

## Chapter No. 4

### GROUP VA AND GROUP VIA ELEMENTS

#### Group VA Elements:

##### Introduction:

The elements of group VA of the periodic table comprise nitrogen, phosphorus, arsenic, antimony and bismuth.

**Electronic Configurations and Physical Properties of Group VA Elements**

Properties	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Electronic configuration	[He]2s <sup>2</sup> 2p <sup>3</sup>	[Ne]3s <sup>2</sup> 3p <sup>3</sup>	[Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>3</sup>	[Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>3</sup>	[Xe]5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>3</sup>
Physical appearance	Colourless gas	Black Solid	Metallic solid	Metallic solid	Metallic solid
Ionization energy (kJ/mol)	1402	1012	950	830	700
Electron affinity (kJ/mol)	-7	71.7	77	101	110
Electronegativity	3.0	2.1	2.0	1.9	1.9
Atomic radius (pm)	70	110	121	141	157
Ionic radius of 3-ion (pm)	171	212	222	245	---
Melting points (°C)	-210	44	817	631	271
Boiling points (°C)	-196	280	613	1750	1560
Density (g/cm <sup>3</sup> )	0.00125	1.83	5.73	6.68	9.80
Principal oxidation states	+3,+5	+3,+5	+3,+5	+3,+5	+3,+5

#### General Characteristics:

##### (i) Metallic Character:

Nitrogen and phosphorus of group VA show the typical properties of non-metals. **For example**, they are poor conductors of heat and electricity and give acidic oxides. Their compounds are predominantly covalent. Arsenic and antimony are metalloids. However bismuth at the bottom of the group shows definite metallic properties. The metallic character increases going down the group.

##### (ii) Bond Nature:

Nitrogen has the greatest tendency to attract the electrons; antimony and bismuth have the least. The trend down the group also shifts from covalent bonding to ionic bonding.

##### (iii) Allotropes:

Phosphorus, arsenic and antimony have allotropes. Allotropes of phosphorus i.e. red and 'white phosphorus' are more important.

(iv) **Common oxidation states:**

Phosphorus and other members of the group can make use of d orbitals in their bonding. This is because the energy of these orbitals is not much greater than those of the other valence shell orbitals. For example, phosphorus can make use of its 3s, 3p and the empty 3d orbitals during bonding with other elements. In phosphorus one of the 3s electrons can be promoted to a vacant 3d orbital giving 5 unpaired electrons in the valence shell. Phosphorus can thus make three or five covalent bonds. Indeed three and five are the common valencies of the group VA elements.

**Nitrogen and its Compound:**

**Nitrogen differs from other elements of its groups as follows**

Nitrogen	Other Elements of V-A Group
(1) It is a gas	(1) Other elements of VA group are solids
(2) It is diatomic molecule	(2) Other elements of VA group are tetra-atomic e.g. $P_4$ , $As_4$ , $Sb_4$ .
(3) It shows a large number of oxidation states. e.g. +5, +4, +3, +2, +1, -1, -2, -3	(3) Other elements show limited no. of oxidation states from +5 to -3.
(4) It occurs in free state as well as in combined states.	(4) The other elements of group V-A occur in combined states only.
(5) It does not form complexes due to non-availability of "d" orbitals.	(5) Other elements which have empty "d" orbitals can accept electron pairs to form complexes.
(6) It is a typical non-metal.	(6) As and Sb are metalloids and Bi is a metal.

**Occurrence:**

- ❖ Nitrogen is present in free state in air as a major constituent 78% by volume. It is an inactive gas in comparison with oxygen which is the next major constituent of air.
- ❖ Inorganic compounds of nitrogen are not commonly found as minerals.
- ❖ In combined state nitrogen is, found in all living matter including, animals and plants in the form of proteins, urea and amino acids.

**Oxides of Nitrogen:**

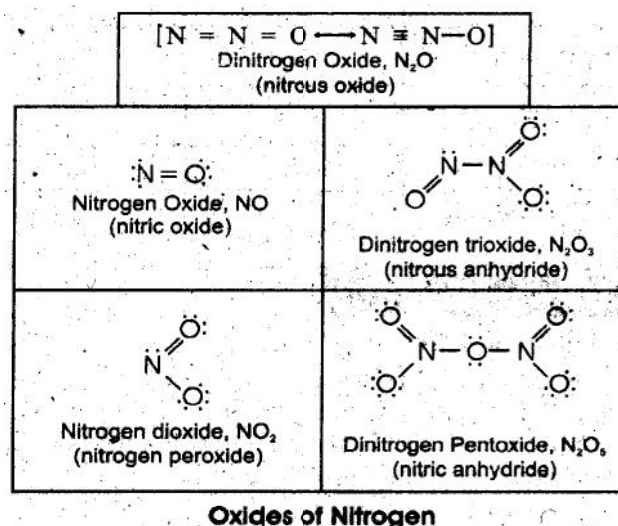
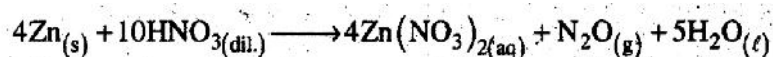
Nitrogen forms several oxides with oxygen.

Common oxides of nitrogen are  $N_2O$ ,  $NO$  and  $NO_2$ . It also forms  $N_2O_3$  and  $N_2O_5$ .

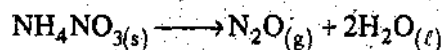
**1. Dinitrogen Oxide ( $N_2O$ ):****Preparation:**

- ❖ Dinitrogen oxide can be prepared by the action of dil.  $HNO_3$  on metallic zinc.

It is usually prepared by heating ammonium nitrate to about  $200^\circ C$



- ❖ It is usually prepared by heating ammonium nitrate to about 200°C



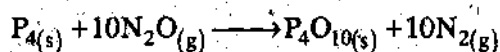
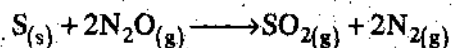
- ❖ To avoid the danger of explosion, ammonium nitrate can be replaced by a mixture of sodium nitrate and ammonium sulphate.

### Properties:

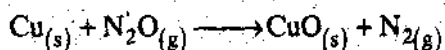
- ❖ Dinitrogen oxide is a colourless gas with a faint, pleasant smell and a sweetish taste.
- ❖ It is fairly soluble in cold water.
- ❖ **Laughing gas:** Its mixture with a little oxygen, if inhaled for a sufficiently long time, produces hysterical laughter, hence it is also known as “laughing gas”.

### Reactions:

- ❖ It is not combustible but resembles oxygen in rekindling a glowing splinter. Similarly, it supports combustion of burning substances, such as sulphur, phosphorus, etc. taken in the cylinder containing this gas.

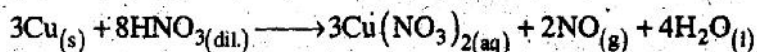


- ❖ When  $\text{N}_2\text{O}$  is passed over red hot copper, it is reduced to nitrogen.

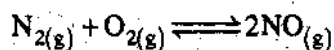


## 2. Nitrogen Oxide (NO):

- ❖ Nitrogen oxide can be prepared by the action of dil.  $\text{HNO}_3$  on copper.



- ❖ It can also be prepared by passing air through an electric arc.

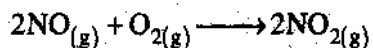


### Properties:

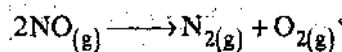
Nitrogen oxide is a colourless gas heavier than air and sparingly soluble in water.

### Reactions:

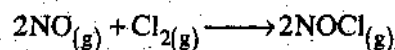
- ❖ With oxygen, it forms reddish brown nitrogen dioxide.



- ❖ It decomposes into  $\text{N}_2$  and  $\text{O}_2$  at about 1000°C and supports combustion.

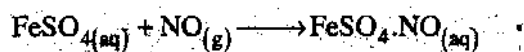


- ❖ It forms nitrosyl chloride and nitrosylbromide with chlorine and bromine, respectively in the presence of charcoal.

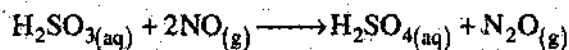
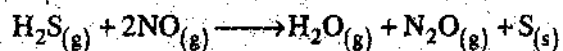


- ❖ **Ring Test:**

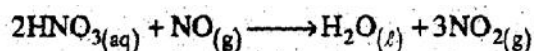
This is a confirmatory test for nitrate  $\text{NO}_3^{-1}$  ion. The respected nitrate is dissolved in water and some fresh  $\text{FeSO}_4$  solution is added to it. Concentrated sulphuric acid is slowly run down the side of the test tube. Brown ring is formed at the junction of two solutions which confirms the presence of nitrate ion.



- ❖ With reducing agents, it is reduced to nitrous oxide or nitrogen.



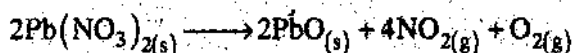
- ❖ Oxidizing agents can oxidize NO to  $\text{NO}_2$  or  $\text{HNO}_3$



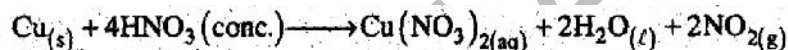
### 3. Nitrogen Dioxide ( $\text{NO}_2$ ):

#### Preparation:

- ❖ It can be prepared in small quantities by heating lead nitrate.



- ❖ It can also be prepared reacting conc.  $\text{HNO}_3$  with copper.



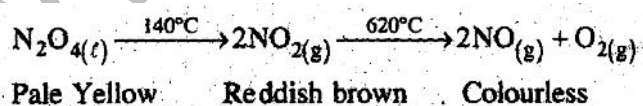
#### Properties of Nitrogen Dioxide:

- ❖ Nitrogen dioxide is a reddish brown gas with a pungent smell.
- ❖ It dissolves readily in water to form a blue acidic solution.

#### Reactions:

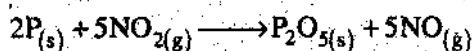
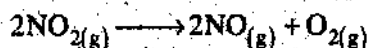
##### ➤ Heating effect:

On cooling,  $\text{NO}_2$  is converted into a yellow liquid which can be frozen to a colourless solid dinitrogen tetraoxide ( $\text{N}_2\text{O}_4$ ). If this solid is heated to  $140^\circ\text{C}$ , the mixture contains  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  but above  $140^\circ\text{C}$   $\text{NO}_2$  is converted to NO and  $\text{O}_2$  molecules which are colourless. This decomposition is complete at  $620^\circ\text{C}$ .



##### ➤ Decomposition:

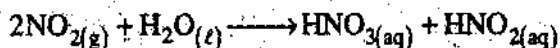
Elements like phosphorus, potassium and carbon continue burning in  $\text{NO}_2$  as it yields  $\text{O}_2$  on decomposition.



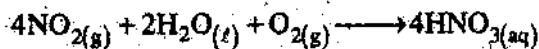


➤ **Dissolution in water:**

In the absence of air, it dissolves in water to form nitric and nitrous acids.

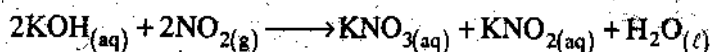
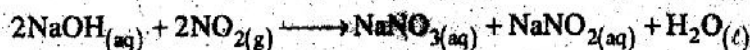


However in the presence of air or oxygen nitric acid is the final, product.



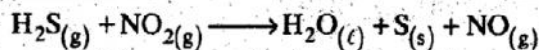
➤ **Reaction with alkalis:**

A mixture of nitrate and nitrite is formed when  $\text{NO}_2$  is passed through strong alkalies.



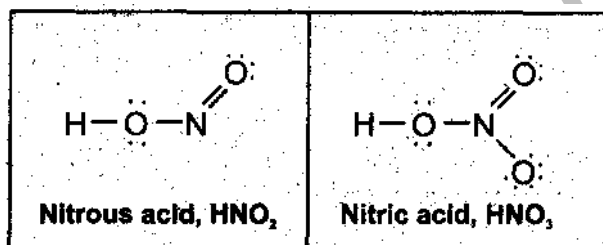
➤ **As an oxidizing agent:**

It is a strong oxidizing agent and oxidizes  $\text{H}_2\text{S}$  to sulphur, ferrous sulphates to ferric sulphates and KI to  $\text{I}_2$ .



**Oxyacids of Nitrogen:**

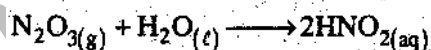
There are two important oxyacids of nitrogen, nitrous acid and nitric acid.



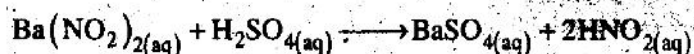
**Nitrous Acid ( $\text{HNO}_2$ ):**

**Preparation:**

- ❖ It can be prepared by dissolving dinitrogen tetroxide in water at  $0^\circ\text{C}$



- ❖ Pure nitrous acid solution can be prepared by reaction between ice cold barium nitrite solution and ice cold dilute sulphuric acid.



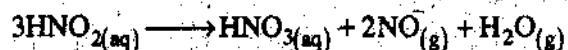
**Properties:**

It is only known in the form of its salts and stable to some extent in a dilute solution.

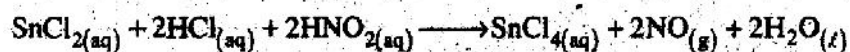
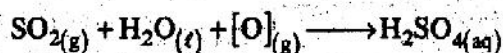
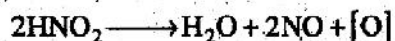
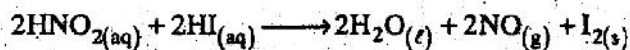
**Reactions:**

**Decomposition:**

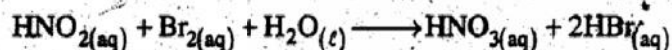
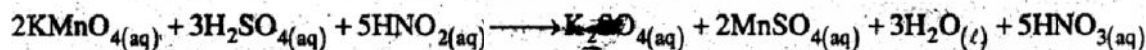
It begins to decompose almost as soon as it is formed even at ordinary temperature

**As an oxidizing agent:**

It acts as an oxidizing agent and oxidizes HI, SO<sub>2</sub> and SnCl<sub>2</sub> into I<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> and SnCl<sub>4</sub> respectively

**As a reducing agent:**

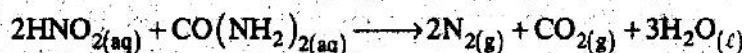
Nitrous acid decolorizes acidified KMnO<sub>4</sub> and bromine water. It readily gets oxidized to nitric acid, so it also behaves as a reducing agent.

**Reaction with alkalis:**

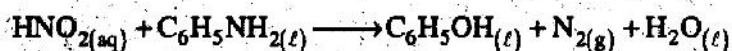
As an acid it reacts with alkalis producing salts.

**Reaction with organic compounds containing NH<sub>2</sub> group:**

It also reacts with organic compounds containing NH<sub>2</sub> group and produces nitrogen.



Urea

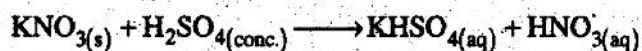


Aminobenzene

Phenol

**Nitric acid (HNO<sub>3</sub>):****Laboratory Preparation:**

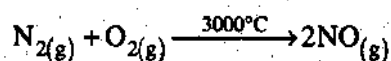
In the laboratory, nitric acid is prepared by heating potassium nitrate crystals with concentrated sulphuric acid.

**Commercial preparation of Nitric Acid:****Birkeland and Eyde's process:**

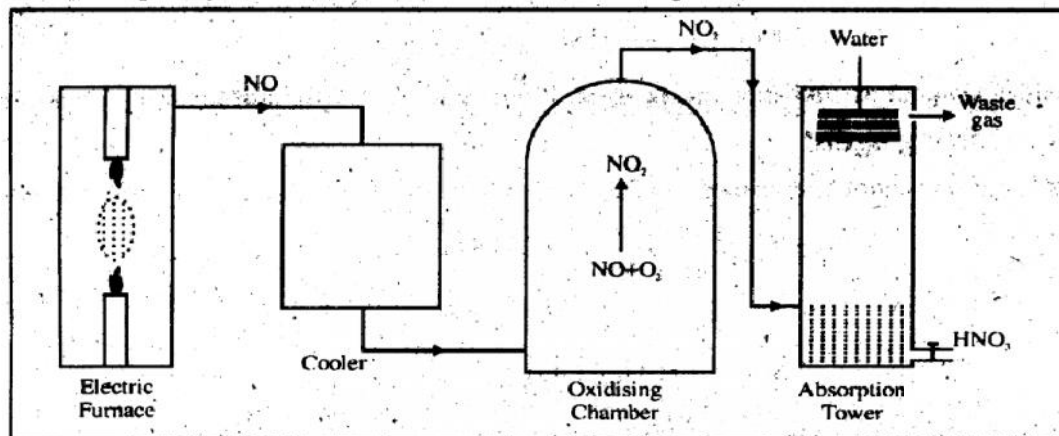
This process consists of the following steps:

- (i) **Formation of nitric oxide:**

Atmospheric nitrogen and oxygen are combined to give nitric oxide in an electric arc (3000°C).



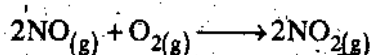
NO formed is cooled quickly to 1000°C at which it does not decompose.



Manufacture of Nitric acid from air

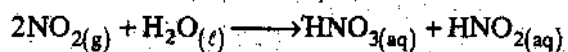
(ii) **Oxidation of nitric oxide:**

At 600°C, combines with  $\text{O}_2$  to form  $\text{NO}_2$



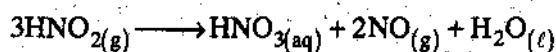
(iii) **Dissolution in water:**

Nitrogen dioxide is absorbed in water to give dilute  $\text{HNO}_3$  along with nitrous acid.



(iv) **Oxidation of nitrous acid:**

Nitrous acid is oxidized to nitric acid and nitric oxide which is re-oxidized to  $\text{NO}_2$ .



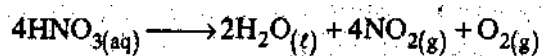
**Properties of Nitric Acid:**

- ❖ Concentrated nitric acid is a colourless volatile liquid which fumes strongly in air.
- ❖ It has a pungent smell.
- ❖ Its specific gravity at 15°C is 1.53.

**Reactions:**

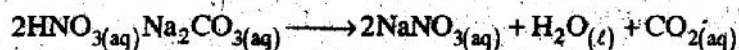
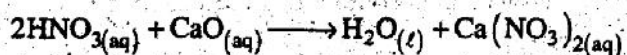
**1. Decomposition:**

Nitric acid is decomposed in the presence of light even at ordinary temperature.



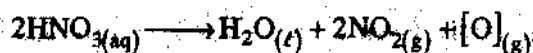
**2. As an acid:**

It is a very strong acid. It exhibits all the usual general properties of acids in all reactions where its oxidizing properties are not shown. It reacts in normal way with basic oxides, hydroxides and carbonates forming respective salts.



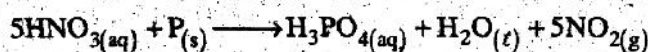
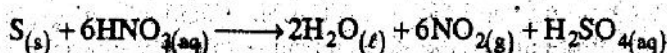
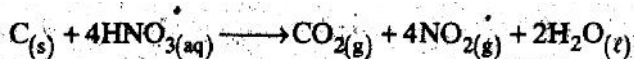
### 3. As an oxidizing agent:

It acts as a strong oxidizing agent due to the ease with which it is decomposed.



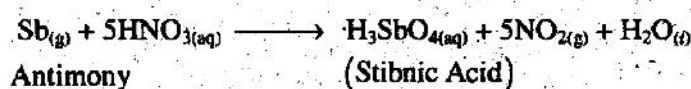
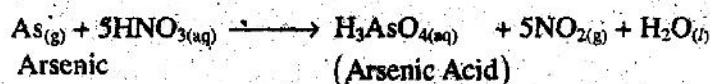
#### (i) With Non-metal:

It oxidizes non-metals to their corresponding oxides.



#### (ii) With Metalloid:

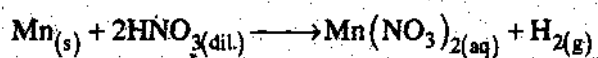
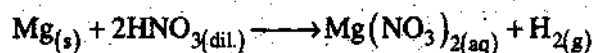
Arsenic and antimony are metalloids they can be oxidized to their corresponding acids when react with Conc. Nitric acid.



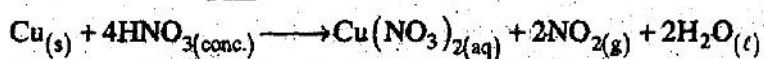
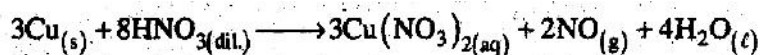
#### (iii) With Metals:

Nitric acid behaves differently with different metals.

- ❖ Gold, platinum, iridium and titanium do not react.
- ❖ Iron, cobalt, nickel, chromium, aluminium are rendered passive by acid due to the formation of a film of their oxides over them
- ❖ Tungsten and uranium are changed into their oxides.
- ❖ Magnesium, calcium and manganese give hydrogen with dilute nitric.

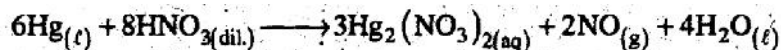


- ❖ Copper and lead give nitric oxide with dilute acid and nitrogen dioxide with concentrated acid.

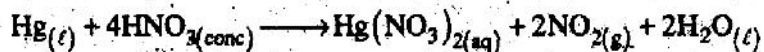




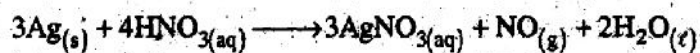
- ❖ Mercury gives mercurous nitrate and nitric oxide with dilute nitric acid.



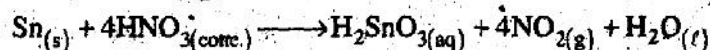
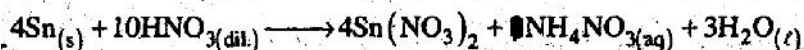
With concentrated acid, it gives mercuric nitrate and  $\text{NO}_2$ .



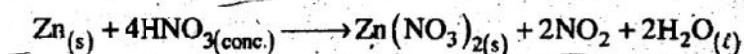
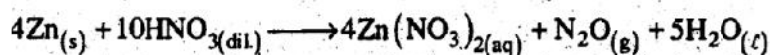
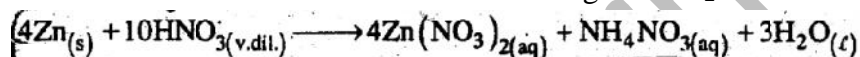
- ❖ Silver reacts with nitric acid to give silver nitrate and nitric oxide.



- ❖ Dilute nitric acid gives ammonium nitrate, when it reacts with tin with concentrated acid meta-stannic acid is produced.

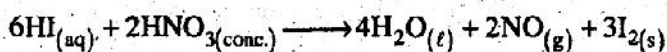
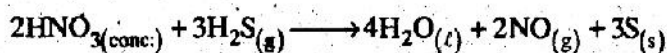
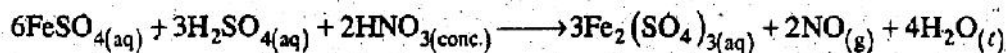


- ❖ Zinc gives different products depending upon the concentration of acid and temperature very dilute nitric acid gives  $\text{NH}_4\text{NO}_3$ . Moderately dilute nitric acid gives nitrous oxide while concentrated nitric acid gives  $\text{NO}_2$ .



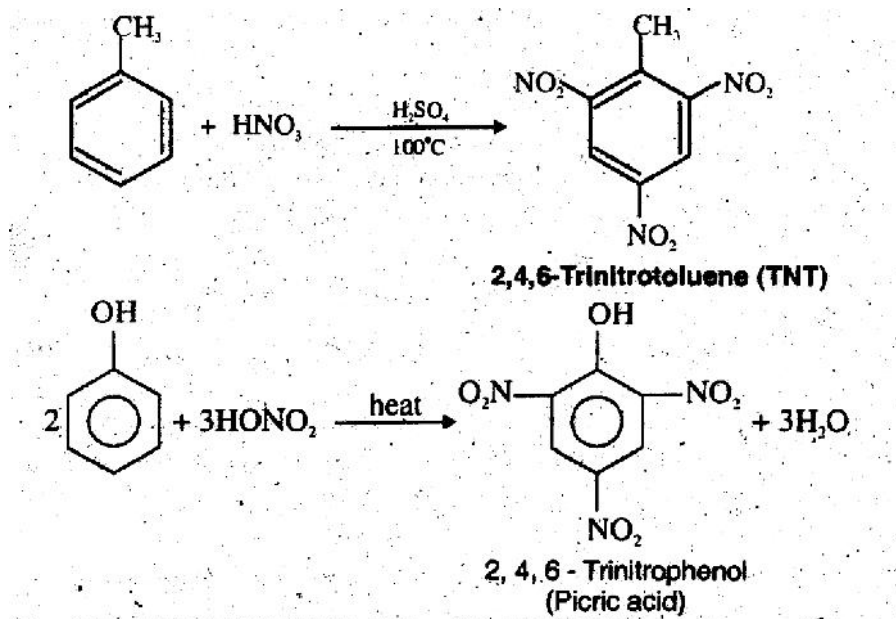
#### 4. With reducing agents:

Reducing agents like  $\text{FeSO}_4$ ,  $\text{H}_2\text{S}$  and  $\text{HI}$  are converted to  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{S}$  and  $\text{I}_2$  respectively, when they react conc.  $\text{HNO}_3$



#### 5. Formation of explosive materials:

Nitric acid reacts with glycerine, toluene and phenol to prepare materials used as explosives like nitroglycerine, trinitrotoluene (TNT) and picric acid, respectively.



### Uses of Nitric acid:

It is used:

1. as a laboratory reagent.
2. in the manufacture of nitrogen fertilizers.
3. in the manufacture explosives.
4. for making organic dyes and varnishes.

### Phosphorus and its Compound:

#### Occurrence:

1. Phosphorus is the second member of group VA. Its name comes from Greek word meaning "Light bearing".
2. Unlike nitrogen it does not occur in free state in nature. Most of the phosphorus is found in deposits of phosphate rocks, i.e. impure  $\text{Ca}_3(\text{PO}_4)_2$  and apatite  $\text{Ca}_5\text{F}(\text{PO}_4)_3$ .
3. As a constituent of plant and animal tissues, it is essential for their normal growth. It occurs especially in seeds, the yolk of eggs, the nerves and brain and bone marrows, usually in the form of lecithins.
4. In the form of calcium phosphate, it is essential constituent of bone. Bone ash which contains 80% calcium phosphate is an important source of phosphorus.

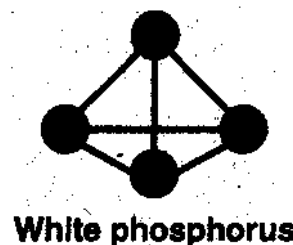
#### Allotropes of phosphorus:

Phosphorus can exist in at least six different solid allotropic forms which are

1. White/Yellow phosphorus.
2. Red phosphorus.
3.  $\alpha$  - black phosphorus.
4. - Black phosphorus.
5. Violet phosphorus.
6. Scarlet phosphorus.

We will mention only three here:

#### 1. White phosphorus:



**White phosphorus**

**Physical properties:** White phosphorus is a waxy, reactive, poisonous, volatile, waxy, yellowish white substance which is soluble in benzene and carbon disulphide. White phosphorus is toxic, and when contacts with skin, produces painful slow healing burns.

**Structure:** It exists in the form of tetra atomic molecules ( $P_4$ ) which have a tetrahedral structure in phosphorus, bond angle is,  $60^\circ$  which is less than normal bond angle. Due to smaller angle, it has strain and very reactive.

**Heating effect:** It boils at  $280^\circ\text{C}$  to  $P_4$  vapours which dissociate above  $700^\circ\text{C}$  to form  $P_2$  molecules.

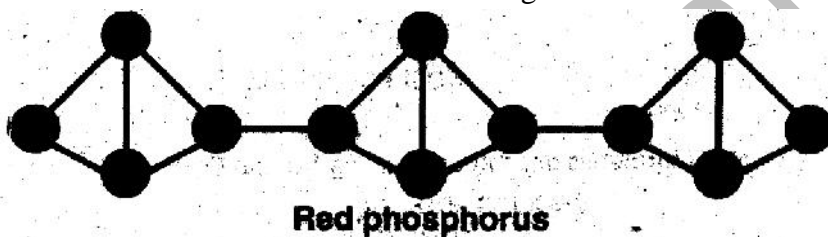
White phosphorus consists of individual tetrahedral  $P_4$  molecules. It is a waxy solid that melts at  $44^\circ\text{C}$  and boils at  $280^\circ\text{C}$ .

## 2. Red phosphorus:

**Physical properties:** Red phosphorus is less reactive and less poisonous than white phosphorus.

**Preparation:** It is prepared by heating white phosphorus in the presence of little iodine or sulphur as a catalyst upto  $250^\circ\text{C}$  in vacuum. The tetra atomic molecules of red phosphorus combine to form macromolecules.

**Uses:** Red phosphorus is used to make incendiary devices (bombs, fireworks etc) red phosphorus when mixed with sand is used as the rubbing surface of the matchbox.



## 3. Black phosphorus:

**Physical properties:** Black phosphorus is the third form which is most stable and least reactive under ordinary conditions. Black phosphorus is prepared by heating red phosphorus to high, temperature and pressure.

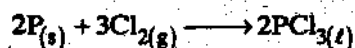
**Structure:** It consists of layers of phosphorus atoms. Within each layer phosphorus atoms are covalently bonded to each other but attraction between the layers is weak like graphite. It has flaky appearance due to layers.

## Halides of Phosphorus:

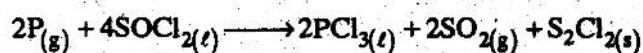
### Phosphorus Trichloride ( $\text{PCl}_3$ ):

#### Preparation:

1. It is usually prepared by melting white phosphorus in a retort in an inert atmosphere of  $\text{CO}_2$  and current of dried chlorine is passed over it. The vapours of  $\text{PCl}_3$  are collected in a flask kept in an ice bath.



2. It may also be prepared by the action of phosphorus with thionyl chloride.

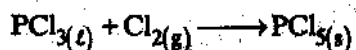


### Properties of $\text{PCl}_3$ :

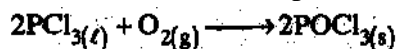
It is a colourless fuming liquid which boils at  $76^\circ\text{C}$  and freezes at  $-112^\circ\text{C}$ .

**Chemical Reactions:**

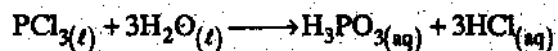
1. It combines with chlorine to form phosphorus pentachloride.



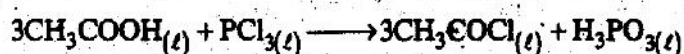
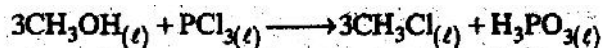
2. It combines with atmospheric oxygen slowly to form phosphorus oxychloride.



3. It is soluble in organic solvents, but readily reacts with water to form phosphorus acid.



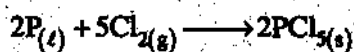
4. It reacts with alcohols and carboxylic acids forming the respective chloro derivatives and  $\text{H}_3\text{PO}_3$ .

**Phosphorus Pentachloride ( $\text{PCl}_5$ ):****Preparation:**

1. By passing dry chlorine through phosphorus trichloride at temperature of about  $0^\circ\text{C}$ , phosphorus pentachloride is formed.



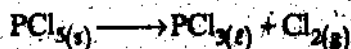
2. It can also be prepared by passing dry chlorine in a well cooled solution of phosphorus in carbon disulphide

**Properties of  $\text{PCl}_5$ :**

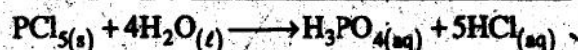
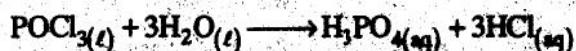
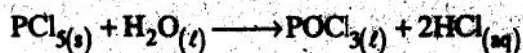
It is yellowish white crystalline solid which sublimates at about  $100^\circ\text{C}$ . It gives fumes in moist air with an irritating smell

**Chemical Reactions:**

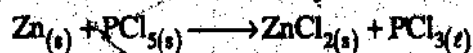
1. It decomposes on heating producing  $\text{PCl}_3$  and chlorine



2. It gets decomposed by water forming phosphorus oxychloride which further reacts with water to produce ortho phosphoric acid.



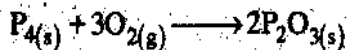
3. It converts metals into their chlorides

**Oxides of Phosphorus:**



**Phosphorus Trioxide  $P_2O_3(P_4O_6)$ :****Preparation:**

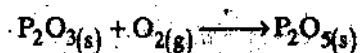
$P_2O_3$  can be prepared by burning white phosphorus in a limited supply of air.

**Properties of  $P_2O_3$ :**

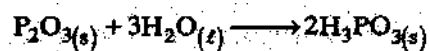
1. It is a white waxy solid with garlic like odour.
2. It melts at  $22.8^\circ\text{C}$  and boils at  $173^\circ\text{C}$ .
3. It is highly poisonous in nature.

**Chemical reactions:**

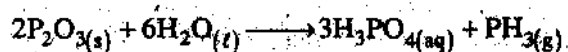
1. When heated in the presence of air oxygen, it is converted into phosphorus pentoxide.



2. It reacts with cold water to give phosphorous acid.



With hot water, it forms phosphine and phosphoric acid

**Phosphorus Pentoxide  $P_2O_5(P_4O_{10})$ :****Preparation:**

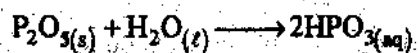
It is prepared by burning phosphorus in excess of dry air.

**Properties of  $P_2O_5$ :**

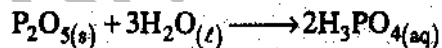
1. It is a white hygroscopic powder having a faint, garlic like odour due to the presence of traces of  $P_2O_3$ .
2. It sublimes at  $360^\circ\text{C}$ .

**Chemical Reactions:**

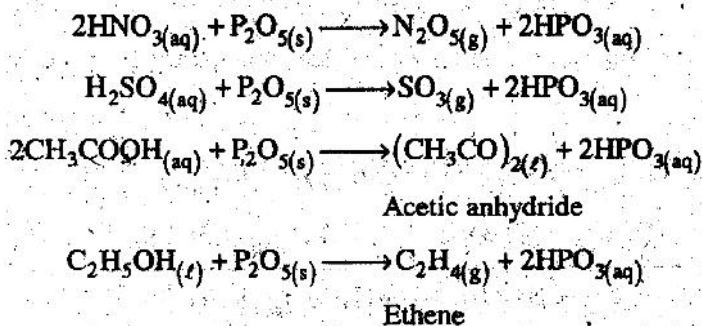
1. With cold water, phosphorus pentoxide forms metaphosphoric acid



With hot water, it forms orthophosphoric acid.



2. It is a powerful dehydrating agent, thus, with  $HNO_3$ ,  $H_2SO_4$ ,  $CH_3COOH$  and  $C_2H_5OH$ , it gives  $N_2O_5$ ,  $(CH_3CO)_2O$  and  $C_2H_4$  respectively.

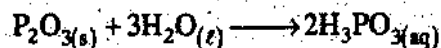


## Oxyacids of Phosphorus:

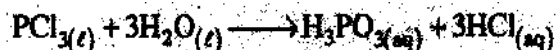
### Phosphorus acid ( $\text{H}_3\text{PO}_3$ ):

#### Preparation:

1. It is prepared by dissolving phosphorus trioxide in cold water.



2. It is also obtained by the hydrolysis of phosphorus trichloride.



### Properties of $\text{H}_3\text{PO}_3$ :

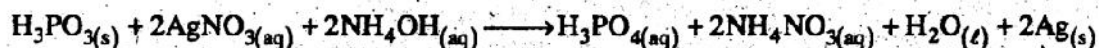
It is a white crystalline solid, which melts at  $73.6^\circ\text{C}$ .

#### Chemical Reactions:

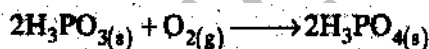
1. It decomposes into phosphine and orthophosphoric acid on heating.



2. It is a powerful reducing agent and reduces  $\text{CuSO}_4$ ,  $\text{AgNO}_3$ , etc. to the metallic state.



3. It reacts with oxygen to form orthophosphoric acid.



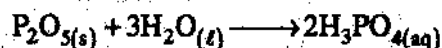
4. Nascent hydrogen produced by  $\text{Zn}/\text{HCl}$  reduces  $\text{H}_3\text{PO}_3$  to phosphine.



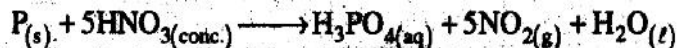
### Orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ):

#### Preparation:

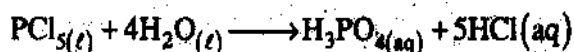
1. It is prepared by dissolving phosphorus pentoxide in hot water.



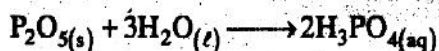
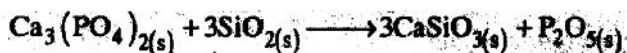
2. It is also obtained by heating red phosphorus with concentrated  $\text{HNO}_3$ .



3. Hydrolysis of phosphorus pentachloride also gives orthophosphoric acid.



4. On large Scale, it can be prepared by heating a mixture of phosphorite (bone ash) and sand in an electric furnace. The phosphorus pentoxide formed is treated with hot water to obtain phosphoric acid.

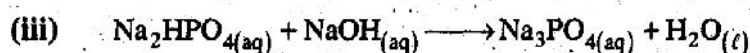
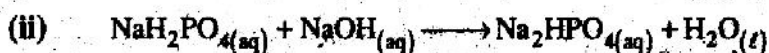
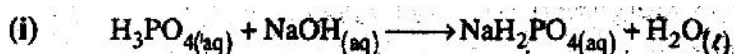


### Properties of $\text{H}_3\text{PO}_4$ :

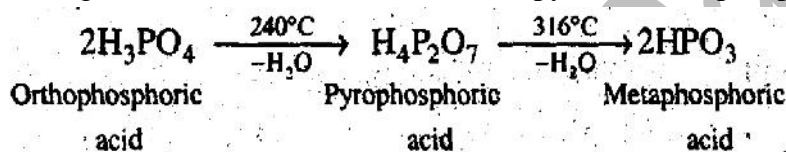
1. It is a colourless, deliquescent crystalline solid.
2. It melts at  $41^\circ\text{C}$ .
3. It is soluble in water.

### Chemical Reactions:

1. It is a weak tribasic acid. It reacts with  $\text{NaOH}$  to give three series of salts



2. On heating, it loses water and is converted into pyro and metaphosphoric acid.



### Group VIA Elements:

#### Introduction:

The members of group VIA are oxygen, sulphur, selenium, tellurium and polonium. These elements are called chalcogens, from the Greek for "copper giver", because they are often found in copper ores;

#### Electronic Configuration and Physical Properties of Group VIA Elements

Physical Properties	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Electronic configuration	$[\text{He}]2s^2 2p^4$	$[\text{Ne}]3s^2 3p^4$	$[\text{Ar}]4s^2 4p^4$	$[\text{Kr}]5s^2 5p^4$	$[\text{Xe}]6s^2 6p^4$
Ionization energy (kJ/mol)	1314	1000	941	869	813
Electron affinity (kJ/mol)	141.1	200.42	197	190	180
Electronegativity	3.5	2.5	2.4	2.1	2.0
Atomic radius (pm)	66	104	117	137	152
Ionic radius 2-ion (pm)	140	184	198	221	---
Melting points ( $^\circ\text{C}$ )	-218	113	217	450	254
Boiling points ( $^\circ\text{C}$ )	-183	444.6	684	990	962
Density ( $\text{g/cm}^3$ )	0.00143	2.06	4.8	6.25	9.4

### General Characteristics of Group VIA:

- (i) Nature of Elements:

All the elements of group VIA are non metals except Po which is a radioactive metal.

**(ii) Periodicity in Physical Properties:**

- ❖ Atomic radii, density, melting and-boiling points generally increase with increase in atomic number down the group.
- ❖ Ionization energies of the group VIA members are very high which shows their reluctance to lose electrons.
- ❖ Oxygen is the most electronegative element (E.N=3.5) after fluorine.

**(iii) Outermost Shell Electronic Configuration:**

The elements of VIA group have six electrons in their valence shell. Their outermost shell electronic configuration is  $ns^2 np^4$ .

**(iv) Allotropy:**

All the elements of group VIA show the property of allotropy.

- ❖ Oxygen has two allotropic forms ( $O_2$  and  $O_3$ ).
- ❖ Sulphur has 3 allotropes i.e: rhombic sulphur ( $\alpha$ -sulphur), monoclinic sulphur ( $\beta$ -sulphur) and plastic sulphur ( $\gamma$ -sulphur).
- ❖ Se has two (red and gray) allotropes.
- ❖ Te has two (metallic and non metallic) allotropes.

**(v) Valency:**

All the elements are polymeric in nature (they form poly-atomic molecules). They attain the electronic configuration of the nearest noble gas by gaining 2 electrons forming  $O^{-2}$ ,  $S^{-2}$ ,  $Se^{-2}$  etc.

**(vi) Catenation:**

Self linking property of an element is called catenation. They also show the property of catenation. This property decreases down the group.

**(vii) Covalency:**

Except oxygen, the other members of the group VIA show a covalency of +2, +4 and +6, **for example**,  $SCl_2$ ,  $SCl_4$ ,  $SCl_6$ . +2 oxidation state is shown due to 2 unpaired electrons in the p-orbitals. +4 oxidation state is shown when 1 electron from p-orbital is promoted to the next vacant d-orbital, while +6 oxidation state is shown when another electron from s-orbital is also promoted to the next vacant d-orbital.

**(viii) Polymeric molecule:**

The elements of this group usually form polymeric molecules. e.g.  $O_2$ ,  $O_3$ ,  $S_4$ ,  $S_8$  etc

**Occurrence:**

**Oxygen:**

- ❖ Oxygen is the most widely distributed and common of all the elements, comprising about 50% of the earth's crust.
- ❖ About one-fourth of the atmospheric air by weight it consists of free oxygen, and water contains nearly 89% of



combined oxygen.

- ❖ The calcium carbonate which occurs as chalk, lime stone, marble etc, contains 48% oxygen
- ❖ Silica which is found in flint, quartz etc contains more than 53% oxygen by weight.

### Sulphur:

- ❖ Sulphur is widely distributed in nature both as free and in combined forms.
- ❖ Many important metallic ores are sulphides, e.g. galena.(PbS), zinc blende (ZnS), cinnabar (HgS), iron pyrite (FeS<sub>2</sub>), stibnite (Sb<sub>2</sub>S<sub>3</sub>) copper pyrite (Cu<sub>2</sub>S. Fe<sub>2</sub>S<sub>3</sub>) etc.
- ❖ Some important sulphates are also found in nature, e.g. gypsum (CaSO<sub>4</sub>), heavy spar (BaSO<sub>4</sub>) etc.
- ❖ Sulphur also occurs in organic compounds present in animals and vegetables. Onions, garlic, mustard, hair, many oils, eggs and proteins consist of compounds containing sulphur in them.
- ❖ It also occurs as a constituent of coal and petroleum.

### Comparison of Oxygen and Sulphur:

#### Similarities:

- ❖ Both oxygen and sulphur have same outer electronic configuration of  $ns^2 np^4$ .
- ❖ Both oxygen and sulphur are usually divalent O<sub>2</sub>, S<sub>2</sub>.
- ❖ Both oxygen and sulphur exhibit allotropic forms. Allotropes of oxygen are O and O<sub>2</sub> while allotropes of sulphur are rhombic, monoclinic and plastic sulphur.
- ❖ Both have polyatomic molecules. Oxygen has diatomic O<sub>2</sub> while sulphur has S<sub>2</sub> and S<sub>8</sub> molecules.
- ❖ Both combine with metals in the form of O<sub>2</sub> and S<sub>2</sub> with oxidation state -2.
- ❖ Both combine with non-metals and form covalent compounds, e.g. H<sub>2</sub>O and H<sub>2</sub>S, CO<sub>2</sub> and CS<sub>2</sub>, etc.
- ❖ Both are found in free and combined states on earth.
- ❖ Both are typical non-metals.

#### Dissimilarities:

Oxygen	Sulphur
There are two allotropic forms of oxygen O <sub>2</sub> and O <sub>3</sub> .	There are 3 allotropic forms of sulphur i.e. rhombic, monoclinic and plastic.
It is gas at ordinary temperature.	It is solid at ordinary temperature.
Oxygen is sparingly soluble in water.	Sulphur is not soluble in water.
Oxygen helps in combustion.	Sulphur is itself combustible.
It is paramagnetic in nature.	It is diamagnetic in nature.
It does not react with water.	When steam is passed through boiling sulphur, a little hydrogen sulphide and sulphur dioxide are formed.
It does not react with acids.	It is readily oxidized by conc. Sulphuric acid or nitric acid.
It does not react with alkalis.	It reacts with alkali solution and forms sulphides and thiosulphates.
It shows -2 oxidation states.	It shows oxidation states of -2, +2, +4 and +6.

### Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>):

Sulphuric acid was first prepared by a Muslim scientist Jabir Bin Hayyan in 8<sup>th</sup> century. In Europe, in 14<sup>th</sup> and 15<sup>th</sup> centuries, its preparation on commercial level was started due to the awareness of its properties and uses. It was called

“oil of vitriol”. It does not occur as such in nature, however small quantities of  $\text{H}_2\text{SO}_4$  are found in the waters of some springs and rivers. Sulphuric acid is also called “King of chemicals” and its production is a parameter for the industrial growth of a country.

### Contact Process (Manufacture of Sulphuric Acid):

This method was developed by Knietzsch in Germany. Basically it involving the catalytic combination of sulphur and oxygen to form  $\text{SO}_2$  which is then dissolved in water to form  $\text{H}_2\text{SO}_4$ .

#### Principle:

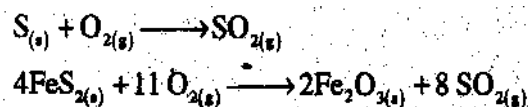
$\text{SO}_2$  obtained by burning sulphur or iron pyrites is oxidized to  $\text{SO}_3$  in the presence of  $\text{V}_2\text{O}_5$  which act as a catalyst. The best yield of  $\text{SO}_3$  can be obtained by using excess of oxygen or air and keeping the temperature between  $400\text{--}500^\circ\text{C}$ .  $\text{SO}_3$  formed is absorbed in concentrated  $\text{H}_2\text{SO}_4$  and “Oleum” ( $\text{H}_2\text{S}_2\text{O}_7$ ) formed can be converted to sulphuric acid of any strength by mixing adequate quantities of water.

#### Steps involved in the contact process:

The process is completed in steps given below:

##### 1. Sulphur burners:

Sulphur or iron pyrites are burnt in excess of air to produce  $\text{SO}_2$ .



##### 2. Purifying unit:

$\text{SO}_2$  is purified from impurities like dust and arsenic oxide, to avoid poisoning of the catalyst.

Purifying unit consists of the following parts.

##### 3. Dust chamber: Steam is injected to remove dust particles from the gases.

##### 4. Cooling pipes: The gases are passed through lead pipes to cool them to $100^\circ\text{C}$ .

##### 5. Scrubbers: The cooled gases are washed by a spray of water, as $\text{SO}_2$ is not soluble in water at high temperature.

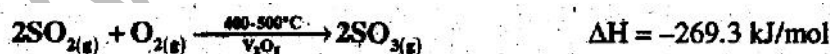
##### 6. Drying Tower: The moisture of gases is removed by concentrated $\text{H}_2\text{SO}_4$ trickling down through the coke filed in this tower.

##### 7. Arsenic Purifier: Arsenic oxide is then removed by passing the gases through chamber provided with shelves packed with freshly prepared ferric hydroxide.

##### 8. Testing box: In this box, a beam of light is introduced which indicates the presence or absence of solid particles. If present the gases are sent back for further purification.

##### 9. Contact chamber:

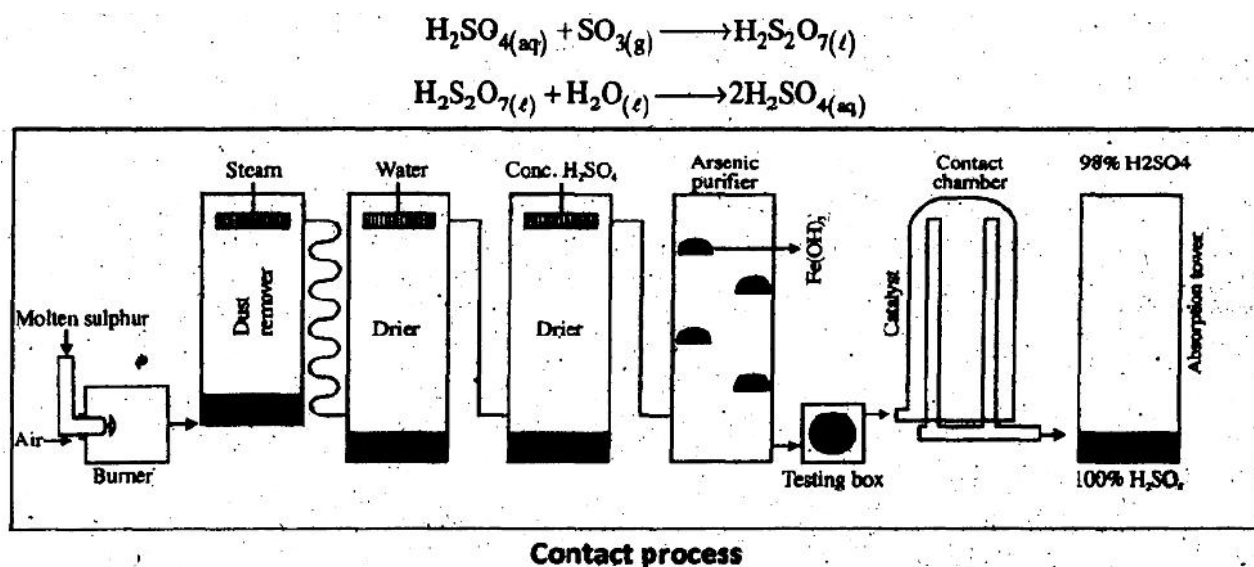
Pre-heated gases at  $400\text{--}500^\circ\text{C}$  are passed through vertical iron columns packed with the catalyst  $\text{V}_2\text{O}_5$ . Here  $\text{SO}_2$  is oxidized to  $\text{SO}_3$ .



The reaction is highly exothermic so no heating is required once the reaction is started.

##### 10. Absorption Unit:

The  $\text{SO}_3$  obtained from the contact tower is dissolved in 98%  $\text{H}_2\text{SO}_4$  to form “oleum” ( $\text{H}_2\text{S}_2\text{O}_7$ ). It can be diluted with water to get any required concentration of sulphuric acid.



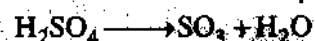
### Physical properties:

1. Pure sulphuric acid is a colourless oily liquid without an odour.
2. Its specific gravity is 1.834 at 18°C.
3. It freezes at 10.5°C.
4. Its boiling point is 338°C.
5. It dissolves in water, liberating a lot of heat which raises the temperature of the mixture up to 120°C.  $\text{H}_2\text{SO}_4$  should always be poured in water in a thin stream to avoid any accident.
6. Pure acid is a nonconductor of electricity but the addition of a little water makes it a good conductor.
7. It is extremely corrosive to skin and causes very serious burns to all the tissues.

### Chemical reactions:

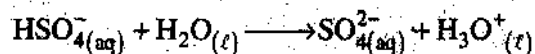
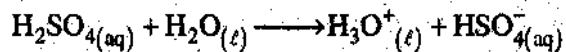
#### 1. Decomposition:

It is stable at ordinary temperature but on strong heating it dissociates into  $\text{SO}_3$  and  $\text{H}_2\text{O}$ .

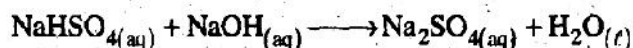
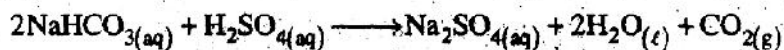
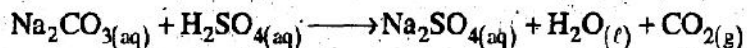
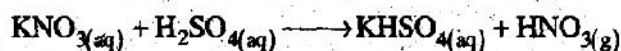
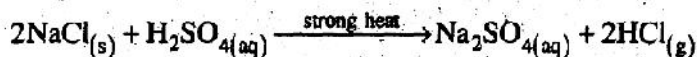


#### 2. Di basic acid:

It is a strong acid. In an aqueous solution, it completely ionizes to give hydrogen, hydrogen sulphate and sulphate ions. The dissociation takes place in two steps.



#### 3. Reactions as acid:

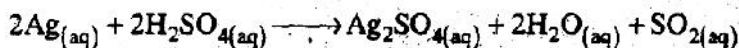
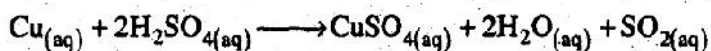
**(i) Reactions with alkalies****(ii) Reactions with carbonates and hydrogen carbonates:****(iii) Reactions with salts****(iv) Reaction with Metals**

(a) Cold dilute acid reacts with almost all metals to produce hydrogen gas.

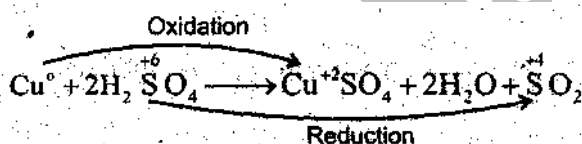


(b). Cold concentrated  $\text{H}_2\text{SO}_4$  does not react with most of the metals like Cu, Ag, Hg, Pb, Au.

(c) With certain metals, hot concentrated sulphuric acid gives metal sulphates, water and  $\text{SO}_2$ .

**Reaction between conc.  $\text{H}_2\text{SO}_4$  and copper:**

Hot Conc. Sulphuric acid reacts with Cu to form copper Sulphate and  $\text{SO}_2$ .



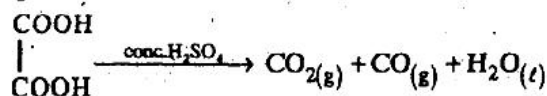
In this reaction, the oxidation state of Cu is changed from “zero” to “2” in  $\text{CuSO}_4$  and thus Cu is oxidized. The oxidation state of S in  $\text{H}_2\text{SO}_4$  is +6 whereas in  $\text{SO}_2$  it is +4. This shows that sulphur is reduced. Therefore the reaction is an oxidation reduction.



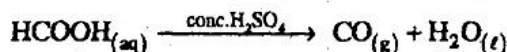
#### 4. Reactions as a dehydrating agent

$\text{H}_2\text{SO}_4$  has a great affinity for water, so it acts as dehydrating agent and eliminates water from different compounds.

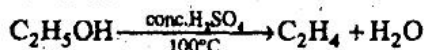
- (i) With oxalic acid it forms  $\text{CO}_2$  and  $\text{CO}$ .



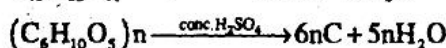
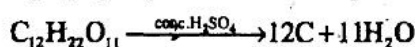
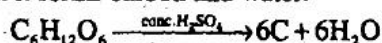
- (ii) With formic acid,  $\text{CO}$  is formed.



- (iii) With ethyl alcohol it forms ethylene or ethane.



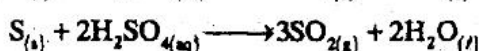
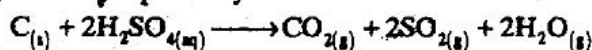
- (iv) With wood, paper, sugar and starch it forms carbon and water.



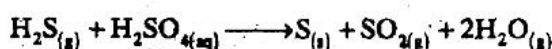
#### 5. As an Oxidizing Agent

$\text{H}_2\text{SO}_4$  acts as a strong oxidizing agent.

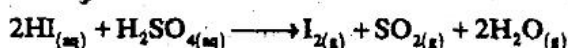
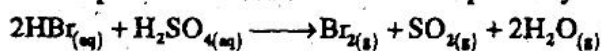
- (i) It oxidizes  $\text{C}$  and  $\text{S}$  giving  $\text{CO}_2$  and  $\text{SO}_2$  respectively.



- (ii)  $\text{H}_2\text{S}$  is oxidized to  $\text{S}$ .

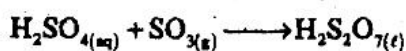


- (iii) Reactions of  $\text{H}_2\text{SO}_4$  with  $\text{HBr}$  and  $\text{HI}$  produce bromine and iodine respectively.

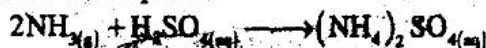


#### 6. Reactions with Gases

- (i) It absorbs  $\text{SO}_3$  and forms oleum.

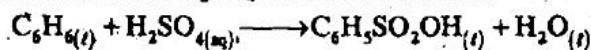


- (ii) It reacts with ammonia forming ammonium sulphate.



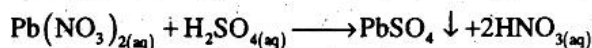
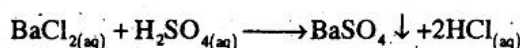
#### 7. Reaction with Benzene

Benzene sulphonic acid is produced when  $\text{H}_2\text{SO}_4$  reacts with benzene.



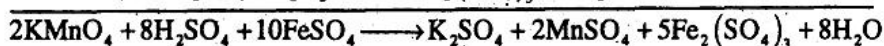
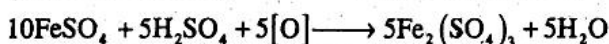
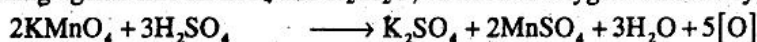
#### 8. Precipitation Reactions

White precipitates are produced when  $\text{H}_2\text{SO}_4$  reacts with aqueous solutions of  $\text{BaCl}_2$ ,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Sr}(\text{NO}_3)_2$ .



#### 9. Reactions with Oxidizing Agents

It reacts with oxidizing agents like  $\text{KMnO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  to liberate oxygen which may oxidize other compounds.



### Uses of Sulphuric Acid:

It is used:

- ❖ in the manufacture of fertilizers like ammonium sulphate  $(\text{NH}_4)_2\text{SO}_4$  and calcium superphosphate  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ .
- ❖ in refining of petroleum to remove nitrogen and sulphur compounds.
- ❖ in the manufacture of  $\text{HCl}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{HNO}_3$ , and sulphates.
- ❖ as a dehydrating agent for drying gases.
- ❖ in electrical batteries and storage cells.
- ❖ in the manufacture of many chemicals, dyes, drugs, plastics, disinfectants, paints, explosives, synthetic fibers etc.
- ❖ as a laboratory reagent.
- ❖ in textile iron steel, leather and paper industries.