

# Formation of ozone is an..?

## 16th GROUP ELEMENTS

➤ Industrially dioxygen is obtained from purified air by fractional distillation

**Physical properties:** It is a colourless and odourless gas.

- Its solubility in water is to the extent of  $3.08 \text{ cm}^3$  in  $100 \text{ cm}^3$  water at 293K
- It liquefies at 90K and freezes at 55K
- Oxygen atom has three stable isotopes  $O^{16}, O^{17}, O^{18}$
- Molecular oxygen is paramagnetic even though it contains even number of electrons.

**Chemical properties:** Oxygen directly reacts with nearly all metals and non-metals except some metals like Au, Pt and noble gases.

With metals :-  $2Ca + O_2 \rightarrow 2CaO$

$4Al + 3O_2 \rightarrow 2Al_2O_3$

With non metals:-  $P_4 + 5O_2 \rightarrow P_2O_5$

$C + O_2 \rightarrow CO_2$

With other compounds

$ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Some compounds are catalytically oxidised.

$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$

$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$

**Uses:** In welding and cutting –oxy-hydrogen or oxy-acetylene torch is used.

- In the manufacture of many metals, particularly steel
- Oxygen cylinder are widely used in hospitals, high altitude flying and in mountaineering
- As a fuel in rockets (Hydrazine in liquid oxygen produces tremendous thrust in rockets)

**Oxides:** A binary compound of oxygen with another element is called oxide.

➤ Oxides are two types:

1. Simple Oxide ( $Na_2O$ ,  $Al_2O_3$  etc..)
2. Mixed Oxides

**Mixed oxides:-** Formed by the combination of two simple oxides eg: Red lead,  $Pb_3O_4$

$(PbO_2 \cdot 2PbO), Fe_3O_4 (FeO + Fe_2O_3)$

➤ Simple oxides classified as

(i) **Acidic oxides** (Non-metal Oxides) oxides of non metals which give acids when dissolved in water are called acidic oxides.

eg.  $CO_2, NO_2, P_2O_5, SO_2, SO_3, Cl_2O_7$  etc..

$CO_2 + H_2O \rightarrow H_2CO_3$  (carbonic acid)

$CO_2 + H_2O \rightarrow H_2CO_3$  (carbonic acid)

$SO_2 + H_2O \rightarrow H_2SO_3$  (Sulphurous acid)

➤ Some metals in high oxidation state also have acidic character (eg  $Mn_2O_7, CrO_3, V_2O_5$ )

ii) **Basic oxides:-** The oxides which give a base with water are known as basic oxides (eg  $Na_2O, CaO, BaO$ )

(iii) **Amphoteric oxides:-** The oxides which can react with both acids and alkalies are known as amphoteric oxides

eg  $ZnO, PbO, Al_2O_3, SnO_2, BeO, Sb_2O_3$

$Al_2O_3 + 6NaOH(aq) + 3H_2O(l) \rightarrow$

$2Na_3[Al(OH)_6]_{(aq)}$

$Al_2O_3 + 6HCl(aq) + 9H_2O(l) \rightarrow$

$2[Al(H_2O)_6]^{3+}_{(aq)} + 6Cl^{-}_{(aq)}$

$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$

$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$

(iv) Neutral oxides - such oxides do not combine with an acid or a base eg:  $NO, N_2O, CO, H_2O$  etc

**Ozone:** Ozone is present in upper atmosphere and absorbs the harmful U.V. rays of sun.

- Ozone is prepared by subjecting silent electric discharge of cold and dry oxygen gas
- Formation of ozone is an endothermic, reversible reaction.

$3O_2 \xrightleftharpoons[discharge]{electric} 2O_3; \Delta H = +284.5kJ$

- Ozone is prepared in the laboratory by using Siemen's and Brodie's ozonisers. In this process around 10% conversion of  $O_2$  to  $O_3$  is possible.
- The obtained gas is a mixture of  $O_2+O_3$  it is called Ozonised oxygen
- Ozonised oxygen is cooled, when  $O_3$  first liquefies and so can be separated from gaseous  $O_2$
- Electrolysis of acidulated water with platinum electrodes gives  $O_3$  at anode. The gases liberated at the anode contain about 95%  $O_3$  and 5%  $O_2$ .

➤ Ozone can also be prepared by heating oxygen to 2773K and cooling it. (thermal method).

**Physical Properties:**  $O_3$  is a pale blue, pungent smelling poisonous gas, dark blue in liquid state, violet black in solid state.

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- $O_3$  harmless in small concentration, however if concentration exceeds 100ppm, breathing becomes uncomfortable resulting in headache and nausea.
- Ozone is thermodynamically unstable. Decomposition is associated with increase in volume.
- In the decomposition heat liberates ( $\Delta H$  is negative) and the entropy increases ( $\Delta S$  is positive) for the decomposition of ozone into oxygen  $\Delta G$  value is negative.
- It is highly soluble in turpentine oil, glacial acetic acid, or carbon tetrachloride.
- It decolorises organic colouring matter by oxidation.
- $O_3$  bleaches by oxidation.

### Chemical properties: Oxidising reactions

OZONE OXIDISES:		
REACTION	ELEMENT WHOSE O.N. CHANGES	CHANGE IN OXIDATION STATE
a) Black PbS to white $PbSO_4$	S	-2 to +6
b) $HCl$ to $Cl_2$	Cl	-1 to 0
c) $KI$ to $I_2$	I	-1 to 0
d) Moist $I_2$ to $HIO_3$ (iodic acid)	I	0 to +5
e) $Ag$ to $Ag_2O$ (blackening of silver)	Ag	0 to +1
f) $Hg$ to $Hg_2O$ (Tailing of mercury)	Hg	0 to +1
g) $K_4[Fe(CN)_6]$ to $K_3[Fe(CN)_6]$	Fe	+2 to +3
h) $SO_2$ to $SO_3$	S	+4 to +6
i) $SnCl_2$ to $SnCl_4$	Sn	+2 to +4

- Oxidising power of  $O_3$  is weaker than  $F_2$  but stronger than  $H_2O_2$  or  $KMnO_4$ .
- Ozone decomposes to give nascent oxygen.  $O_3 \rightarrow O_2 + (O)$ .

Thus in all oxidation reactions if one mole of ozone is consumed, one mole of oxygen is formed. (in presence of  $HCl$ )

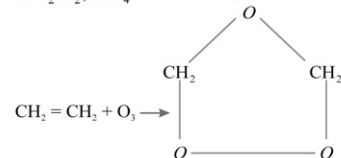
- Ozone reduces: a)  $BaO_2$  to  $BaO$
- b)  $H_2O_2$  to  $H_2O$  c)  $Ag_2O$  to  $Ag$
- When  $O_3$  reacts with an excess eg:  $KI$  solution buffered with a borate buffer ( $P^H=9.2$ ), Iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is the quantitative method for estimating  $O_3$  gas.

$2KI + H_2O + O_3 \rightarrow I_2 + 2KOH + O_2$

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

- When ozone is bubbled through the solution of an alkene or alkyne in an inert solvent like  $CH_2Cl_2, CCl_4$  etc at 195 K, ozonides are formed

$CH_2=CH_2 + O_3 \rightarrow$



**Structure:**



- Ozone is an angular molecule and diamagnetic
- The two oxygen - oxygen bond lengths in the ozone molecule are identical (128 pm)
- **Uses of Ozone:** It is used as germicide and disinfectant.
- It is used for sterilizing water.
- it is used in improving the quality of atmosphere at crowded places (tube railways, mines, cinema halls etc..).
- It is used for bleaching oils, oil paintings, ivory articles, flour, starch etc.
- It is used in the manufacture of artificial silk and synthetic camphor.
- It is used to locate multiple bonds in carbon compounds.
- It acts as an oxidising agent in the manufacture of potassium permanganate
- A mixture of  $O_3$  and  $C_2N_2$  is known as cyanogen and is used as Rocket fuel.

### Sulphur - Allotropic forms :

- All VI A group elements exhibit allotropism except Te
- Oxygen occurs in two non metallic forms (a) Oxygen ( $O_2$ ) (b) Ozone ( $O_3$ )
- Oxygen is paramagnetic as it contains two unpaired electrons in anti bonding M.O (as per Molecular Orbital Theory).
- Ozone is a triatomic diamagnetic allotropic form of oxygen. It is unstable and decomposes to  $O_2$ .  $2O_3 \rightarrow 3O_2$
- Sulphur has more number of allotropic forms all these are non-metallic.
- Allotropes of Sulphur are :

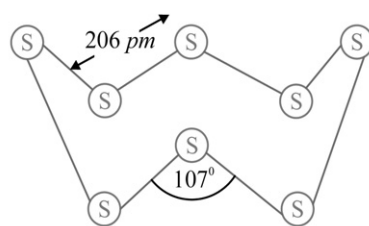
- $\alpha$  - Sulphur or Rhombic sulphur.
  - $\beta$  - Sulphur or monoclinic sulphur or prismatic sulphur.
  - $\gamma$  - Monoclinic sulphur.
  - $\chi$  - Sulphur or plastic sulphur.
- At 369K both Rhombic and monoclinic forms can co-exist in equilibrium. This temperature is called **transition temperature** of sulphur.
  - The stable form at room temperature is rhombic
  - a) Yellow (or)  $\alpha$  - sulphur
  - above 369K Rhombic sulphur transforms to monoclinic sulphur
  - Rhombic sulphur is yellow in colour, M.P 385.8 K and specific gravity 2.06.
  - Rhombic sulphur crystals are formed by evaporating the solution of roll sulphur in  $CS_2$ . It is insoluble in water but dissolves to some extent in benzene, alcohol and ether. It readily soluble in  $CS_2$



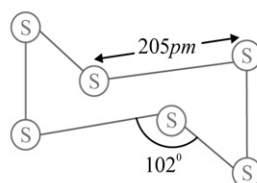
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- $\beta$  - Sulphur melts at 392 K and its specific gravity is 1.98
- It is soluble in  $CS_2$
- $\beta$  form of sulphur is prepared by melting Rhombic sulphur in a dish and cooling, till crust is formed. Two holes are made in the crust and the remaining liquid poured out on removing the crust, colourless needle shaped crystals of  $\beta$  - sulphur are formed.
- $\alpha, \beta$  and  $\gamma$  forms of sulphur are crystalline in nature and possess puckered ring structures ( $S_8$ ) (crown structure)
- Sulphur persists with the  $S_8$  units, just above the boiling point of sulphur ( $160^\circ C$ ). Further increase in temperature leads to the dissociation of  $S_8$  units successively into  $S_6$  (Engel's sulphur),  $S_4$  and  $S_2$  units.
- In cyclo -  $S_6$  the ring adopts the chair form. At elevated temperatures ( $1000K$ )  $S_2$  is the dominant species and is paramagnetic like  $O_2$ .
- $S_2$  molecule has two unpaired electron in the antibonding  $\pi^*$  orbitals like  $O_2$ .
- Structure of  $S_8$  ring (crown)  
Structure of  $S_6$  ring (chair)



Puckered ring  $S_8$  molecule



$S_6$  Chair molecule

**Sulphur Dioxide:** When sulphur is burnt in air or oxygen  $SO_2$  is formed along with 6-8% sulphur trioxide

- In the laboratory  $SO_2$  is prepared by treating a sulphite with dilute sulphuric acid
- $SO_3^{2-} + 2H^+ \rightarrow SO_2(g) + H_2O(l)$
- Industrially it is produced as a by-product of the roasting of sulphide ores
- $4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$
- Liquefied  $SO_2$  is stored in steel cylinders