HPO_3)_n$  is formed by dehydration of  $H_3PO_4$  at  $316^\circ C$ .

Table : 18.6 Oxyacids of phosphorus

Name	Oxidation state of P and Basicity	Structure
Hypophosphorous acid $H_3PO_2$	+1 Monobasic	
Phosphorous acid $H_3PO_3$	+3 Dibasic	
Hypophosphoric acid $H_4P_2O_6$	+4 Tetrabasic	
Orthophosphoric acid $H_3PO_4$	+5 Tribasic	
Metaphosphoric acid $(HPO_3)_n$	+5 Monobasic	
Pyrophosphoric acid (Diphosphoric acid). $H_4P_2O_7$	+5 Tetrabasic	

(5) Chemical Fertilizers : The chemical substances which are added to the soil to keep up the fertility of soil are called fertilizers.

Types of fertilizers : Chemical fertilizers are mainly of four types,

(i) Nitrogenous fertilizers : e.g. Ammonium sulphate  $(NH_4)_2SO_4$ , Calcium cyanamide  $CaCN_2$ , Urea  $NH_2CONH_2$  etc.

(ii) Phosphatic fertilizers : e.g.  $Ca(H_2PO_4)_2 \cdot H_2O$  (Triple super phosphate), Phosphatic slag etc.

(iii) Potash fertilizers : e.g. Potassium nitrate  $(KNO_3)$ , Potassium sulphate  $(K_2SO_4)$  etc.

(iv) Mixed fertilizers : These are made by mixing two or more fertilizers in suitable proportion. e.g. NPK (contains nitrogen, phosphorus and potassium).

NPK is formed by mixing ammonium phosphate, super phosphate and some potassium salts.

## Oxygen Family

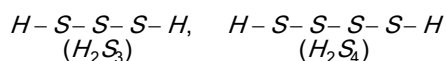
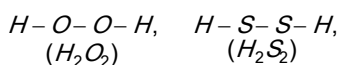
Oxygen is the first member of group 16 or VIA of the periodic table. It consists of five elements Oxygen (*O*), sulphur (*S*), selenium (*Se*), tellurium (*Te*) and polonium (*Po*). These (except polonium) are the ore forming elements and thus called **chalcogens**.

(1) Electronic configuration

Elements	Electronic configuration ( $ns^2 np^4$ )
${}_8 O$	$[He] 2s^2 2p^4$
${}_{16} S$	$[Ne] 3s^2 3p^4$
${}_{34} Se$	$[Ar] 3d^{10} 4s^2 4p^4$
${}_{52} Te$	$[Kr] 4d^{10} 5s^2 5p^4$
${}_{84} Po$	$[Xe] 4f^{14} 5d^{10} 6s^2 6p^4$

### Physical properties

- Physical state** : Oxygen is gas while all other are solids.
- Atomic radii** : Down the group atomic radii increases because the increases in the number of inner shells overweighs the increase in nuclear charge.
- Ionisation energy** : Down the group the ionisation energy decrease due to increase in their atomic radii and shielding effect.
- Electronegativity** : Down the group electronegativity decreases due to increase in atomic size.
- Electron affinity** : Element of this group have high electron affinity, electron affinity decreases down the group.
- Non – metallic and metallic character** : These have very little metallic character because of their higher ionisation energies.
- Nature of bonding** : Compound of oxygen with non metals are predominantly covalent. *S*, *Se*, and *Te* because of low electronegativities show more covalent character.
- Melting and boiling points** : The melting point and boiling points increases on moving down the group.
- Catenation** : Oxygen has some but sulphur has greater tendency for catenation.



### (10) Allotropy

- Oxygen –  $O_2$  and  $O_3$
- Sulphur – Rhombic, monoclinic, plastic sulphur
- Selenium – Red (non-metallic) grey (metallic)
- Tellurium – Non-metallic and metallic (more stable)
- Polonium –  $\alpha$  and  $\beta$  (both metallic)

(11) **Oxidation states** : Oxygen shows  $-2$ ,  $+2$  and  $-1$  oxidation states. Other elements show  $+2$ ,  $+4$  and  $+6$  oxidation states.

### Chemical properties

(1) **Hydrides** : The elements of this group form hydrides such as  $H_2O$ ,  $H_2S$ ,  $H_2Se$ ,  $H_2Te$  and  $H_2Po$ . Following are their characteristics.

(i) **Physical states** : Water is colourless and odourless while hydrides of the rest of the elements of this group are colourless, unpleasant smelling poisonous gases.

(ii) **Volatile nature** : Volatility increases from  $H_2O$  to  $H_2S$  and then decreases. The low volatility and abnormally high boiling point of water is due to the association of water molecules on account of hydrogen bonding because of strongly electronegative oxygen atom linked to hydrogen atom. thus, water is liquid while  $H_2S$  and other hydrides are gases under normal condition of temperature and pressure.

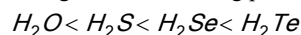
(iii) **Acidic character** : The hydrides of this group behave as weak diprotic acids in aqueous solution, the acidic character increasing from  $H_2S$  to  $H_2Te$  when  $H_2O$  is neutral.

(iv) **Thermal stability** : The thermal stability decreases from  $H_2O$  to  $H_2Po$  because the size of the central atom (from *O* to *Po*) increases resulting in longer and weaker *M-H* bond consequently the bond strength decreases. This results in the decrease of the thermal stability.

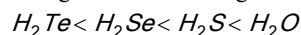
(v) **Reducing character** : The reducing power of the hydrides increases from  $H_2O$  to  $H_2Po$  due to the decreasing bond strength from  $H_2O$  to  $H_2Po$ .

(vi) **Bond angle** : All these hydrides are angular molecules and the bond angle  $H-X-H$  (*X* is *O*, *S*, *Se*, *Te*) decreases from  $H_2O$  to  $H_2Te$ .

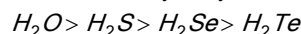
Increasing order of reducing power of hydrides :



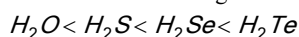
Increasing order of bond angles in hydrides :



The order of stability of hydrides :



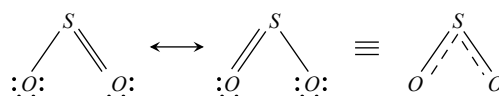
The order of increasing acidic nature of hydrides :



(2) **Oxides** : These elements form monoxides (*MO*), dioxides ( $MO_2$ ) and trioxides ( $MO_3$ ).

(i) **Dioxides** : Sulphur, selenium and tellurium burn in air to form  $SO_2$ ,  $SeO_2$  and  $TeO_2$ . The dioxide molecules contain  $p\pi-p\pi$  bonds which become weaker with increase in atomic number because of the increase in the bond length.

(a) Sulphur dioxide,  $SO_2$  is a gas at room temperature and exists as individual molecules even in the solid state. Its molecule has bent structure and is a resonance hybrid of the following canonical structures.



$SO_2$  is acidic in nature and also called the anhydride of sulphurous acid. It can act as reducing and oxidising agent.  $SO_2$  also acts as a bleaching agent in the presence of moisture, but in contrast to  $Cl_2$ , its bleaching action is temporary.

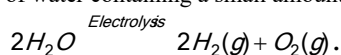


Colouring matter  $+2[H] =$  Colourless compound

Hence,  $SO_2$  bleaches due to reduction and the bleaching action is temporary.



of water containing a small amount of acid or alkali,



**Physical properties of  $O_2$**  : It is a colourless, tasteless and odourless gas. It is slightly soluble in water and its solubility is about  $30\text{ cm}^3$  per litre of water at 298 K.

**Table : 18.7 Physical properties of atomic and molecular oxygen**

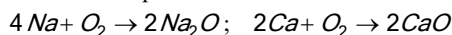
Atomic properties	Molecular properties
Atomic radius (pm) – 73	Bond length (pm) – 120.7
Ionic radius $O^{2-}$ (pm) – 140	Bond energy ( $\text{kJ mol}^{-1}$ ) – 493
Electronegativity – 3.5	Density at S.T.P. ( $\text{g cm}^{-3}$ ) – 1.429
Ionisation energy ( $\text{kJ mol}^{-1}$ ) – 1310	Melting point (K) – 54.4
Electron affinity ( $\text{kJ mol}^{-1}$ ) – 140	Boiling point (K) – 90.2

**Chemical properties of  $O_2$**  : It does not burn itself but helps in burning. It is quite stable in nature and its bond dissociation energy is very high. Therefore, it is not very reactive as such,  $O_2 \rightarrow O + O$ .

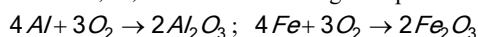
Therefore, dioxygen reacts at higher temperatures. However, once the reaction starts, it proceeds of its own. This is because the chemical reactions of dioxygen are exothermic and the heat produced during the reaction is sufficient to sustain the reactions.

(1) **Action with litmus** : Like dihydrogen, it is also neutral and has no action on blue or red litmus.

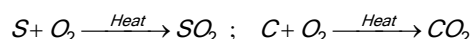
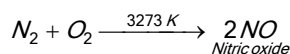
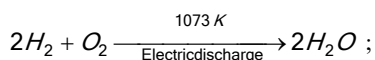
(2) **Reaction with metals** : Active metals like *Na*, *Ca* react at room temp. to form their respective oxides.



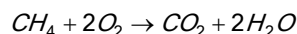
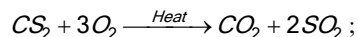
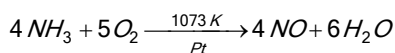
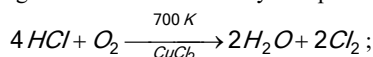
It reacts with *Fe*, *Al*, *Cu* etc. metals at high temperature



(3) **Action with Non-metals** : It form oxides.



(4) **Reaction with compounds** : Dioxygen is an oxidising agent and it oxidises many compounds under specific conditions. e.g.



Uses of dioxygen

(1) It is used in the oxy-hydrogen or oxy-acetylene torches which are used for welding and cutting of metals.

(2) It is used as an oxidising and bleaching agent,

(3) Liquid  $O_2$  is used as rocket fuel.

(4) It is used in metallurgical processes to remove the impurities of metals by oxidation.

### Compounds of Oxygen

(1) **Oxides** : A binary compound of oxygen with another element is called oxide. On the basis of acid-base characteristics, the oxides may be classified into the following four types,

(i) **Basic oxides** : Alkali, alkaline earth and transition metals form basic oxides -  $Na_2O$ ,  $MgO$ ,  $Fe_2O_3$  etc. their relative basic character decreases in the order : alkali metal oxides > alkaline earth metal oxides > transition metal oxides.

(ii) **Acidic oxides** : Non-metal oxides are generally acidic -  $CO_2$ ,  $SO_2$ ,  $SO_3$ ,  $NO_2$ ,  $N_2O_5$ ,  $P_4O_{10}$ ,  $Cl_2O_7$  etc.

(iii) **Amphoteric oxides** :  $Al_2O_3$ ,  $SnO_2$  etc.

(iv) **Neutral oxides** :  $H_2O$ ,  $CO$ ,  $N_2O$ ,  $NO$  etc.

**Trends of oxides in the periodic Table** : On moving from left to the right in periodic table, the nature of the oxides change from basic to amphoteric and then to acidic. For example, the oxides of third period has the following behaviour,

$Na_2O$ strongly basic	$MgO$ basic	$Al_2O_3$ amphote ric	$SiO_2$ weakly acidic	$P_4O_{10}$ acidic	$SO_2$ strongly acidic	$Cl_2O_7$ very strongly acidic
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Basic to acidic character increases 

However, on moving down a group, acidic character of the oxides decreases. For example in the third group, the acidic character of oxides decreases as:

$B_2O_3$ acidic	$Al_2O_3$ amphoteric	$Ga_2O_3$ (weakly basic)	$In_2O_3, Tl_2O_3$ basic
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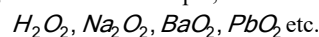
Acidic to basic character increases 

On the basis of oxygen content the oxides may be classified into the following types,

**Normal oxides** : These contain oxygen atoms according to the normal oxidation number *i.e.* - 2. For example,  $MgO$ ,  $H_2O$ ,  $CaO$ ,  $Li_2O$ ,  $Al_2O_3$  etc.

**Polyoxides** : These contain oxygens atoms more than permitted by the normal valency. Therefore, these contain oxygen atoms in oxidation state different than -2.

**Peroxides** : These contains  $O_2^{2-}$  ion having oxidation number of oxygen as -1. For example,



**Superoxides** : These contains  $O_2^-$  ion having oxidation number of oxygen as -1/2. For example,  $KO_2$ ,  $PbO_2$ , etc.

**Suboxides** : These oxides contain less oxygen than expected from the normal valency. For example,  $N_2O$ .

**Mixed oxides** : These oxides are made up of two simple oxides. For example, red lead  $Pb_3O_4 (2PbO_2 + PbO_2)$ , magnetic oxide of iron,  $Fe_3O_4 (FeO + Fe_2O_3)$  and mixed oxide of manganese,  $Mn_3O_4 (MnO_2 + 2MnO)$ .

### Ozone or trioxigen

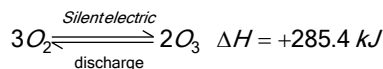
Ozone is an allotrope of oxygen. It is present in the upper atmosphere, where it is formed by the action of U. V. radiations on  $O_2$ ,  $3O_2 \xrightarrow[\text{Ozone}]{U.V. radiation} 2O_3$ .

$O_3$  protects us from the harmful U. V. radiations which causes skin cancer. Now a days, ozone layer in the atmosphere is depleting due to  $NO$  released by supersonic aircrafts and chlorofluoro carbons



(CFC'S) *i.e.* freon which is increasingly being used in aerosols and as a refrigerant.

**Preparation :** Ozone is prepared by passing silent electric discharge through pure, cold and dry oxygen in a specially designed apparatus called ozoniser. The formation of ozone from oxygen is an endothermic reaction.



Ozone is prepared in the laboratory by the following two types of ozonisers,

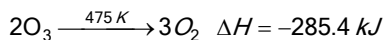
(a) Siemen's ozoniser, (b) Brodie's ozoniser

*For the better yield of ozone :* (a) Only pure and dry oxygen should be used. (b) The ozoniser must be perfectly dry. (c) A fairly low temperature ( $\approx 273 \text{ K}$ ) must be maintained. (d) The electric discharge must be sparkless.

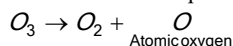
**Physical properties :** Ozone is a light blue coloured gas, having pungent odour. It is heavier than air. Its vapour density is 24. It is slightly soluble in water.

**Chemical properties :** The important chemical properties of ozone are discussed below,

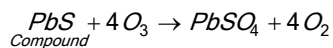
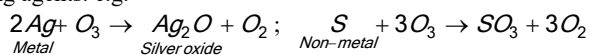
(1) **Decomposition :** Pure ozone decomposes on heating above  $475 \text{ K}$  to form  $O_2$  gas.



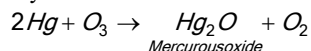
(2) **Oxidising agent :** Ozone is one of the most powerful oxidising agent with the liberation of dioxygen. In fact, ozone is a stronger oxidising agent than molecular oxygen because ozone has higher energy content and decomposes to give atomic oxygen as:



Therefore, ozone oxidises a number of non-metals and other reducing agents. e.g.

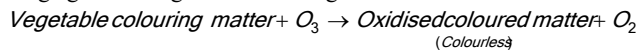


Mercury is oxidised to mercurous oxide,



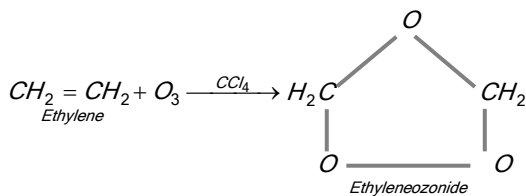
During this reaction mercury loses its meniscus and starts sticking to the sides of the glass. This is known as tailing of mercury. Mercurous oxide formed in this reaction dissolves in mercury and starts sticking to the glass surface.

(3) **Bleaching agent :** Due to the oxidising action of ozone, it acts as a mild bleaching agent as well as a sterilizing agent. It acts as a bleaching agent for vegetable colouring matter.

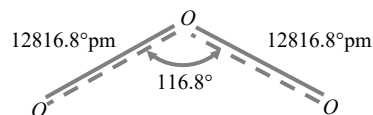


For example, ozone bleaches indigo, ivory, litmus, delicate fabrics etc.

(4) **Formation of ozonides :** Ozone reacts with alkenes in the presence of  $CCl_4$  to form an ozonide. e.g.



**Structure of  $O_3$  :** The structure of  $O_3$  molecule is angular as shown in fig. The  $O-O-O$  bond angle is  $116.8^\circ$  and  $O-O$  bond length is  $128 \text{ pm}$ .



#### Uses of ozone

(1)  $O_3$  is used for disinfecting water for drinking purposes because ozone has germicidal properties.

(2) It is used for purifying air of crowded places such as cinemas, under ground railway, auditoriums, tunnels, mines etc.

(3) It is used in industry for the manufacture of  $KMnO_4$ , artificial silk, synthetic camphor etc.

#### Sulphur and its compounds

Sulphur is the second member of oxygen family and belongs to group-16 (VI A) of the periodic table.

**Occurrence :** Sulphur occurs in the earth's crust to the extent of 0.05%. It occurs in the free state as well as in combined state. Sulphur occurs mainly as sulphides and sulphates. eg.

**Table 18.8**

Sulphide Ores	Sulphate Ores
Iron pyrites (fool's gold) – $FeS_2$	Gypsum – $CaSO_4 \cdot 2H_2O$
Galena – $PbS$	Epsom salt – $MgSO_4 \cdot 7H_2O$
Copper pyrites – $CuFeS_2$	Barytes – $BaSO_4$
Cinnabar – $HgS$	Zinc blende – $ZnS$

**Extraction of sulphur (Frasch process) :** Sulphur is generally extracted from underground deposits by drilling three concentric pipes upto the beds of sulphur (700 – 1200 feet deep).

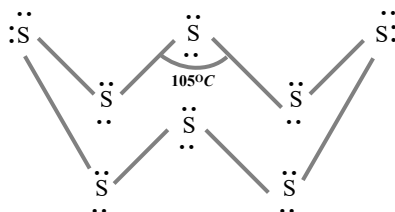
**Allotropy in sulphur :** Sulphur exists in four allotropic forms,

(1) **Rhombic or octahedral or  $\alpha$ -sulphur :** It is a bright yellow solid, soluble in  $CS_2$  and stable at room temp. All other varieties of sulphur gradually change into this form on standing.

(2) **Monoclinic sulphur or prismatic or  $\beta$ -sulphur:** It is prepared by melting the sulphur and then cooling it till a crust is formed. On removing the crust, needle shaped crystals of monoclinic sulphur separate out. It is dull yellow in colour, soluble in  $CS_2$  and stable only above  $369 \text{ K}$ . Below this temperature it changes into rhombic form.

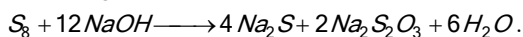
Thus, at  $369 \text{ K}$  both these varieties co-exist. This temperature is called transition temperature and the two sulphurs are called enantiotropic substances. It also exist as molecules similar to that of rhombic sulphur but the symmetry of the crystals is different.

(3) **Plastic or amorphous or  $\gamma$ -sulphur :** It is a super cooled liquid insoluble in  $CS_2$ , soft and amorphous. It consists of long zig-zag chains of S-atoms.



(4) **Colloidal or δ-sulphur** : It is prepared by passing  $H_2S$  through a solution of an oxidizing agent or water or by treating sodium thiosulphate with dil.  $HCl$ .

**Properties of sulphur** : It burns in air with a blue flame forming  $SO_2$ , gives sulphur hexafluoride with  $F_2$  and sulphur monochloride with  $Cl_2$ , sulphides with metals like  $Na, Ca, Zn, Hg, Fe, Cu$  etc., reduces  $HNO_3$  to  $NO_2$  and  $H_2SO_4$  to  $SO_2$ . With  $NaOH$  solution on heating,

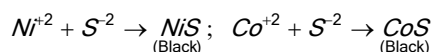
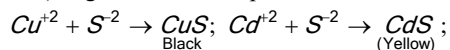


It gives sodium sulphide and sodium thiosulphate, with excess of sulphur,  $2Na_2S + S_8 \longrightarrow 2Na_2S_5$ .

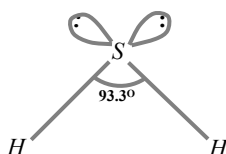
**Uses of sulphur** : It is used in the manufacture of matches, gun powder (mixture of charcoal, sulphur and potassium nitrate), explosives and fire works  $SO_2, H_2SO_4, CS_2$  and dyes, sulphur drugs and ointment for curing skin diseases and in the vulcanization of rubber.

#### Compounds of Sulphur

(1) **Hydrogen Sulphide** : It is prepared in the laboratory by the action of dil.  $H_2SO_4$  on ferrous sulphide in kipp's apparatus,  $FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$ . It is colourless gas having foul smell resembling that of rotten eggs. It reacts with many cations (of group II and IV) to give coloured sulphides,

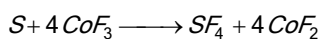


The solubility of sulphides can be controlled by the  $H^+$  ions concentration and therefore,  $H_2S$  finds extensive use in qualitative analysis of cation radicals.



(2) **Halides of sulphur** : Two important halides of sulphur are  $SF_4$  and  $SF_6$ .

(i) **Sulphur tetrafluoride** :  $SF_4$  is formed by the reaction of sulphur with  $CoF_3$ .

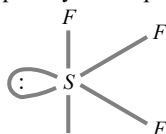


It is a colour gas which is quite reactive. It is hydrolysed with water.



It is used for fluorinating inorganic and organic compounds.

**Structure** : It has see-saw structure with  $sp^3d$ -hybridization and is derived from trigonal bipyramid geometry in which an equatorial position is occupied by a lone pair of electrons.

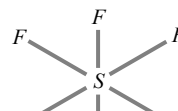


(ii) **Sulphur hexafluoride** :  $SF_6$  is prepared by burning sulphur in a stream of fluorine.  $OF_6$  is not known though sulphur forms  $SF_6$ . This is because oxygen has no  $d$ -orbitals in its valence shell.

$SF_6$  is a colourless gas. It is extremely inert substance even at red heat. It does not react with water. on account of its chemical inertness and dielectric strength, it is used as an insulator in high voltage generators and switch-gears.

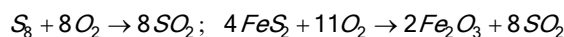
**Structure** : It has an octahedral structure with  $sp^3d^2$ -hybridisation around the central sulphur atom.

Therefore, all  $S-F$  bond distances are equal in its structure.



(3) **Oxides of sulphur** : Sulphur forms several oxides of which sulphur dioxide ( $SO_2$ ) and sulphur trioxide ( $SO_3$ ) are most important.

(i) **Sulphur dioxide ( $SO_2$ )** : It is prepared by burning sulphur or iron pyrites in air.

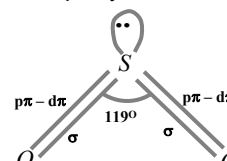


In laboratory, it is prepared by heating copper turnings with conc.  $H_2SO_4$

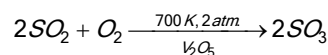


It is a colourless gas with irritating and suffocating smell.

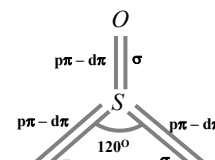
$SO_2$  molecule has a bent structure with a  $O-S-O$  bond angle of  $119^\circ$ . Sulphur is  $sp^2$  hybridized.



(ii) **Sulphur trioxide ( $SO_3$ )** : It is formed by the oxidation of  $SO_2$ .



In the gaseous phase, it exists as planar triangular molecular species involving hybridization of the  $S$ -atom. It has three  $S-O$   $\sigma$  bonds and three  $S-O$   $\pi$  bonds. The  $O-S-O$  bond angle is of  $120^\circ$ .



(4) **Oxyacids of sulphur** : Sulphur forms many oxyacids. Some of these are,

Table : 18.9 Oxyacids of sulphur

Formula	Name	Important properties	Structural formula
$H_2SO_3$ (+4)	Sulphurous acid	Free acid does not exist diprotic, strong reducing agent	$\begin{array}{c} \cdot\cdot \\ O = \overset{\cdot\cdot}{S} - OH \\   \\ OH \end{array}$
$H_2SO_4$ (+6) (Oil of vitriol)	Sulphuric acid	Stable diprotic, dehydrating agent	$\begin{array}{c} O \\    \\ O = \overset{O}{S} - OH \\   \\ OH \end{array}$
$H_2S_2O_3$ (-2 and +6)	Thiosulphuric acid	Free acid does not exist but its salts e.g. $Na_2S_2O_3$ All quite stable reducing agent	$\begin{array}{c} S \\    \\ O = \overset{O}{S} - OH \\   \\ OH \end{array}$
$H_2S_2O_4$ (+3)	Dithionous acid		$\begin{array}{c} O \quad O \\    \quad    \\ HO - S - S - OH \end{array}$
$H_2S_2O_6$ (+5)	Dithionic acid	Free acid is moderately stable but its salts are quite stable.	$\begin{array}{c} O \quad O \\    \quad    \\ O = S - S = O \\   \quad   \\ OH \quad OH \end{array}$
$H_2S_2O_7$ (+6) (Oleum)	Disulphuric acid (Pyrosulphuric acid)	Strong oxidising agent	$\begin{array}{c} O \quad O \\    \quad    \\ O = S - O - S = O \\   \quad   \\ OH \quad OH \end{array}$
$H_2SO_5$ (+6) (Caro's acid)	Peroxomonosulphuric acid (Its salts known as persulphates)	Stable crystalline solid, powerful oxidising agent	$\begin{array}{c} O \\    \\ HO - S - OOH \\   \\ O \end{array}$
$H_2S_2O_8$ (+6) (Marshals acid)	Peroxodisulphuric acid (its salts are known as disulphates)	Strong oxidising agent.	$\begin{array}{c} O \quad O \\    \quad    \\ O = S - O - O - S = O \\   \quad   \\ OH \quad OH \end{array}$