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**ENTHUSE**

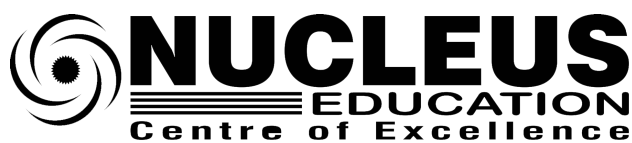
# **IIT CHEMISTRY**

**INORGANIC CHEMISTRY**

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**p-block Elements**

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**C.O.: NAIVEDHYAM, Plot No. SP-11, Old INOX, Indira Vihar, Kota (Raj.) 324005 Ph. 0744-2799900**

## p-BLOCK ELEMENT

### GROUP 13 ELEMENTS: THE BORON FAMILY :

Boron is a typical non-metal, aluminium is a metal but gallium, indium and thallium are almost exclusively metallic in character.

### OCCURANCE

**Boron:** Boron is a fairly rare element, mainly occurs as orthoboric acid, ( $\text{H}_3\text{BO}_3$ ),

borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , and kernite,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ .

There are two isotopic forms of boron  $^{10}\text{B}$  (19%) and  $^{11}\text{B}$  (81%).

### ALUMINIUM :

Aluminium is the most abundant metal.

Third most abundant element in the earth's crust (8.3% by mass) after oxygen (45.5%) and Si (27.7%).

Bauxite,  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  and cryolite,  $\text{Na}_3\text{AlF}_6$  are the important minerals of aluminium.

### ELECTRONIC CONFIGURATION :

The outer electronic configuration of these elements is  $ns^2np^1$ .

### ATOMIC RADII :

On moving down the group, for each successive member one extra shell of electrons is added and, therefore, atomic radius is expected to increase. However, a deviation can be seen.

#### Atomic and Ionic radii order

$\text{B} < \text{Ga} < \text{Al} < \text{In} < \text{Tl}$

#### Ionization Enthalpy

The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group.

#### Ionization Enthalpies order

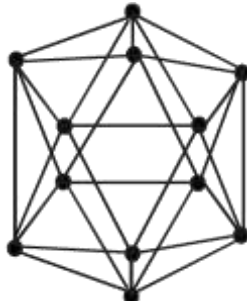
$\text{B} > \text{Tl} > \text{Ga} > \text{Al} > \text{In}$

#### Electronegativity

$\text{B} > \text{Tl} > \text{In} > \text{Ga} > \text{Al}$

### Physical Properties

- (i) Boron is non-metallic in nature.
  - It is extremely hard and black coloured solid.
  - Boron exists in many allotropic forms. All the allotropes have basic building  $B_{12}$  icosahedral units made up of polyhedron having 20 faces and 12 corners. For example one is the simplest form :  $\alpha$  - rhombohedral boron.



But Al, In & Tl all have close packed metal structure.

- (ii) Rest of the members are soft metals with low melting point and high electrical conductivity.
- (iii) Gallium with unusually low melting point (303K), could exist in liquid state during summer.
- (iv) Density of the elements increases down the group from boron to thallium.

### Melting and Boiling points order

M.P.  $B > Al > Tl > In > Ga$

B.P.  $B > Al > Ga > In > Tl$

### Electropositive Character

$B < Al < Ga < In < Tl$

Non  
metal

metals

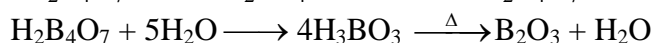
### Chemical Properties

#### Oxidation state and trends in chemical reactivity

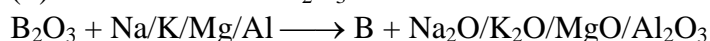
- (i) Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form +3 ions and forces it to form only covalent compounds.
- (ii) The relative stability of +1 oxidation state progressively increases for heavier elements:  $Al < Ga < In < Tl$ . In thallium +1 oxidation state is predominant whereas the +3 oxidation state is highly oxidizing in character.
- (iii) The compounds in +1 oxidation state, as expected from energy considerations, are more ionic than those in +3 oxidation state.

### Preparation of Boron :

- (i) Preparation of  $B_2O_3$  from Borax or Colemanite



- (ii) Reduction of  $B_2O_3$



**Chemical Properties :**

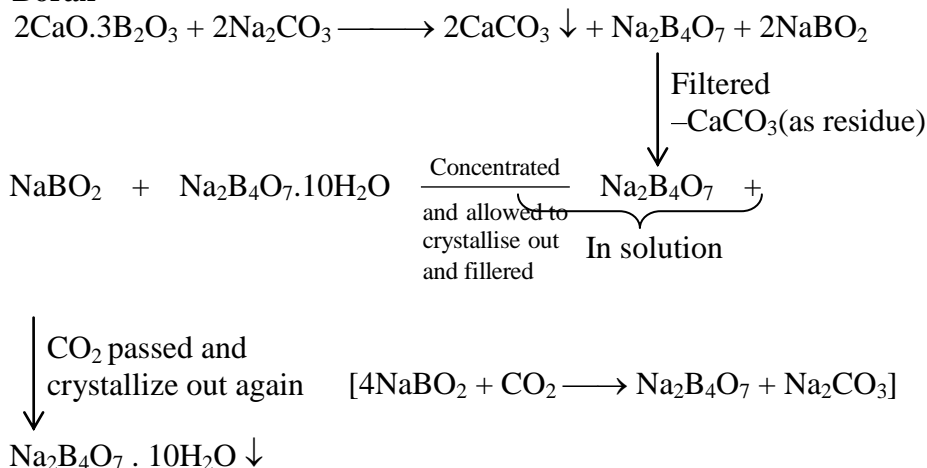
- (i) Burning in air :  $4\text{B} + 3\text{O}_2 \longrightarrow 2\text{B}_2\text{O}_3$   
 $4\text{Al} + 3\text{O}_2 \longrightarrow 2\text{Al}_2\text{O}_3$
- (ii) Reaction with water  
 $\text{B} + \text{H}_2\text{O}$  (Cold & hot)  $\longrightarrow$  no reaction  
 $2\text{B} + 3\text{H}_2\text{O} \longrightarrow \text{B}_2\text{O}_3 + \text{H}_2$   
 $(\text{Al} + 3\text{H}_2\text{O} \longrightarrow \text{Al}(\text{OH})_3 + \frac{3}{2} \text{H}_2)$   
 (red hot)
- (iii)  $\text{B} + \text{HCl} \longrightarrow$  no reaction  
 $\text{B} + \text{H}_2\text{SO}_4$  (dil)  $\longrightarrow$  no reaction  
 $2\text{B} + 3\text{H}_2\text{SO}_4$  (conc.)  $\longrightarrow 2\text{H}_3\text{BO}_3 + 3\text{SO}_2$   
 $(2\text{Al} + 6\text{H}_2\text{SO}_4 \longrightarrow \text{Al}_2(\text{SO}_4)_3 + 3\text{SO}_2 + 6\text{H}_2\text{O})$   
 $\text{B} + 3\text{HNO}_3 \longrightarrow \text{H}_3\text{BO}_3 + 3\text{NO}_2$   
 $[\text{Al} + \text{HNO}_3(80\%) \longrightarrow \text{Al}_2\text{O}_3 \text{ (passive layer) and does not react further.}]$
- (vi) Ga, In, Tl dissolve in dilute acids liberating  $\text{H}_2$  Ga is amphoteric like Al and it dissolves in aq. NaOH liberating  $\text{H}_2$  and forming gallates.  
 $2\text{B} + 2\text{NaOH} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaBO}_2 + 3\text{H}_2$   
 $2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaAlO}_2 + 3\text{H}_2$
- (v)  $2\text{B} + \text{N}_2 \longrightarrow 2\text{BN}$  ( $2\text{Al} + \text{N}_2 \longrightarrow 2\text{AlN}$ )  
 $4\text{B} + \text{C} \longrightarrow \text{B}_4\text{C}$  ( $4\text{Al} + 3\text{C} \longrightarrow \text{Al}_4\text{C}_3$ )
- (vi)  $3\text{Mg} + 2\text{B} \longrightarrow \text{Mg}_3\text{B}_2$

**SOME IMPORTANT COMPOUNDS OF BORON**

Some useful compounds of boron are borax, orthoboric acid and diborane. We will briefly study their chemistry.

**Preparation of Borax :**

**Borax**



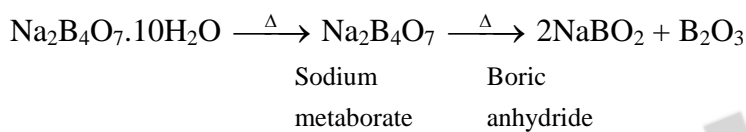
**Properties :**

- (i) It is a white crystalline solid of formula  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ . In fact it contains the tetranuclear units  $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$  and correct formula; therefore, is  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ .
- (ii) Borax dissolves in water to give an alkaline solution.  

$$\text{Na}_2\text{B}_4\text{O}_7 + 7\text{H}_2\text{O} \rightarrow 2\text{NaOH} + 4\text{H}_3\text{BO}_3$$

**Orthoboric acid**

- (iii) On heating, borax first loses water molecules and swells up. On further heating it turns into a transparent liquid, which solidifies into glass like material known as borax bead.



The metaborates of many transition metals have characteristic colours and, therefore, borax bead test can be used to identify them in the laboratory. For example, when borax is heated in a Bunsen burner flame with  $\text{CoO}$  on a loop of platinum wire, a blue coloured  $\text{Co}(\text{BO}_2)_2$  bead is formed.

**Orthoboric acid :**

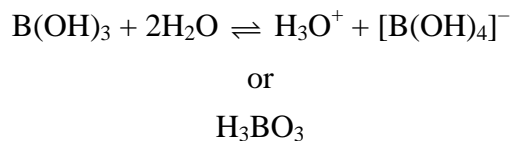
**Preparation :**

- (i) It can be prepared by acidifying an aqueous solution of borax.  

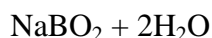
$$\text{Na}_2\text{B}_4\text{O}_7 + 2\text{HCl} + 5\text{H}_2\text{O} \rightarrow 2\text{NaCl} + 4\text{B}(\text{OH})_3$$
- (ii) It is also formed by the hydrolysis (reaction with water or dilute acid) of most boron compounds (halides, hydrides, etc.)

**Property :**

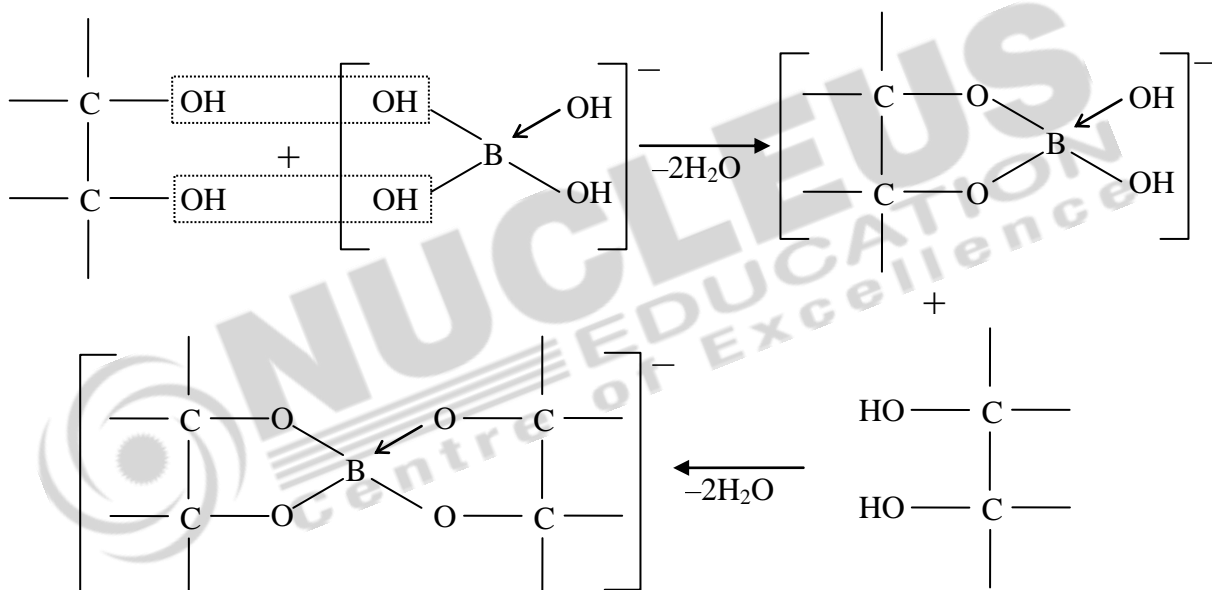
- (i) Orthoboric acid,  $\text{H}_3\text{BO}_3$  is a white crystalline solid, with soapy touch.
- (ii) It is sparingly soluble in water but highly soluble in hot water.
- (iii)  $\text{H}_3\text{BO}_3$  is soluble in water and behaves as weak monobasic acid. It does not donate protons like most the acids, but rather it accepts  $\text{OH}^-$ . It is therefore is Lewis acid ( $\text{B}(\text{OH})_3$ )



Since  $\text{B(OH)}_3$  only partially reacts with water to form  $\text{H}_3\text{O}^+$  and  $[\text{B(OH)}_4]^-$  it behaves as a weak acid. Thus it cannot be titrated satisfactorily with  $\text{NaOH}$  as a sharp end point is not obtained. If certain polyhydroxy compounds such as glycerol, mannitol or sugar are added to the titration mixture then  $\text{B(OH)}_3$  behaves as a strong monobasic acid. and hence can now be titrated with  $\text{NaOH}$  and end point is diluted using phenolphthalein as indicator.

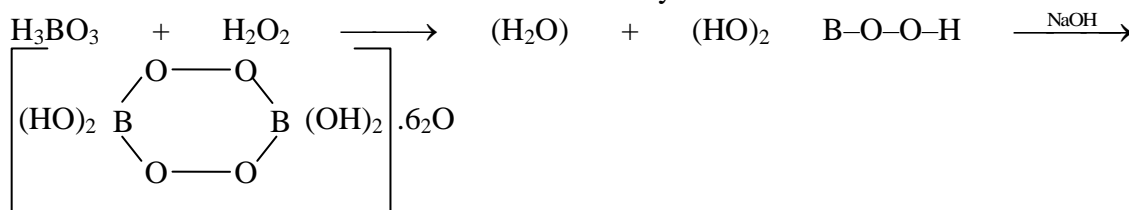
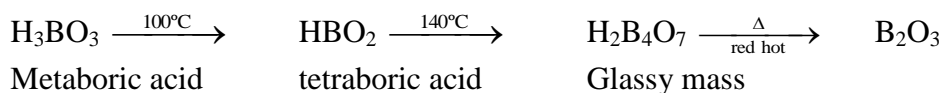


The added compound must be a as diol to enhance the acidic proprieties in this way the cis-diol forms very stable complexes with  $[\text{B(OH)}_4]^-$  formed in forward direction above, thus effectively removing it from solution. Hence reaction proceeds in forward direction (Le-Chatelier principle.)



On heating, orthoboric acid above 370K forms metaboric acid,  $\text{HBO}_2$  which on further heating yields boric oxide,  $\text{B}_2\text{O}_3$ .

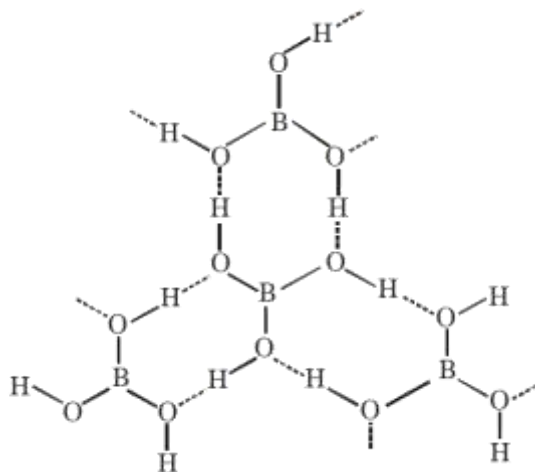
• **Heating of boric acid :**



Sodium peroxy borate used in washing powder as brightner

### STRUCTRE

It has a layer structure in which planar  $\text{BO}_3$  units are joined by hydrogen bonds as shown in figure.



Structure of boric acid; the dotted lines represent hydrogen bonds.

#### Uses of boric acid :

- (i) Boric acid is used in manufacturing of optical glasses
- (ii) With borax, it is used in the preparation of a buffer solution.

#### Diborane, $\text{B}_2\text{H}_6$

The simplest boron hydride known, is diborane.

#### Preparation :

- (i) It is prepared by treating boron trifluoride with  $\text{LiAlH}_4$  in diethyl ether.  

$$3\text{LiAlH}_4 + 4\text{BF}_3 \longrightarrow 3\text{LiF} + 3\text{AlF}_3 + 2\text{B}_2\text{H}_6$$

or  $\text{LiBH}_4$  or  $3(\text{BF}_3)$
- (ii) **Laboratory method :** For the preparation of diborane involves the oxidation of sodium borohydride with iodine.  

$$2\text{NaBH}_4 + \text{I}_2 \rightarrow \text{B}_2\text{H}_6 + 2\text{NaI} + \text{H}_2$$
- (iii) **Industrial scale :** By the reaction of  $\text{BF}_3$  with sodium hydride.  

$$2\text{BF}_3 + 6\text{NaH} \xrightarrow{450\text{K}} \text{B}_2\text{H}_6 + 6\text{NaF}$$

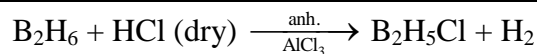
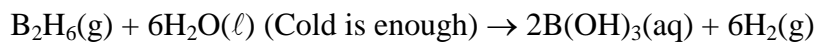
#### Properties :

- (i) Diborane is a colourless, highly toxic gas with a b.p. of 180 K.
- (ii) Diborane catches fire spontaneously upon exposure to air.
- (iii) It burns in oxygen releasing an enormous amount of energy.  

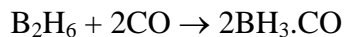
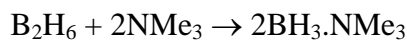
$$\text{B}_2\text{H}_6 + 3\text{O}_2 \rightarrow \text{B}_2\text{O}_3 + 3\text{H}_2\text{O} ; \Delta_c H^\ominus = -1976 \text{ kJ mol}^{-1}$$

Most of the higher boranes are also spontaneously flammable in air.

- (iv) Boranes are readily hydrolysed by water to give boric acid.



- (v) Diborane undergoes cleavage reactions with Lewis bases(L) to give borane adducts,  $\text{BH}_3\cdot\text{L}$



Reaction of ammonia with diborane gives initially  $\text{B}_2\text{H}_6\cdot 2\text{NH}_3$  which is formulated as  $[\text{BH}_2(\text{NH}_3)_2]^+ [\text{BH}_4]^-$ ; further heating gives borazine,  $\text{B}_3\text{N}_3\text{H}_6$  known as “inorganic benzene” in view of its ring structure with alternate BH and NH groups.

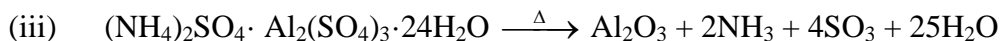
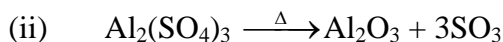
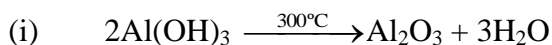


- (VI) **Metal hydrido borates :** Boron also forms a series of hydridoborates; the most important one is the tetrahedral  $[\text{BH}_4]^-$  ion. Tetrahydridoborates of several metals are known. Lithium and sodium tetrahydridoborates, also known as borohydrides, are prepared by the reaction of metal hydrides with  $\text{B}_2\text{H}_6$  in diethyl ether.



Both  $\text{LiBH}_4$  and  $\text{NaBH}_4$  are used as reducing agents in organic synthesis. They are useful starting materials for preparing other metal borohydrides.

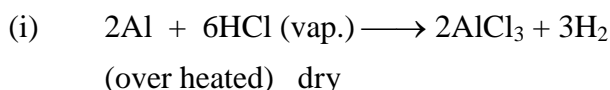
• ***Al<sub>2</sub>O<sub>3</sub> preparation :***



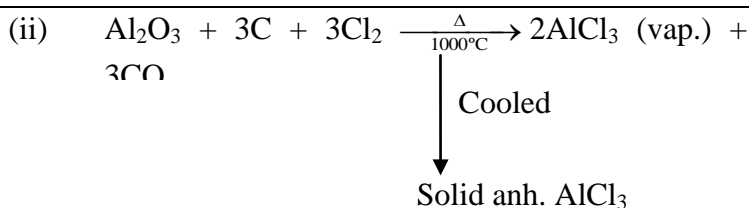
**Uses:**

- (i) In making refractory brick
- (ii) as abrasive
- (iii) To make high alumina cement

• ***AlCl<sub>3</sub> preparation :***

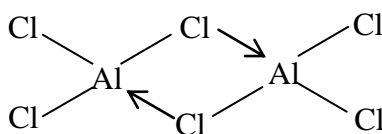






**Properties :**

- (i) Its anhydrous form is deliquescent and fumes in air.
- (ii) It sublimes at  $180^\circ\text{C}$ .
- (iii) It is covalent and exists in the form of dimer even if in non polar solvents e.g. alcohol, ether, benzene, where it is soluble in fair extent.



**Uses:**

- (i) Friedel-Craft reaction
  - (ii) Dyeing, drug. & perfumes etc.
- **Alumns :**  $\text{M}_2\text{SO}_4, \text{M}'_2 (\text{SO}_4)_3 \cdot 24 \text{H}_2\text{O}$

**Props:**

Swelling characteristics

where  $\text{M} = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{As}^+, \text{Tl}^+, \text{NH}_4^+$

$\text{M}' = \text{Al}^{+3}, \text{Cr}^{+3}, \text{Fe}^{+3}, \text{Mn}^{+3}, \text{Co}^{+3}$

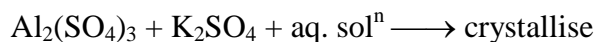
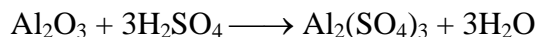
$\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  Potash alum

$(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  Ammonium alum

$\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  Chrome alum

$(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  Ferric alum

**Preparation:**



**Uses:**

- (i) Act as coagulant
- (ii) Purification of water
- (iii) Tanning of leather
- (iv) Mordant in dying
- (v) Antiseptic

**USES OF BORON AND ALUMINIUM AND THEIR COMPOUNDS****Boron :**

- (i) Boron being extremely hard refractory solid of high melting point, low density and very low electrical conductivity, finds many applications.
- (ii) Boron fibres are used in making bullet-proof vest and light composite material for aircraft.
- (iii) The boron-10 ( $^{10}\text{B}$ ) isotope has high ability to absorb neutrons and, therefore, metal borides are used in nuclear industry as protective shields and control rods.
- (iv) The main industrial application of borax and boric acid is in the manufacture of heat resistant glasses(e.g., Pyrex), glass-wool and fibreglass.
- (v) Borax is also used as a flux for soldering metals, for heat, scratch and stain resistant glazed coating to earthenwares and as constituent of medicinal soaps.
- (vi) An aqueous solution of orthoboric acid is generally used as a mild antiseptic.

**Aluminium :**

- (i) Aluminium is a bright silvery-white metal, with high tensile strength.
- (ii) It has a high electrical and thermal conductivity.
- (iii) On a weight-to-weight basis, the electrical conductivity of aluminium is twice that of copper.
- (iv) Aluminium is used extensively in industry and every day life.
- (v) It forms alloys with Cu, Mn, Mg, Si and Zn.
- (vi) Aluminium and its alloys can be given shapes of pipe, tubes, rods, wires, plates or foils and, therefore, find uses in packing, utensil making, construction, aeroplane and transportation industry.
- (vii) The use of aluminium and its compounds for domestic purposes is now reduced considerably because of their toxic nature.

## GROUP 14 ELEMENTS

### The carbon family

Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14.

### Occurrence of element

- (i) **Carbon** : Carbon is the seventeenth most abundant element by mass in the earth's crust. Naturally occurring carbon contains two stable isotopes:  $^{12}\text{C}$  and  $^{13}\text{C}$ . In addition to these, third isotope,  $^{14}\text{C}$  is also present. It is a radioactive isotope with half-life 5770 years and used for radiocarbon dating.
- (ii) **Silicon** : Silicon is the second (27.7 % by mass) most abundant element on the earth's crust.
- (iii) **Germanium** : Germanium exists only in traces.
- (iv) **Tin** : Tin occurs mainly as cassiterite,  $\text{SnO}_2$
- (v) **Lead** : Lead as galena,  $\text{PbS}$ .

**Note** : Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices.

### Electronic Configuration

The valence shell electronic configuration of these elements is  $ns^2np^2$ .

- **Covalent Radius**

Covalent radii :  $\text{C} < \text{Si} < \text{Ge} < \text{Sn} < \text{Pb}$

- **Ionization Enthalpy**

$\text{C} > \text{Si} > \text{Ge} > \text{Pb} > \text{Sn}$  ( $\text{IE}_1$  values)

- **Melting and Boiling Points**

M.P. :  $\text{C} > \text{Si} > \text{Ge} > \text{Pb} > \text{Sn}$

B.P. :  $\text{Si} > \text{Ge} > \text{Sn} > \text{Pb}$

- **Electronegativity**

$\text{C} > \text{Si} = \text{Ge} = \text{Sn} = \text{Pb}$

Due to small size, the elements of this group are slightly more electronegative than group 13 elements.

The electronegativity values for elements from Si to Pb are almost the same.

- **Physical Properties**

All group 14 members are solids. Carbon and silicon are non-metals, germanium is a metalloid, whereas tin and lead are soft metals with low melting points.

**Chemical Properties****Oxidation states and trends in chemical reactivity**

- (i) The group 14 elements have four electrons in outermost shell.
- (ii) The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states.
- (iii) In heavier members the tendency to show +2 oxidation state increases in the sequence  $\text{Ge} < \text{Sn} < \text{Pb}$ . It is due to the inability of  $ns^2$  electrons of valence shell to participate in bonding. The relative stabilities of these two oxidation states vary down the group.
- (iv) Carbon and silicon mostly show +4 oxidation state.
- (v) Germanium forms stable compounds in +4 state and only few compounds in +2 state.
- (vi) Tin forms compounds in both oxidation states (Sn in +2 state is a reducing agent).
- (vii) Lead compounds in +2 state are stable and in +4 state are strong oxidising agents.

**Reactivity towards oxygen**

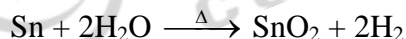
There are mainly two types of oxides, *i.e.*, monoxide and dioxide of formula MO and  $\text{MO}_2$  respectively. SiO only exists at high temperature.

The dioxides —  $\text{CO}_2$ ,  $\text{SiO}_2$  and  $\text{GeO}_2$  are acidic, whereas  $\text{SnO}_2$  and  $\text{PbO}_2$  are amphoteric in nature.

Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.

**Reactivity towards water**

Carbon, silicon and germanium are not affected by water. Tin decomposes steam to form dioxide and dihydrogen gas.



Lead is unaffected by water, probably because of a protective oxide film formation.

**Reactivity towards halogen**

- (i) These elements can form halides of formula  $\text{MX}_2$  and  $\text{MX}_4$  (where  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ). Except carbon, all other members react directly with halogen under suitable condition to make halides.
- (ii) Most of the  $\text{MX}_4$  are covalent in nature. The central metal atom in these halides undergoes  $sp^3$  hybridisation and the molecule is tetrahedral in shape. Exceptions are  $\text{SnF}_4$  and  $\text{PbF}_4$ , which are ionic in nature.
- (iii)  $\text{PbI}_4$  does not exist.
- (iv) Heavier members Ge to Pb are able to make halides of formula  $\text{MX}_2$ .
- (v) Stability of dihalides increases down the group. Considering the thermal and chemical stability,  $\text{GeX}_4$  is more stable than  $\text{GeX}_2$ , whereas  $\text{PbX}_2$  is more than  $\text{PbX}_4$ .
- (vi) Except  $\text{CCl}_4$ , other tetrachlorides are easily hydrolysed by water.

### Catenation Property

Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called catenation. This is because C—C bonds are very strong. The order of catenation is  $C \gg Si > Ge \approx Sn$ . Lead does not show catenation.

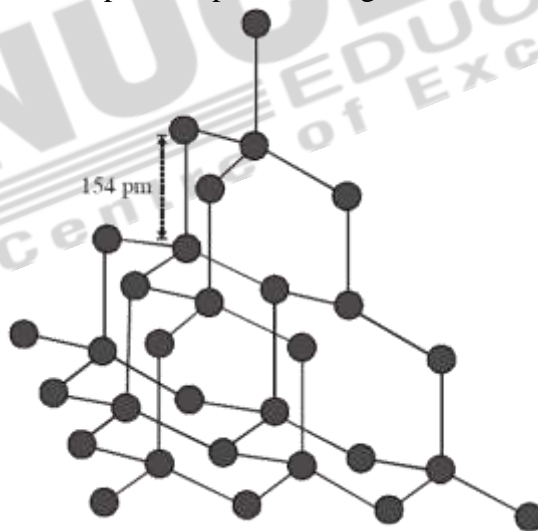
| Bond    | Bond enthalpy/kJ mol <sup>-1</sup> |
|---------|------------------------------------|
| C – C   | 348                                |
| Si – Si | 297                                |
| Ge – Ge | 260                                |
| Sn – Sn | 240                                |

Due to property of catenation and  $p\pi-p\pi$  bond formation, carbon is able to show allotropic forms.

### ALLOTROPES OF CARBON

#### Diamond

- It has a crystalline lattice.
- In diamond each carbon atom undergoes  $sp^3$  hybridisation.
- The C—C bond length is 154 pm.
- The structure extends in space and produces a rigid three-dimensional network of carbon atoms.



The structure of diamond

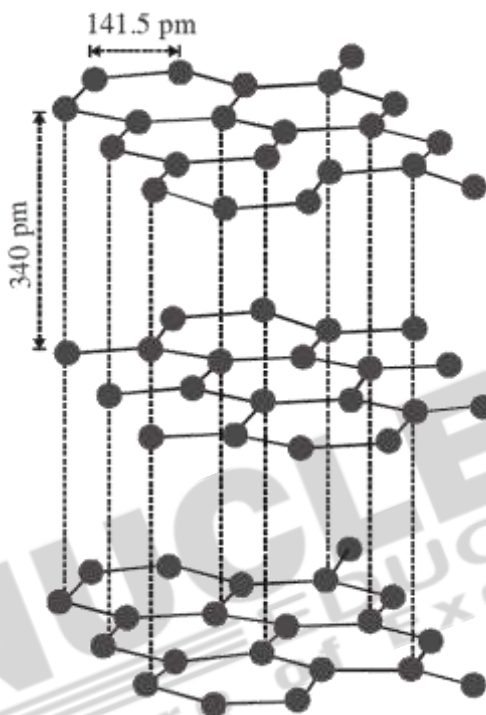
It is very difficult to break extended covalent bonding and, therefore, diamond is a hardest substance on the earth.

**Use :** It is used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.

#### Graphite

- Graphite has layered structure figure.
- Layers are held by van der Waals forces.

- (iii) Each layer is composed of planar hexagonal rings of carbon atoms. C—C bond length within the layer is 141.5 pm.
- (iv) Each carbon atom in hexagonal ring undergoes  $sp^2$  hybridisation and makes three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a p bond. The electrons are delocalized over the whole sheet. Electrons are mobile and, therefore, graphite conducts electricity along the sheet.



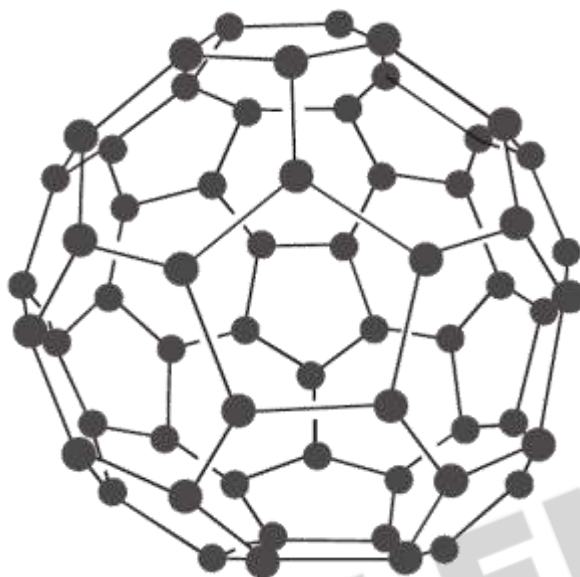
The Structure of Graphite

- (v) Graphite cleaves easily between the layers and, therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

### Fullerenes

- (i) Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourised  $C^n$  small molecules consists of mainly  $C_{60}$  with smaller quantity of  $C_{70}$  and traces of fullerenes consisting of even number of carbon atoms up to 350 or above. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules.  $C_{60}$  molecule has a shape like soccer ball and called **Buckminsterfullerene**.
- (ii) It contains twenty six- membered rings and twelve five membered rings.
- (iii) All the carbon atoms are equal and they undergo  $sp^2$  hybridisation.

- (iv) This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C–C distances of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called *bucky balls* in short.



*The structure of  $C_{60}$ , Buckminsterfullerene : Note that molecule has the shape of a soccer ball (football).*

**Note:** It is very important to know that graphite is thermodynamically most stable allotrope of carbon.

**Note:** Other forms of elemental carbon like carbon black, coke, and charcoal are all impure forms of graphite or fullerenes.

Carbon black is obtained by burning hydrocarbons in a limited supply of air.

Charcoal and coke are obtained by heating wood or coal respectively at high temperatures in the absence of air.

### ***Uses of Carbon***

- (i) Used in products such as tennis rackets, fishing rods, aircrafts and canoes.
- (ii) Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis.
- (iii) Crucibles made from graphite are inert to dilute acids and alkalies.
- (iv) Being highly porous, activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contaminators and in airconditioning system to control odour.
- (v) Carbon black is used as black pigment in black ink and as filler in automobile tyres.
- (vi) Coke is used as a fuel and largely as a reducing agent in metallurgy.
- (vii) Diamond is a precious stone and used in jewellery. It is measured in carats (1 carat = 200 mg).

**SOME IMPORTANT COMPOUNDS OF CARBON AND SILICON**

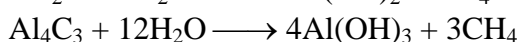
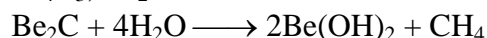
**Types of Carbide**

(i) Ionic and salt like:

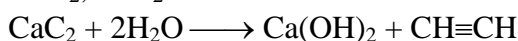
Classification on basis of  
no. of carbon atoms  
present in hydrocarbon  
found on their hydrolysis

- (a) C<sub>1</sub> unit  
(b) C<sub>2</sub> unit  
(c) C<sub>3</sub> unit

**C<sub>1</sub> unit:** Al<sub>4</sub>C<sub>3</sub>, Be<sub>2</sub>C



**C<sub>2</sub> unit:** CaC<sub>2</sub>, BaC<sub>2</sub>



**C<sub>3</sub> unit:** Mg<sub>2</sub>C<sub>3</sub>



(ii) Covalent carbide : SiC & B<sub>4</sub>C

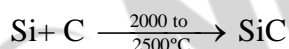
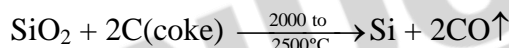
(iii) Interstitial carbide :

(Transition element or inner transitional elements forms this kind of carbide)

Interstitial carbide formation doesn't affect the metallic lusture and electrical conductivity. (∵ no chemical bond is present, no change in property)

**SiC (Carborandum)**

**Preparation**



**Note :**

(i) SiC has diamond like or wurtzite structure

(ii) SiC is often dark purple, black or dark green due to traces Fe and other impurities but pure sample are pale yellow to colourless

**Properties**

(i) It is very hard and is used in cutting tools and abrassive powder(polishing material)

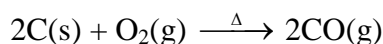
(ii) It is very much inert

(iii) It is not being affected by any acid except H<sub>3</sub>PO<sub>4</sub>

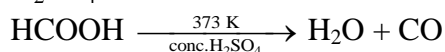
**Carbon Monoxide**

**Preparation :**

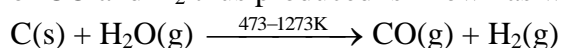
(i) Direct oxidation of C in limited supply of oxygen or air yields carbon monoxide.



(ii) On small scale pure CO is prepared by dehydration of formic acid with concentrated H<sub>2</sub>SO<sub>4</sub> at 373 K

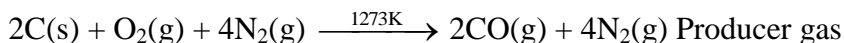


(iii) On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and H<sub>2</sub> thus produced is known as water gas or synthesis gas.



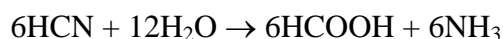
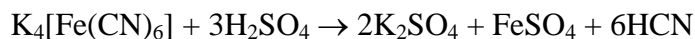


When air is used instead of steam, a mixture of CO and N<sub>2</sub> is produced, which is called producer gas.

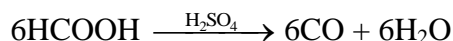
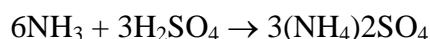


Water gas and producer gas are very important industrial fuels. Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat.

(iv) **By heating potassium ferrocyanide with conc. H<sub>2</sub>SO<sub>4</sub> :** When potassium ferrocyanide in powdered state is heated with concentrated H<sub>2</sub>SO<sub>4</sub>, CO is evolved. Dilute H<sub>2</sub>SO<sub>4</sub> should never be used because it shall evolve highly poisonous gas HCN.

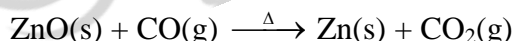


Formic acid



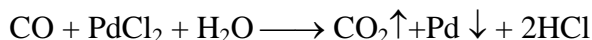
#### Properties :

- Carbon monoxide is a colourless, odourless and almost water insoluble gas.
- It is a powerful reducing agent and reduces almost all metal oxides other than those of the alkali and alkaline earth metals, aluminium and a few transition metals. This property of CO is used in the extraction of many metals from their oxides ores.



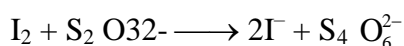
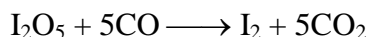
#### DETECTION

- burns with blue flame
- CO is passed through PdCl<sub>2</sub> solution giving rise to black ppt.

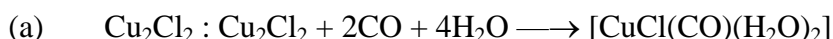


Black metallic  
deposition

#### ESTIMATION



#### ABSORBERS



- **Bonding in CO mole**

In CO molecule, there are one sigma and two p bonds between carbon and oxygen. Because of the presence of a lone pair on carbon, CO molecule acts as a donor and reacts with certain metals when heated to form **metal carbonyls**.

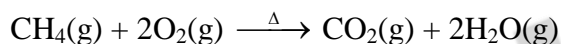
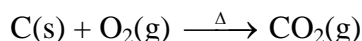
- **Poisonous nature of CO**

The highly poisonous nature of CO arises because of its ability to form a **complex with haemoglobin**, which is about 300 times more stable than the oxygen-haemoglobin complex. This prevents haemoglobin in the red blood corpuscles from carrying oxygen round the body and ultimately resulting in death.

### Carbon Dioxide

#### Preparation :

- (i) It is prepared by complete combustion of carbon and carbon containing fuels in excess of air.



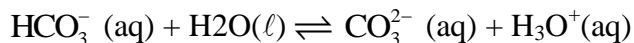
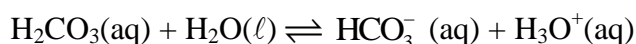
- (ii) **Laboratory** by the action of dilute HCl on calcium carbonate.



- (iii) Commercial scale by heating limestone.

#### Properties :

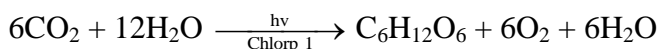
- (i) It is a colourless and odourless gas.
- (ii) Its low solubility in water makes it of immense biochemical and geo-chemical importance.
- (iii) With water, it forms carbonic acid,  $\text{H}_2\text{CO}_3$  which is a weak dibasic acid and dissociates in two steps:



$\text{H}_2\text{CO}_3/\text{HCO}_3^-$  buffer system helps to maintain pH of blood between 7.26 to 7.42. Being acidic in nature, it combines with alkalies to form metal carbonates.

#### Use of $\text{CO}_2$

Carbon dioxide, which is normally present to the extent of ~ 0.03 % by volume in the atmosphere, is removed from it by the process known as **photosynthesis**. It is the process by which green plants convert atmospheric  $\text{CO}_2$  into carbohydrates such as glucose.



By this process plants make food for themselves as well as for animals and human beings.

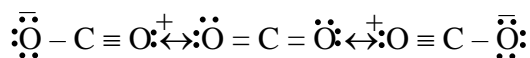
### Harmful effect of CO<sub>2</sub>

It is not poisonous.

CO<sub>2</sub> lead to increase in **green house effect**.

- Carbon dioxide can be obtained as a solid in the form of **dry ice** by allowing the liquified CO<sub>2</sub> to expand rapidly and dry ice is used as a refrigerant for ice-cream and frozen food.
- Gaseous CO<sub>2</sub> is extensively used to carbonate soft drinks.
- A substantial amount of CO<sub>2</sub> is used to manufacture urea.

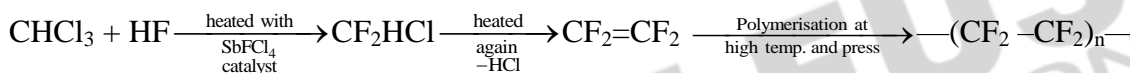
The resonance structures are shown below:



Resonating structures of carbon dioxide

**Note : Carbongene has 95% O<sub>2</sub> and 5% CO<sub>2</sub> and is used as an antidote for posining of CO.**

Teflon —(CF<sub>2</sub> — CF<sub>2</sub>)<sub>n</sub>—



### Purpose

Temperature with standing capacity upto 500–550°C (1<sup>st</sup> organic compound withstand this kind of high temperature)

### SILICON (Si)

### Occurrence

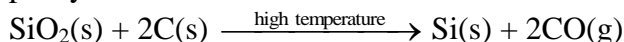
Silicon is the second most abundant (27.2%) element.

Silica is found in the free state in sand, flint and quartz and in the combined state as silicates like

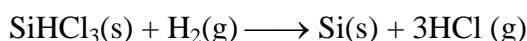
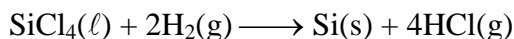
- Feldspar — K<sub>2</sub>O. Al<sub>2</sub>O<sub>3</sub>. 6SiO<sub>2</sub>
- Kaolinite — Al<sub>2</sub>O<sub>3</sub>. 2SiO<sub>2</sub>. 2H<sub>2</sub>O
- Asbestos — CaO. 3MgO. 4SiO<sub>2</sub>

### Preparation

- From silica (sand): Elemental silicon is obtained by the reduction of silica (SiO<sub>2</sub>) with high purity coke in an electric furnace.



- From silicon tetrachloride (SiCl<sub>4</sub>) or silicon chloroform (SiHCl<sub>3</sub>) : Silicon of very high purity required for making semiconductors is obtained by reduction of highly purified silicon tetrachloride or silicon chloroform with dihydrogen followed by purification by zone refining.

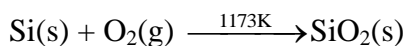


**Physical Properties :**

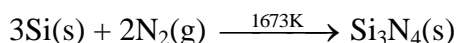
- (i) Elemental silicon is very hard having diamond like structure.
- (ii) It has shining luster with a melting point of 1793 K and boiling point of about 3550 K.
- (iii) Silicon exists in three isotopes, i.e.  ${}_{14}^{28}\text{Si}$ ,  ${}_{14}^{29}\text{Si}$  and  ${}_{14}^{30}\text{Si}$  but  ${}_{14}^{28}\text{Si}$  is the most common isotope.

**Chemical Properties :**

- (i) **Action of air :** Silicon reacts with oxygen of air at 1173 K to form silicon dioxide and with nitrogen of air at 1673 K to form silicon nitride,.

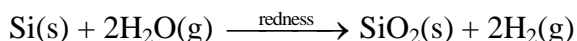


Silicon dioxide



Silicon nitride

- (ii) **Action of steam :** It is slowly attacked by steam when heated to redness liberating dihydrogen gas.

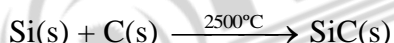


- (iii) **Reaction with halogens:** It burns spontaneously in fluorine gas at room temperature to form silicon tetrafluoride ( $\text{SiF}_4$ ).



However, with other halogens, it combines at high temperatures forming tetrahalides.

- (iv) **Reaction with carbon :** Silicon combines with carbon at 2500 °C forming silicon carbide ( $\text{SiC}$ ) known as carborundum.



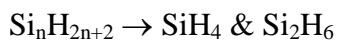
Carborundum is an extremely hard substance next only to diamond. It is mainly used as an abrasive and as a refractory material.

**Uses :**

It is used in the preparation of alloys such as silicon-bronze, magnesium silicon bronze and ferrosilicon.

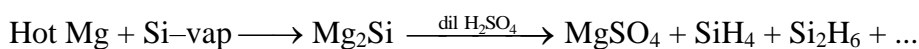
**Compounds of Silicon :**

**Silane :**



Only these two are found

Higher molecules are not formed.  $\therefore$  Si can't show catanation property

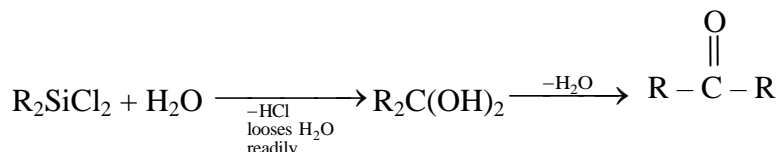
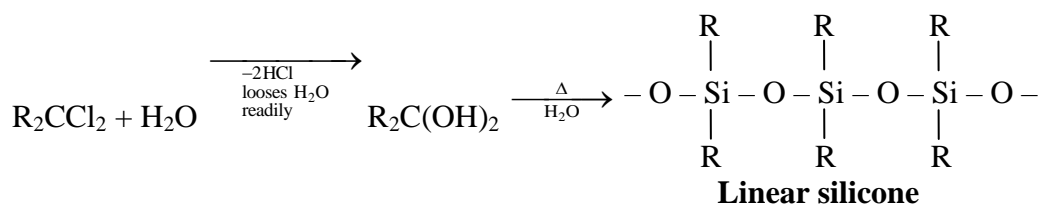


**Silicones**

It is organo silicon polymer

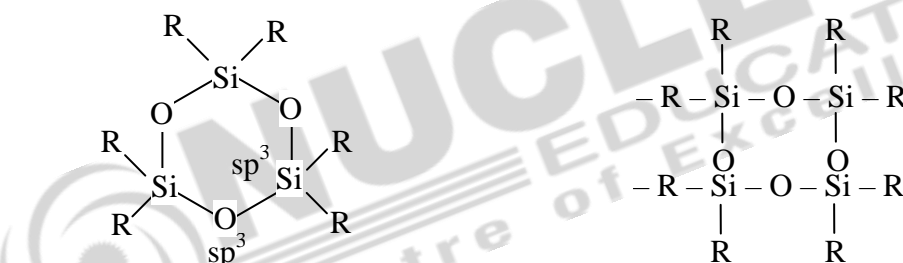
### TYPES OF SILICONES

#### (i) Linear silicones



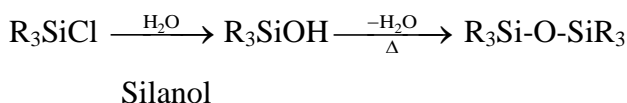
#### (ii) Cyclic silicones

Silicones may have the cyclic structure also having 3, 4, 5 and 6 nos. of silicon atoms within the ring. Alcohol analogue of silicon is known as silanol

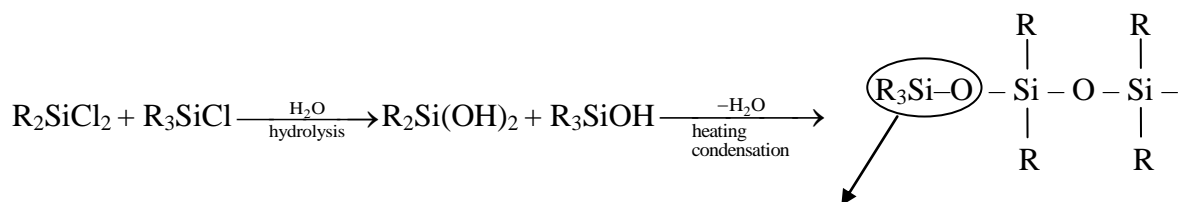


cyclic silicone not planar

#### (iii) Dimer silicones



**Note :**

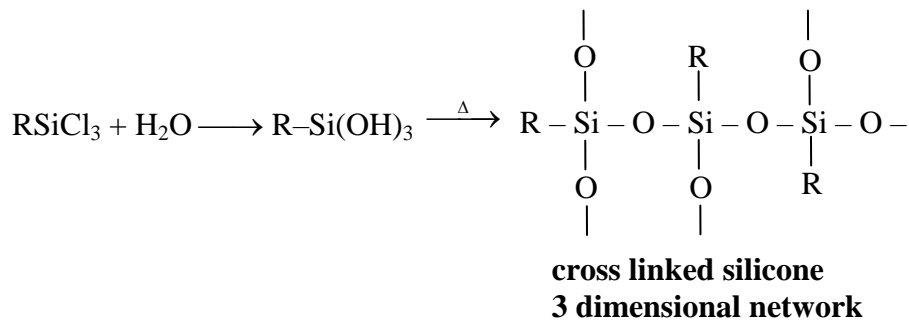


This end of the chain can't be extended hence

$R_3SiCl$  is called as chain stopping unit

\* Using  $R_3SiCl$  in a certain proportion we can control the chain length of the polymer

(iv) **Crossed linked silicones**



It provides the crosslinking among the chain making the polymer more hard and hence controlling the proportion of  $\text{RSiCl}_3$  we can control the hardness of polymer.

**Uses**

- (1) It can be used as electrical insulator (due to inertness of Si-O-Si bonds)
- (2) It is used as water repellent (Q surface is covered) eg. car polish, shoe polish, masonry works in buildings
- (3) It is used as antifoaming agent in sewage disposal, beer making and in cooking oil used to prepare potato chips.
- (4) As a lubricant in the gear boxes.

**SILICA ( $\text{SiO}_2$ )**

**Occurrence :**

Silica or silicon dioxide occurs in nature in the free state as sand, quartz and flint and in the combined state as silicates like, Feldspar :  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ , Kaolinite :  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  etc.

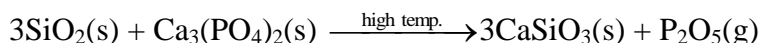
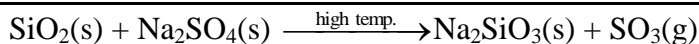
**Properties :**

- (i) Pure silica is colourless, but sand is usually coloured yellow or brown due to the presence of ferric oxide as an impurity.
- (ii) Silicon dioxide is insoluble in water and all acids except hydrofluoric acid.  

$$\text{SiO}_2(\text{s}) + 4\text{HF}(\ell) \longrightarrow \text{SiF}_4(\ell) + 2\text{H}_2\text{O}(\ell)$$
- (iii) It also combines with metallic oxides at high temperature giving silicates e.g.  

$$\text{SiO}_2(\text{s}) + \text{CaO}(\text{s}) \xrightarrow{\Delta} \text{CaSiO}_3(\text{s})$$
- (iv) When silica is heated strongly with metallic salts, silicates are formed and the volatile oxides are driven off as vapours.  

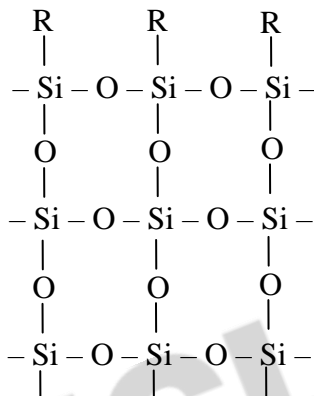
$$\text{SiO}_2(\text{s}) + \text{Na}_2\text{CO}_3(\text{s}) \xrightarrow{\text{high temp.}} \text{Na}_2\text{SiO}_3(\text{s}) + \text{CO}_2(\text{g})$$



The first two examples quoted here are important in glass making.

### Structures of Silica :

Silica has a three-dimensional network structure. In silica, silicon is  $\text{sp}^3$ -hybridized and is thus linked to four oxygen atoms and each oxygen atom is linked to two silicon atoms forming a three-dimensional giant molecule as shown in figure.



### Uses :

- (i) Sand is used in large quantities to make mortar and cement.
- (ii) Being transparent to ultraviolet light, large crystal of quartz are used for making lenses for optical instruments and for controlling the frequency of radio-transmitters.
- (iii) Powdered quartz is used for making silica bricks.
- (iv) Silica gel ( $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ ) is used as a desiccant (for absorbing moisture) and as an adsorbent in chromatography.

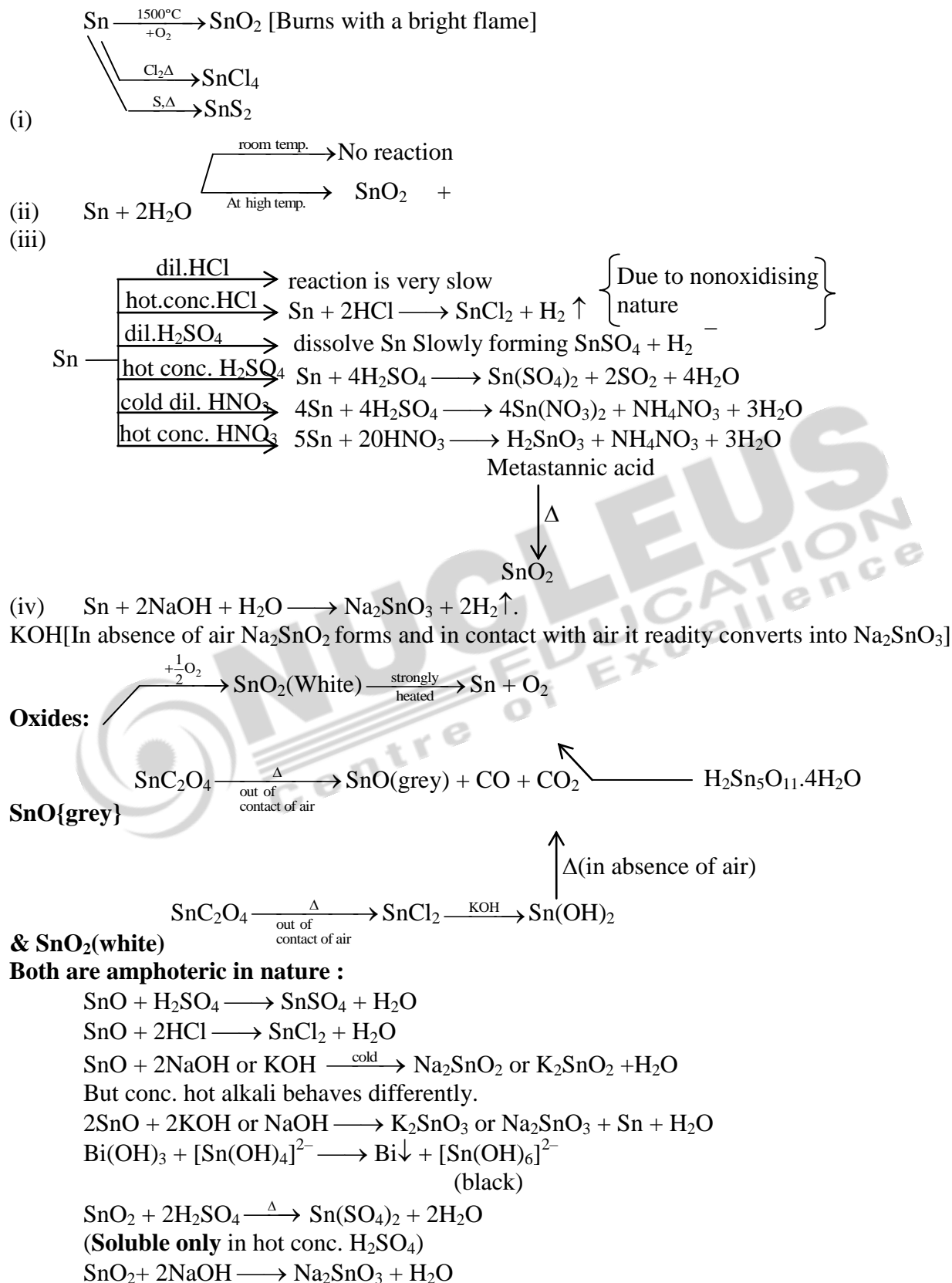
### Silicates

A large number of silicates minerals exist in nature. Some of the examples are feldspar, zeolites, mica and asbestos. Two important man-made silicates are glass and cement.

### Zeolites

If aluminium atoms replace few silicon atoms in three-dimensional network of silicon dioxide, overall structure known as aluminosilicate, acquires a negative charge. Cations such as  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{Ca}^{2+}$  balance the negative charge. Examples are feldspar and zeolites. Zeolites are widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation, e.g., ZSM-5 (A type of zeolite) used to convert alcohols directly into gasoline. Hydrated zeolites are used as ion exchangers in softening of "hard" water.

**TIN & ITS COMPOUND**





**SnCl<sub>2</sub> & SnCl<sub>4</sub> :**

- (1)  $\text{Sn} + 2\text{HCl (hot conc.)} \longrightarrow \text{SnCl}_2 + \text{H}_2\uparrow$   
 $\text{SnCl}_2 \cdot 2\text{H}_2\text{O} \xrightarrow{\Delta} \text{Sn(OH)Cl} + \text{HCl} + \text{H}_2\text{O}\uparrow \Rightarrow \text{Hence anh. SnCl}_2 \text{ cannot be obtained.}$   
 $\downarrow$   
 $\text{SnO} + \text{HCl}$   
 $\{\text{SnCl}_4 + 4\text{H}_2\text{O} \longrightarrow \text{Sn(OH)}_4 + 4\text{HCl}\uparrow \text{ fumes comes out}\}$
- (2) A piece of Sn is always added to preserve a solution of SnCl<sub>2</sub>. Explain.  
 $6\text{SnCl}_2 + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 2\text{SnCl}_4 + 4\text{Sn(OH)Cl}\downarrow \text{ (white ppt)}$   
 $\text{SnCl}_4 + \text{Sn} \longrightarrow 2\text{SnCl}_2$   
 $\text{SnCl}_4 + 4\text{H}_2\text{O} \longrightarrow \text{Sn(OH)}_4\downarrow \text{ (white ppt.)} + 4\text{HCl}$
- (3)  $\text{SnCl}_2 + \text{HCl} \longrightarrow \text{HSnCl}_3 \xrightarrow{\text{HCl}} \text{H}_2\text{SnCl}_4$   
 $\text{SnCl}_4 + 2\text{HCl} \longrightarrow \text{H}_2\text{SnCl}_6 \text{ (Hexachloro stannic (IV) acid)}$   
 $\text{SnCl}_4 + 2\text{NH}_4\text{Cl} \longrightarrow (\text{NH}_4)_2 \text{SnCl}_6 \text{ (colourless crystalline compound known as "pink salt")}$
- (4) Reducing Properties of SnCl<sub>2</sub> :  
 $\text{Sn}^{+2} + 2\text{Fe}^{+3} \longrightarrow 2\text{Fe}^{+2} + \text{Sn}^{+4}$   
 $2\text{Cu}^{+2} + \text{Sn}^{+2} \longrightarrow 2\text{Cu}^{+} + \text{Sn}^{+4}$   
 $\text{Hg}^{+2} + \text{Sn}^{+2} \longrightarrow \text{Hg}\downarrow + \text{Sn}^{+4}$   
 $\text{PhNO}_2 + \text{SnCl}_2 / \text{HCl} \longrightarrow \text{PhNH}_2 + \text{Sn}^{+4}$   
 $\text{K}_2\text{Cr}_2\text{O}_7 + \text{SnCl}_2 + \text{HCl} \longrightarrow \text{Cr}^{+3} + \text{Sn}^{+4} + \text{KCl} + \text{H}_2\text{O}$
- (5) Readily combines with I<sub>2</sub> to form SnCl<sub>2</sub>I<sub>2</sub>. This reaction is used to estimate tin.

**Formation of SnCl<sub>4</sub> :**

- (i)  $\text{Sn} + \text{Cl}_2 \text{ (Excess)} \longrightarrow \text{SnCl}_4$   
 (molten) (dry)
- (ii)  $2\text{HgCl}_2 + \text{SnCl}_2 \longrightarrow 2\text{Hg}\downarrow + \text{SnCl}_4$
- (iii)  $\text{Sn} + \text{Aq. regia} \longrightarrow \text{SnCl}_4 + \text{NO} + \text{H}_2\text{O}$   
 $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  is known as butter of tin  $\Rightarrow$  used as mordant.  
 $(\text{NH}_4)_2 \text{SnCl}_6$  is known as 'pink salt'  $\Rightarrow$  used in calico printing.

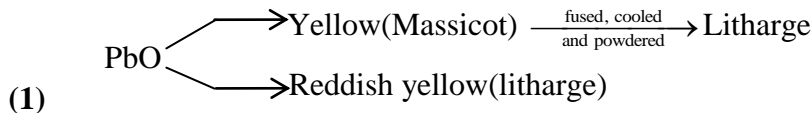
**Distinction of Sn<sup>+2</sup> / Sn<sup>+4</sup> :**

- (i) H<sub>2</sub>S      (ii) Hg<sup>+2</sup>      (iii)  $\text{Fe}^{+3} + \text{K}_3[\text{Fe(CN)}_6] \xrightarrow{\text{Sn}^{+2}} \text{Blue ppt.}$

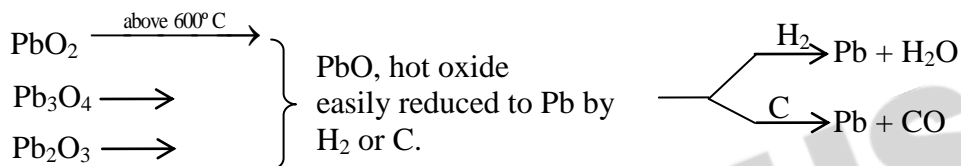
**COMPOUNDS OF LEAD**

**Oxides of lead :**

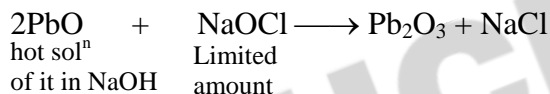
- (i) PbO (ii) Pb<sub>3</sub>O<sub>4</sub> (Red)  
(iii) Pb<sub>2</sub>O<sub>3</sub> (reddish yellow) (Sesquioxide)  
(iv) PbO<sub>2</sub> (dark brown)



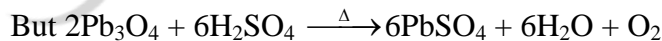
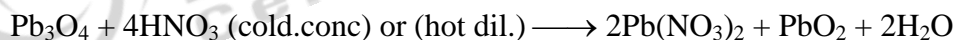
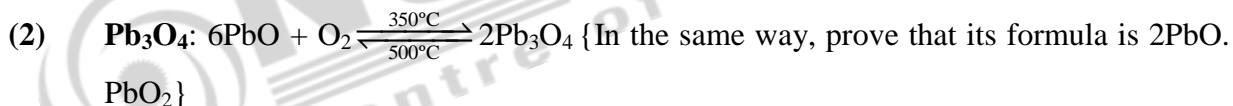
**Laboratory Prep<sup>n</sup> :**



**Preparation of Pb<sub>2</sub>O<sub>3</sub> :**

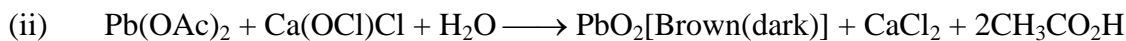
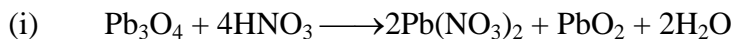


This reaction suggests that Pb<sub>2</sub>O<sub>3</sub> contains PbO<sub>2</sub>.

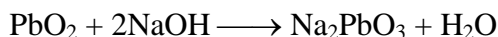
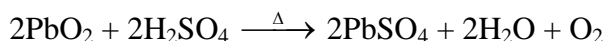


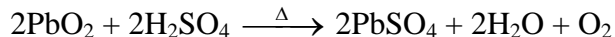
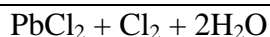
(3) **PbO<sub>2</sub> :** Insoluble in water :

HNO<sub>3</sub>, But reacts with HCl and H<sub>2</sub>SO<sub>4</sub> (hot conc.) but does not react with HNO<sub>3</sub> and soluble in hot NaOH / KOH.



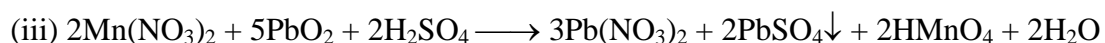
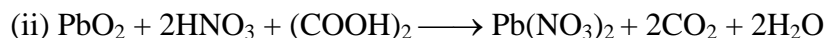
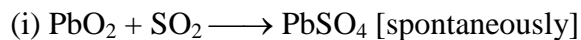
↓  
Excess bleaching powder  
is being removed by stirring with  
HNO<sub>3</sub>



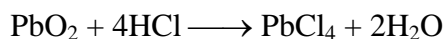


### INORGANIC CHEMISTRY

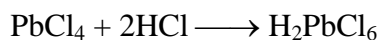
**PbO<sub>2</sub>** : Powerful oxidising agent :



**PbCl<sub>4</sub>** : Exists as H<sub>2</sub>[PbCl<sub>6</sub>]



{ice cold conc. saturated with Cl<sub>2</sub>}



**TetraEthyl lead :**



It is antiknocking agent.

## NITROGEN FAMILY

### GROUP-15 ELEMENTS (N, P, As, Sb, Bi)

#### Occurrence :

**Nitrogen** : Molecular nitrogen comprises 78% by volume of the atmosphere. It occurs as sodium nitrate,  $\text{NaNO}_3$  (called Chile saltpetre) and potassium nitrate (Indian saltpetre).

#### Phosphorus :

- (i) It is eleventh most abundant element in earth's crust occurs in minerals of the apatite family,  $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{CaX}_2$  ( $\text{X} = \text{F}, \text{Cl}$  or  $\text{OH}$ ) (e.g., fluorapatite  $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{CaF}_2$ ) and also found as chlorapatite  $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{CaCl}_2$  .
- (ii) Arsenic , antimony and bismuth are found mainly as sulphide minerals.

#### Electronic Configuration :

The valence shell electronic configuration of these elements is  $ns^2 np^3$ .

#### Atomic and Ionic Radii :

Covalent radius :  $\text{N} < \text{P} < \text{As} < \text{Sb} < \text{Bi}$

#### Ionisation Enthalpy :

$\text{N} > \text{P} > \text{As} > \text{Sb} > \text{Bi}$  (IE1 values)

#### Electronegativity :

$\text{N} > \text{P} > \text{As} > \text{Sb} = \text{Bi}$   
(1.9)      (1.9)

#### Metallic Character

|                       |               |                         |
|-----------------------|---------------|-------------------------|
| $\text{N} < \text{P}$ | $\text{As} <$ | $\text{Sb} < \text{Bi}$ |
| None                  | Metalloid     | Metals                  |
| metal                 |               |                         |

#### Physical Properties :

- (i) All the elements of this group are polyatomic. Dinitrogen is a diatomic gas while all others are solids.
- (ii) Metallic character increases down the group.
- (iii) The boiling points, in general, increase from top to bottom in the group but the melting point increases upto arsenic and then decreases upto bismuth.
- (iv) Except nitrogen all the elements show allotropy.  
 $\text{P} \rightarrow$  exists in three allotropic form as white, red and black  
 $\text{As}, \text{Sb} \rightarrow$  exist as yellow and grey  
 $\text{Bi} \rightarrow$  exist as  $\alpha, \beta, \gamma, \delta$  allotropic form

#### Catenation

- \* The group 15 elements also show catenation property but to much smaller extent than carbon. For example hydrazine ( $\text{H}_2\text{NNH}_2$ ) has two N atoms bonded together  $\text{HN}_3$  has three N atoms.



- \* Among group 15 elements P has the maximum tendency for catenation forming cyclic as well as open chain compounds consisting of many phosphorous atoms.

$P_2H_4$  has two P atoms bonded together the lesser tendency of elements of group 15 to show catenation in comparison to carbon is their low dissociation enthalpies.

|         |                 |
|---------|-----------------|
| C – C   | 353.3 kJ /mole  |
| N – N   | 160.8 kJ / mole |
| P – P   | 201.6 kJ / mole |
| As – As | 147.4 kJ / mole |

### Chemical Properties :

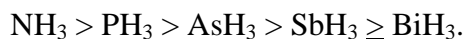
#### *Oxidation states and trends in chemical reactivity*

- The common oxidation states of these elements are  $-3$ ,  $+3$  and  $+5$ .
- The tendency to exhibit  $-3$  oxidation state decreases down the group due to increase in size and metallic character. Bismuth hardly forms any compound in  $-3$  oxidation state.
- The stability of  $+5$  oxidation state decreases down the group. The only well characterised Bi(V) compound is  $BiF_5$ .
- The stability of  $+5$  oxidation state decreases and that of  $+3$  state increases (due to inert pair effect) down the group.
- Nitrogen exhibits  $+1$ ,  $+2$ ,  $+4$  oxidation states also when it reacts with oxygen. Phosphorus also shows  $+1$  and  $+4$  oxidation states in some oxoacids.
- In the case of nitrogen, all oxidation states from  $+1$  to  $+4$  tend to disproportionate in acid solution. For example,
  - $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$
- Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into  $+5$  and  $-3$  both in alkali and acid.
  - $4H_3PO_3 \xrightarrow{Heat} 3H_3PO_4 + PH_3$
- $+3$  oxidation state in case of arsenic, antimony and bismuth becomes increasingly stable with respect to disproportionation.
- Nitrogen is restricted to a maximum covalency of 4 since only four (one s and three p) orbitals are available for bonding.
- The heavier elements have vacant d orbitals in the outermost shell which can be used for bonding 6 (covalency) and hence, expand their covalency as in  $PF_6^-$ .

#### **Anomalous properties of nitrogen**

- Nitrogen has unique ability to form  $p_\pi - p_\pi$  multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C, O).
- Heavier elements of this group do not form pp-pp bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping.
- Nitrogen exists as a diatomic molecule with a triple bond (one s and two p) between the two atoms.  
 $N_2$  bond enthalpy ( $941.4 \text{ kJ mol}^{-1}$ ) is very high.
- Phosphorus, arsenic and antimony form single bonds as P–P, As–As and Sb–Sb while bismuth forms metallic bonds in elemental state.

(i) **Reactivity towards hydrogen:**



(ii) **Reactivity towards oxygen:** All these elements form two types of oxides:  $\text{E}_2\text{O}_3$  and  $\text{E}_2\text{O}_5$ .

Their acidic character decreases down the group. The oxides of the type  $\text{E}_2\text{O}_3$  of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth predominantly basic.

(iii) **Reactivity towards halogens:** These elements react to form two series of halides:  $\text{EX}_3$  and  $\text{EX}_5$ . In case of nitrogen, only  $\text{NF}_3$  is known to be stable. Trihalides except  $\text{BiF}_3$  are predominantly covalent in nature.

(iv) **Reactivity towards metals:** All these elements react with metals to form their binary compounds exhibiting  $-3$  oxidation state, such as,  $\text{Ca}_3\text{N}_2$  (calcium nitride)  $\text{Ca}_3\text{P}_2$  (calcium phosphide),  $\text{Na}_3\text{As}$  (sodium arsenide),  $\text{Zn}_3\text{Sb}_2$  (zinc antimonide) and  $\text{Mg}_3\text{Bi}_2$  (magnesium bismuthide).

## DINITROGEN

### Preparation :

(a) **Commercial preparation :**

Dinitrogen is produced commercially by the liquefaction and fractional distillation of air. Liquid dinitrogen (b.p. 77.2 K) distils out first leaving behind liquid oxygen (b.p. 90 K).

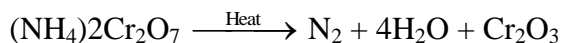
(b) **Laboratory preparation :**

(i) Dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.

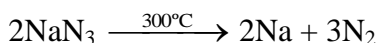


Small amounts of  $\text{NO}$  and  $\text{HNO}_3$  are also formed in this reaction; these impurities can be removed by passing the gas through aqueous sulphuric acid containing potassium dichromate.

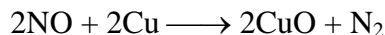
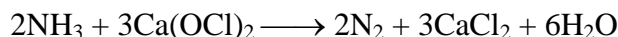
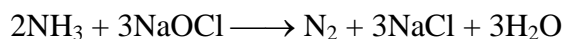
(ii) Dinitrogen can also be obtained by the thermal decomposition of ammonium dichromate.



**Note :** Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide.

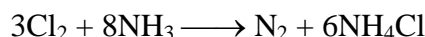
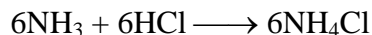
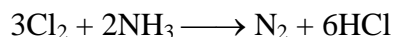


(c) **Other preparation**

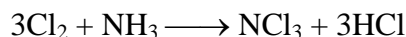


(red, overheated) (Black)

$\text{Cl}_2$  passed into liquor  $\text{NH}_3$



In this method conc. of  $\text{NH}_3$  should not be lowered down beyond a particular limit.



↓

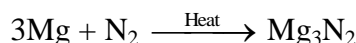
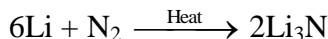
(Trimendously explosive)

**Physical properties :**

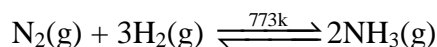
- (i) Dinitrogen is a colourless, odourless, tasteless and non-toxic gas.
- (ii) Nitrogen atom has two stable isotopes:  $^{14}\text{N}$  and  $^{15}\text{N}$ .
- (iii) It has a very low solubility in water ( $23.2 \text{ cm}^3$  per litre of water at 273 K and 1 bar pressure)
- (iv) Dinitrogen has low freezing and boiling points.

**Chemical properties**

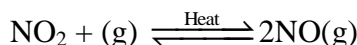
**Reaction with metal :** At higher temperatures, it directly combines with some metals to form predominantly ionic nitrides and with non-metals, covalent nitrides. A few typical reactions are:



**Reaction with metal :** It combines with hydrogen at about 773 K in the presence of a catalyst (Haber's Process) to form ammonia:

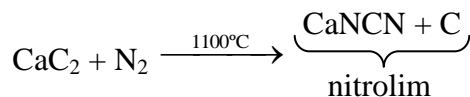


Dinitrogen combines with dioxygen only at very high temperature (at about 2000 K) to form nitric oxide, NO.

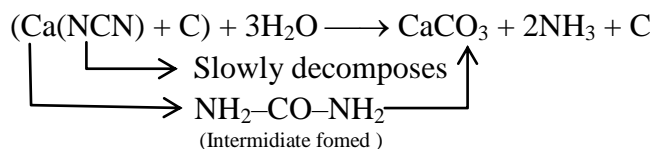
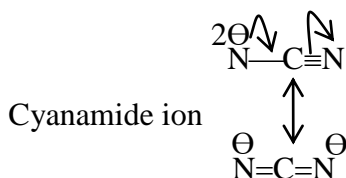


### Absorption on calcium carbide

N<sub>2</sub> can be absorbed by calcium carbide at the temperature around 1000°C.



It is a very good fertiliser.



**Qus. Why dinitrogen is inert at room temperature ?**

**Ans.** Dinitrogen is inert at room temperature because of the high bond enthalpy of N  $\equiv$  N bond. Reactivity, however, increases rapidly with rise in temperature.

### TYPES OF NITRIDE

Salt like or ionic : Li<sub>3</sub>N, Na<sub>3</sub>N, K<sub>3</sub>N (?), Ca<sub>3</sub>N<sub>2</sub>, Mg<sub>3</sub>N<sub>2</sub>, Be<sub>3</sub>N<sub>2</sub>

Covalent : AlN, BN, Si<sub>3</sub>N<sub>4</sub>, Ge<sub>3</sub>N<sub>4</sub>, Sn<sub>3</sub>N<sub>4</sub>

Interstitial :  $\underbrace{\text{M} = \text{Sc, Ti, Zr, Hf, La}}_{\text{HCP or FCC}}$

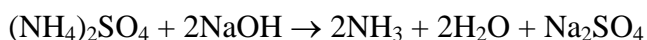
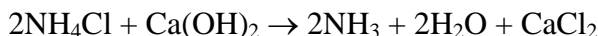
## AMMONIA

### Preparation :

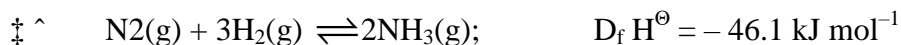
- (i) Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.



- (ii) Small scale preparation By the decomposition of ammonium salts when treated with caustic soda or calcium hydroxide.

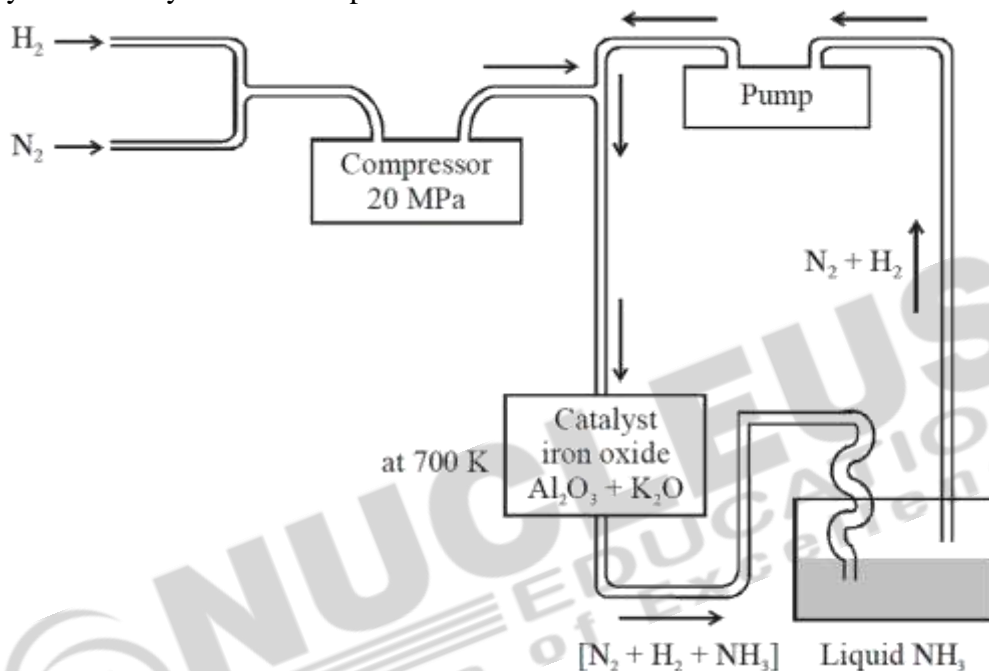


- (iii) Large scale manufacturing (Haber's Process)





- \* According to Le Chatelier's principle, high pressure and low temperature would favour the formation of ammonia.
- \* The optimum conditions for the production of ammonia are a pressure of  $200 \times 10^5$  Pa (about 200 atm), a temperature of  $\sim 700$  K.
- \* Use of a catalyst such as iron oxide with small amounts of  $K_2O$  and  $Al_2O_3$  to increase the rate of attainment of equilibrium.
- \* The flow chart for the production of ammonia is shown in figure. Earlier, iron was used as a catalyst with molybdenum as a promoter.



Flow chart for the manufacture of ammonia

#### Other preparation :

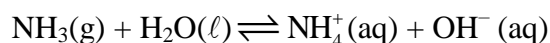
- (i) Nitrate or nitrite reduction :  $NO_3^- / NO_2^- + Zn \text{ or } Al + NaOH \longrightarrow NH_3 + [Zn(OH)_4]^{2-} \text{ or } [Al(OH)_4]^-$
- (ii) Metal nitride hydrolysis :  $N^{3-} + 3H_2O \longrightarrow NH_3 \uparrow + 3OH^-$

#### Properties :

- (i) Ammonia is a colourless gas with a pungent odour.
- (ii) Its freezing and boiling points are 198.4 and 239.7 K respectively.
- (iii) In the solid and liquid states, it is associated through hydrogen bonds.
- (iv) Ammonia gas is highly soluble in water.

#### Basic character :

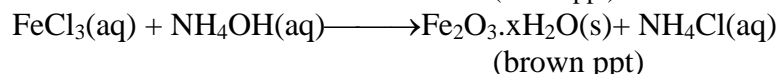
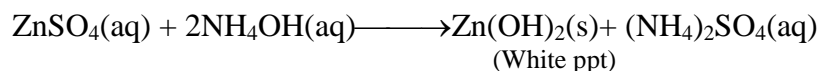
Its aqueous solution is weakly basic due to the formation of  $OH^-$  ions.



It forms ammonium salts with acids, e.g.,  $NH_4Cl$ ,  $(NH_4)_2SO_4$ , etc.

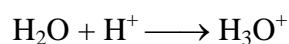
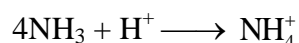
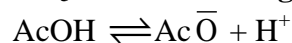
As a weak base, it precipitates the hydroxides (hydrated oxides in case of some metals) of many metals from their salt solutions.

For example,



**Note - 1: Other reactions**

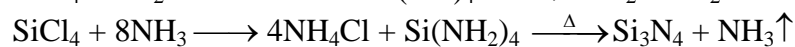
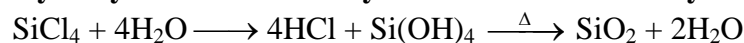
**CH<sub>3</sub>COOH is strong acid in liq. NH<sub>3</sub> while in water is weak acid.**



Basidity order  $\text{NH}_3 > \text{H}_2\text{O}$

more solvation of  $\text{H}^+$  in  $\text{NH}_3$ .

**Note - 2: Hydrolysis and Ammonolysis occurs in a same way.**



Rate of hydrolysis and Ammonolysis will be affected by the presence of HCl vapour & NH<sub>4</sub>Cl vapour respectively.

**Uses :**

- (i) Ammonia is used to produce various nitrogenous fertilisers.
- (ii) In the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid.
- (iii) Liquid ammonia is also used as a refrigerant.

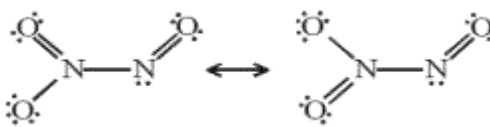
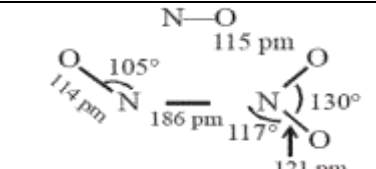
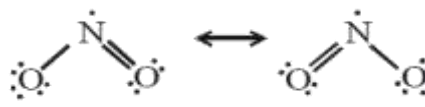
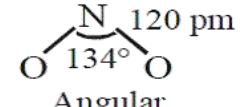
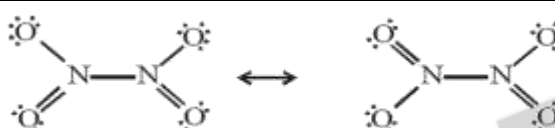
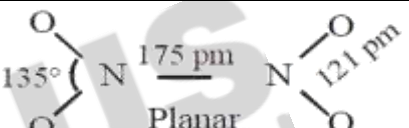
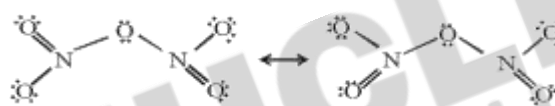
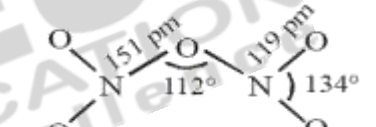
### OXIDES OF NITROGEN

Nitrogen forms a number of oxides in different oxidation states. The names, formulas, preparation and physical appearance of these oxides are given in Table.

**Oxides of Nitrogen**

| Name  | Formula                       | Oxidation state of nitrogen | Common Methods of Preparation  | Physical Appearance and Chemical nature   |
|---|-------------------------------|-----------------------------|--|---|
| Dinitrogen oxide<br>[Nitrogen oxide]          | N <sub>2</sub> O              | +1                          | $\text{NH}_4\text{NO}_3 \xrightarrow{\text{Heat}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$  | Colourless gas, neutral                   |
| Nitrogen monoxide<br>[Nitrogen (II) oxide]    | NO                            | +2                          | $2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O} + 2\text{NO}$ | Colourless gas, neutral                   |
| Dinitrogen trioxide<br>[Nitrogen (III) oxide] | N <sub>2</sub> O <sub>3</sub> | +3                          | $2\text{NO} + \text{N}_2\text{O}_4 \xrightarrow{250\text{K}} 2\text{N}_2\text{O}_3$  | Blue solid, acidic<br>Blue liquid (–30°C) |
| Nitrogen dioxide<br>[Nitrogen (IV) oxide]     | NO <sub>2</sub>               | +4                          | $2\text{Pb}(\text{NO}_3)_2 \xrightarrow{673\text{K}} 4\text{NO}_2 + 2\text{PbO} + \text{O}_2$  | Brown gas.<br>Acidic                      |
| Nitrogen tetroxide<br>[Nitrogen (IV) oxide]   | N <sub>2</sub> O <sub>4</sub> | +4                          | $2\text{NO}_2 \xrightleftharpoons[\text{Heat}]{\text{Cool}} \text{N}_2\text{O}_4$  | Colourless solid / liquid, acidic         |
| Nitrogen pentaoxide<br>[Nitrogen (V) oxide]   | N <sub>2</sub> O <sub>5</sub> | +5                          | $4\text{HNO}_3 + \text{P}_4\text{O}_{10} \rightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$  | Colourless solid, acidic                  |

**Structure of Oxides of Nitrogen**

| Formula                       | Resonance structures   | Bond Parameters  |
|-------------------------------|--|--|
| N <sub>2</sub> O              | $\ddot{\text{N}}=\text{N}=\ddot{\text{O}} \leftrightarrow :\text{N}=\text{N}-\ddot{\text{O}}:$ | $\text{N}-\text{N}-\text{O}$<br>113 pm    119 pm<br>Linear                                     |
| NO                            | $:\text{N}=\ddot{\text{O}} \leftrightarrow :\ddot{\text{N}}=\ddot{\text{O}}:$                  |  |
| N <sub>2</sub> O <sub>3</sub> |               |             |
| NO <sub>2</sub>               |               | <br>Angular |
| N <sub>2</sub> O <sub>4</sub> |              | <br>Planar  |
| N <sub>2</sub> O <sub>5</sub> |             | <br>Planar |

**Preparations:**

- N<sub>2</sub>O

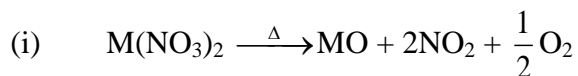
  - $\text{NH}_4\text{NO}_3 \longrightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$
  - $\text{Zn} + \text{HNO}_3 \longrightarrow \text{Zn}(\text{NO}_3)_2 + \text{N}_2\text{O} + \text{H}_2\text{O}$   
(dil. & cold)
- NO

  - $\text{Cu} + \text{HNO}_3 (1 : 1) \xrightarrow{\text{hot}} \text{Cu}(\text{NO}_3)_2 + \text{NO} + \text{H}_2\text{O}$
  - $\text{KNO}_3 + \text{FeSO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + \text{NO} + \text{H}_2\text{O}$   
 $\text{FeSO}_4 + \text{NO} \longrightarrow \text{FeSO}_4 \cdot \text{NO} \xrightarrow{\Delta} \text{FeSO}_4 + \text{NO} \uparrow$
  - Oswald process—Restricted oxidation of NH<sub>3</sub>.  
 Industrial process.  
 $4\text{NH}_3 + 5\text{O}_2 \xrightarrow[750^\circ\text{C, Pt-Cat}]{6 \text{ atm}} 4\text{NO} + 6\text{H}_2\text{O}$
- N<sub>2</sub>O<sub>3</sub>

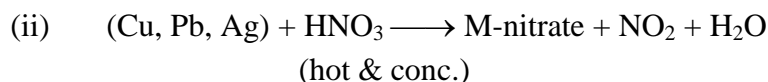
  - $\text{HNO}_3 + \text{As}_2\text{O}_3 \longrightarrow \text{H}_3\text{AsO}_4 + \text{N}_2\text{O}_3$
  - $\text{Cu} + \text{HNO}_3(6\text{M}) \longrightarrow \text{Cu}(\text{NO}_3)_2 +$ 

$\text{NO} + \text{NO}_2$   
 $\downarrow$  Cool (-30°C)  
 Blue liq (N<sub>2</sub>O<sub>3</sub>)

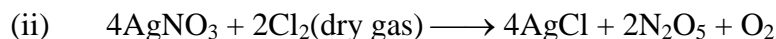
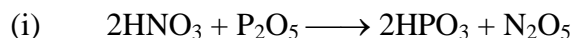
4. NO<sub>2</sub>



M = Pb, Cu, Ba, Ca

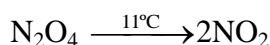
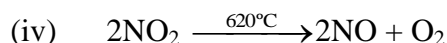
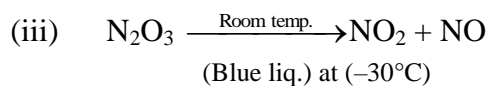
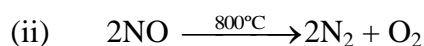
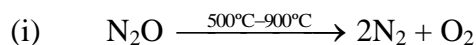


5. N<sub>2</sub>O<sub>5</sub>

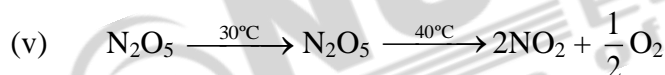


### Properties:

#### (I) Decomposition Behaviour



(white solid)      Brown gas  
at(-11°C)

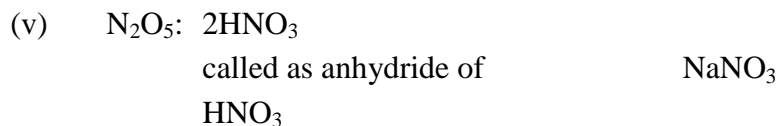
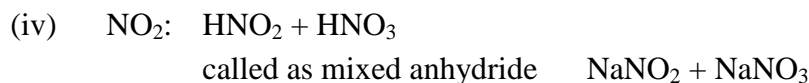
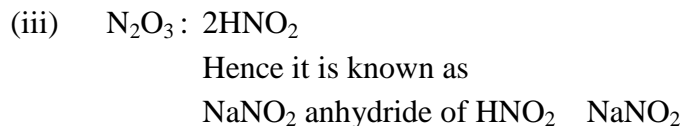
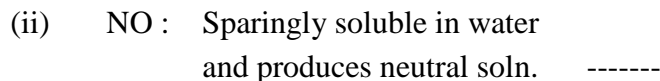
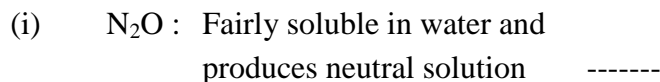


Colourless      yellow  
Solid      liq.

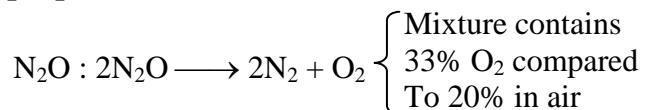
#### (II) Reaction with H<sub>2</sub>O & NaOH

H<sub>2</sub>O

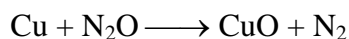
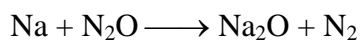
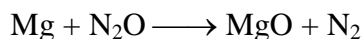
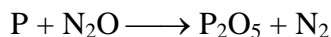
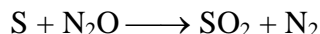
NaOH



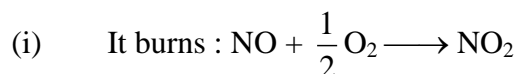
**Other properties:**



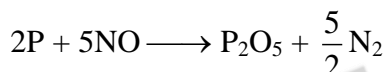
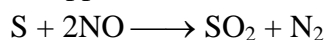
Hence it is better supporter for combustion



**NOTE: -**



(ii) It supports combustion also for molten sulphur and hot phosphorous.

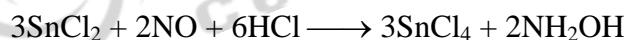
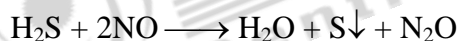
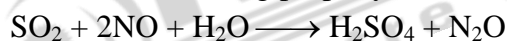


(iii) It is being absorbed by  $\text{FeSO}_4$  solution.

(iv) It is having reducing property.

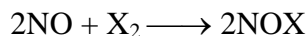


(v) NO shows oxidising property also.



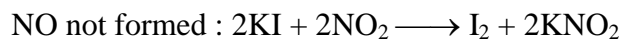
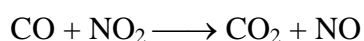
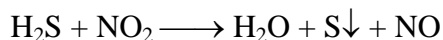
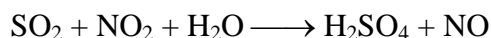
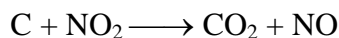
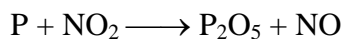
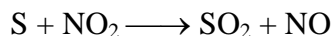
(Used for  $\text{NH}_2\text{OH}$  preparation)

(vi) NO combines with  $\text{X}_2$  ( $\text{X}_2 = \text{Cl}_2, \text{Br}_2, \text{F}_2$ ) to produce NO X

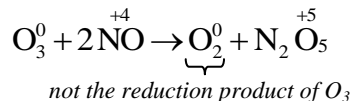


$\text{N}_2\text{O}_3$  : No more properties.

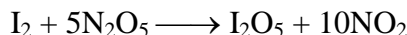
(1) It is having oxidising property.



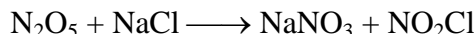
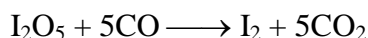
(2) Reducing property of  $\text{NO}_2$ .



$\text{N}_2\text{O}_5$  :



$\text{I}_2\text{O}_5$  is used for the estimation of CO



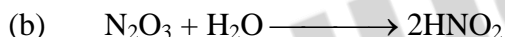
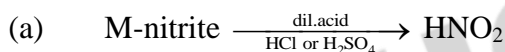
This likes proves that  $\text{N}_2\text{O}_5$  is consisting of ion pair of  $\text{NO}_2^+$  &  $\text{NO}_3^-$

### OXOACIDS OF NITROGEN

$\text{H}_2\text{N}_2\text{O}_2$  (hyponitrous acid),  $\text{HNO}_2$  (nitrous acid) and  $\text{HNO}_3$  (nitric acid). Amongst them  $\text{HNO}_3$  is the most important.

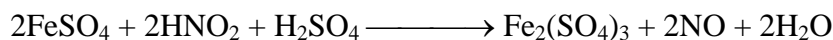
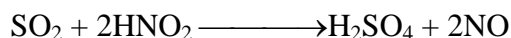
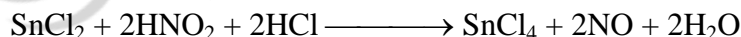
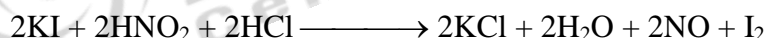
### NITROUS ACID ( $\text{HNO}_2$ )

#### Preparation

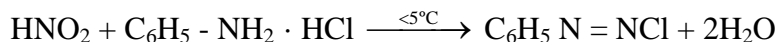
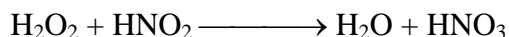
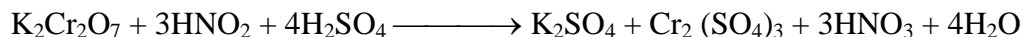
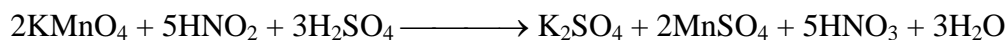
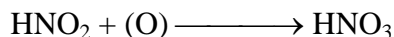


#### Properties

(a) **Oxidising property** : Because of its easy oxidation to liberate nascent oxygen, it acts as a strong oxidant  $2\text{HNO}_2 \longrightarrow \text{H}_2\text{O} + 2\text{NO} + (\text{O})$



(b) **Reducing property** : Nitrous acid also acts as a reducing agent as it can be oxidised into nitric acid.



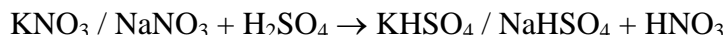
Benzene diazonium chloride

## NITRIC ACID

It was named aqua fortis (means strong water) by alchemists.

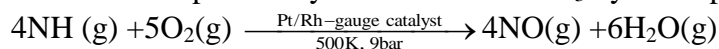
### Preparation :

Laboratory Method : By heating  $\text{KNO}_3$  or  $\text{NaNO}_3$  and concentrated  $\text{H}_2\text{SO}_4$  in a glass retort.

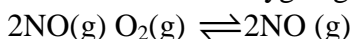


### Large scale preparation (Ostwald's process) :

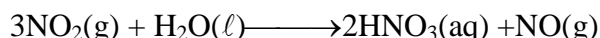
(i) This method is based upon catalytic oxidation of  $\text{NH}_3$  by atmospheric oxygen.



(ii) Nitric oxide thus formed combines with oxygen giving  $\text{NO}_2$ .

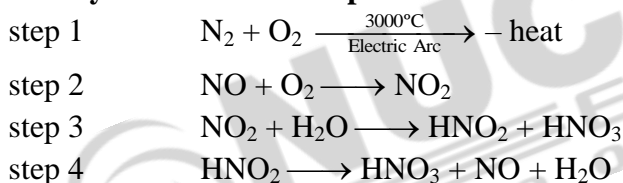


(iii) Nitrogen dioxide so formed, dissolves in water to give  $\text{HNO}_3$ .



$\text{NO}$  thus formed is recycled and the aqueous  $\text{HNO}_3$  can be concentrated by distillation upto ~ 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated  $\text{H}_2\text{SO}_4$ .

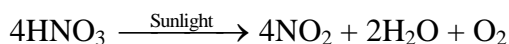
### Birkel and Eyde Process or arc process



### Properties

#### Physical properties

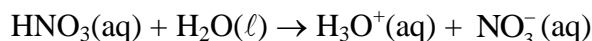
- (i) It is a colourless liquid (f.p. 231.4 K and b.p. 355.6 K).
- (ii) Nitric acid usually acquires yellow or brown colour due to its decomposition by sunlight into  $\text{NO}_2$ .



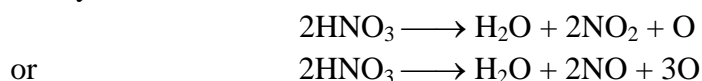
The yellow or brown colour of the acid can be removed by warming it to 60-80°C and bubbling dry air through it.

#### Chemical properties

**Acidic character** in aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.



**Oxidising nature:** Nitric acid acts as a strong oxidising agent as it decomposes to give nascent oxygen easily.



(i) **Oxidation of non-metals** : The nascent oxygen oxidises various non-metals to their corresponding oxyacids of highest oxidation state.

- (1) Sulphur is oxidised to sulphuric acid  

$$\text{S} + 6\text{HNO}_3 \xrightarrow{\text{conc. and hot}} \text{H}_2\text{SO}_4 + 6\text{NO}_2 + 2\text{H}_2\text{O}$$
- (2) Carbon is oxidised to carbonic acid  

$$\text{C} + 4\text{HNO}_3 \rightarrow \text{H}_2\text{CO}_3 + 4\text{NO}_2 + 2\text{H}_2\text{O}$$
- (3) Phosphorus is oxidised to orthophosphoric acid.  

$$2\text{P} + 10\text{HNO}_3 \rightarrow 2\text{H}_3\text{PO}_4 + 10\text{NO}_2 + 2\text{H}_2\text{O}$$
  
conc. and hot
- (4) Iodine is oxidised to iodic acid  

$$\text{I}_2 + 10\text{HNO}_3 \rightarrow 2\text{HIO}_3 + 10\text{NO}_2 + 4\text{H}_2\text{O}$$
  
conc. and hot

(ii) **Oxidation of metalloids**

Metalloids like non-metals also form oxyacids of highest oxidation state.

- (1) Arsenic is oxidised to arsenic acid  

$$2\text{As} + 10\text{HNO}_3 \rightarrow 2\text{H}_3\text{AsO}_4 + 10\text{NO}_2 + 2\text{H}_2\text{O}$$
  
or  

$$\text{As} + 5\text{HNO}_3 \rightarrow \text{H}_3\text{AsO}_4 + 5\text{NO}_2 + \text{H}_2\text{O}$$
  
conc. and hot
- (2) Antimony is oxidised to antimononic acid  

$$\text{Sb} + 5\text{HNO}_3 \rightarrow \text{H}_3\text{SbO}_4 + 5\text{NO}_2 + \text{H}_2\text{O}$$
  
conc. and hot
- (3) Tin is oxidised to meta-stannic acid.  

$$\text{Sn} + 2\text{HNO}_3 \rightarrow \text{H}_2\text{SnO}_3 + 4\text{NO}_2 + \text{H}_2\text{O}$$

(iii) **Oxidation of Compounds:**

- (1) Sulphur dioxide is oxidised to sulphuric acid  

$$\text{SO}_2 + 2\text{HNO}_3 \rightarrow \text{H}_2\text{SO}_4 + 2\text{NO}_2$$
- (2) Hydrogen sulphide is oxidised to sulphur  

$$\text{H}_2\text{S} + 2\text{HNO}_3 \rightarrow 2\text{NO}_2 + 2\text{H}_2\text{O} + \text{S}$$
- (3) Ferrous sulphate is oxidised to ferric sulphate in presence of  $\text{H}_2\text{SO}_4$   

$$6\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 + 2\text{HNO}_3 \rightarrow 3\text{Fe}_2(\text{SO}_4)_3 + 2\text{NO} + 4\text{H}_2\text{O}$$
- (4) Iodine is liberated from KI.  

$$6\text{KI} + 8\text{HNO}_3 \rightarrow 6\text{KNO}_3 + 2\text{NO} + 3\text{I}_2 + 4\text{H}_2\text{O}$$
- (5) HBr, HI are oxidised to  $\text{Br}_2$  and  $\text{I}_2$ , respectively.  

$$2\text{HBr} + 2\text{HNO}_3 \rightarrow \text{Br}_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$$
  
Similarly,  $2\text{HI} + 2\text{HNO}_3 \rightarrow \text{I}_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
- (6) Ferrous sulphide is oxidised to ferric sulphate  

$$\text{FeS} + \text{HNO}_3 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 8\text{NO}_2 + 4\text{H}_2\text{O}$$
- (7) Stannous chloride is oxidised to stannic chloride in presence of HCl.  

$$2\text{HNO}_3 + 14\text{H} \rightarrow \text{NH}_2\text{OH} + \text{NH}_3 + 5\text{H}_2\text{O}$$
  
Hydroxylamine  

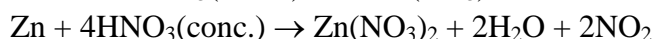
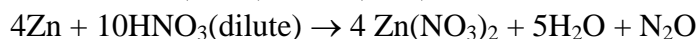
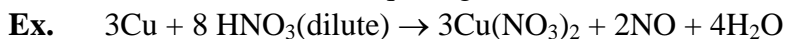
$$\text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3$$
  
-----  

$$7\text{SnCl}_2 + 14\text{HCl} + 3\text{HNO}_3 \rightarrow 7\text{SnCl}_4 + \text{NH}_2\text{OH} + \text{NH}_4\text{NO}_3 + 5\text{H}_2\text{O}$$



(ii) **Reaction with metal** concentrated nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum.

Au & Pt dissolve in aqua regia a mixture of 25% conc.  $\text{HNO}_3$  & 75% conc.  $\text{HCl}$ .



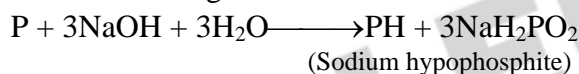
Some metals (e.g., Cr, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

### Action on Proteins :

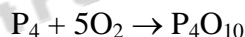
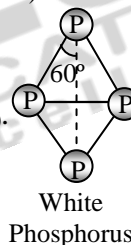
Nitric acid attacks proteins forming a yellow nitro compound called xanthoprotein. It, therefore, stains skin and renders wool yellow. This property is utilized for the test of proteins.

### ALLOTROPIC FORMS OF PHOSPHORUS

Phosphorus is found in many allotropic forms, the important ones being white, red and black. White phosphorus dissolves in boiling  $\text{NaOH}$  solution in an inert atmosphere giving  $\text{PH}_3$ .

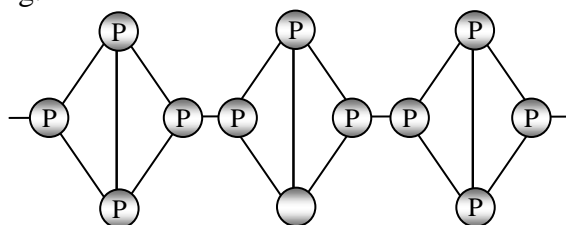


It readily catches fire in air to give dense white fumes of  $\text{P}_4\text{O}_{10}$ .



It consists of discrete tetrahedral  $\text{P}_4$  molecule as shown in Fig.

**Red phosphorus :** It is polymeric, consisting of chains of  $\text{P}_4$  tetrahedra linked together in the manner as shown in Fig.



Red Phosphorus

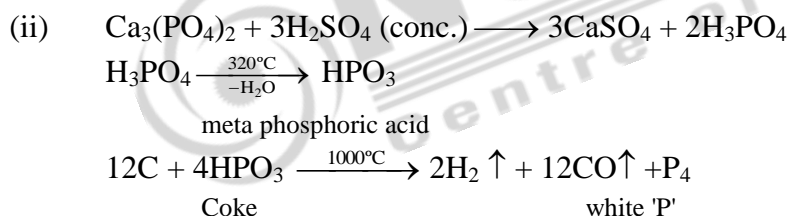
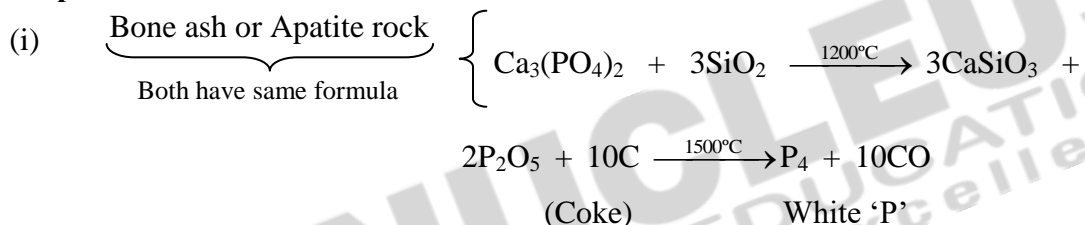
### Black phosphorus :

- (i) It has two forms  $\alpha$ -black phosphorus and  $\beta$ -black phosphorus.
- (ii)  $\alpha$ -Black phosphorus is formed when red phosphorus is heated in a sealed tube at 803K.
- (iii) It can be sublimed in air and has opaque monoclinic or rhombohedral crystals.
- (iv) It does not oxidise in air.  $\beta$ -Black phosphorus is prepared by heating white phosphorus at 473 K under high pressure.
- (v) It does not burn in air upto 673 K.

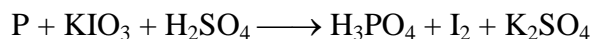
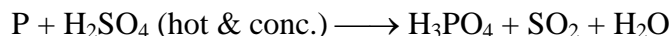
**Comparison between White and Red Phosphorus**

| Property                      | White phosphorus  | Red phosphorus         |
|-------------------------------|---|------------------------|
| Physical state                | Soft waxy solid.  | Brittle powder.        |
| Colour                        | White when pure.<br>Attains yellow colour<br>On standing. | Red.                   |
| Odour                         | Garlic  | Odourless.             |
| Solubility in water           | Insoluble.  | Insoluble.             |
| Solubility in CS <sub>2</sub> | Soluble   | Insoluble.             |
| Physiological action          | Poisonous.  | Non-poisonous.         |
| Chemical activity             | Very active.  | Less active.           |
| Stability                     | Unstable.   | Stable                 |
| Phosphorescence               | Glow in dark  | Does not glow in dark. |
| Molecular formula             | P <sub>4</sub>  | Complex polymer.       |

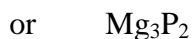
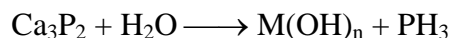
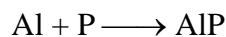
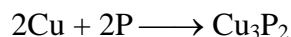
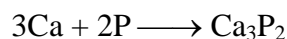
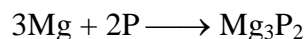
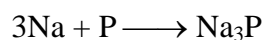
**Preparation of white 'P'**



**Reactions of 'P'**



Reaction with hot metal —



**PHOSPHINE**

**Preparation**

- (i) Phosphine is prepared by the reaction of calcium phosphide with water or dilute HCl.  

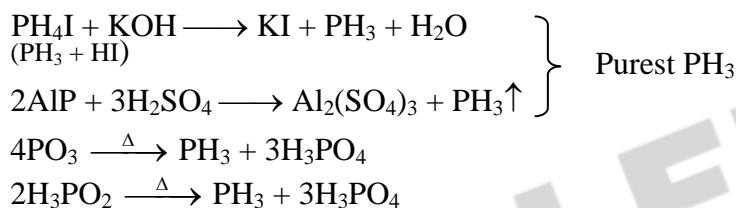
$$\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Ca}(\text{OH})_2 + 2\text{PH}_3$$

$$\text{Ca}_3\text{P}_2 + 6\text{HCl} \rightarrow 3\text{CaCl}_2 + 2\text{PH}_3$$
- (ii) Laboratory preparation it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of  $\text{CO}_2$ .  

$$\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2$$
(sodium hypophosphite)

Pure  $\text{PH}_3$  is non inflammable but becomes inflammable owing to the presence of  $\text{P}_2\text{H}_4$  or  $\text{P}_4$  vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide ( $\text{PH}_4\text{I}$ ) which on treating with KOH gives off phosphine.

**Other preparation**



**Physical Properties :**

- (i) It is a colourless gas with rotten fish smell and is highly poisonous.  
 (ii) It explodes in contact with traces of oxidising agents like  $\text{HNO}_3$ ,  $\text{Cl}_2$  and  $\text{Br}_2$  vapours.  
 (iii) It is slightly soluble in water but soluble in  $\text{CS}_2$ . The solution of  $\text{PH}_3$  in water decomposes in presence of light giving red phosphorus and  $\text{H}_2$ .

**Chemical Properties :**

- (i) It absorbed in copper sulphate or mercuric chloride solution, the corresponding phosphides are obtained.  

$$3\text{CuSO}_4 + 2\text{PH}_3 \rightarrow \text{Cu}_3\text{P}_2 + 3\text{H}_2\text{SO}_4$$

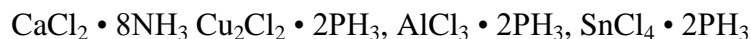
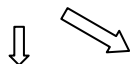
$$3\text{HgCl}_2 + 2\text{PH}_3 \rightarrow \text{Hg}_3\text{P}_2 + 6\text{HCl}$$
 Phosphine is weakly basic and like ammonia, gives phosphonium compounds with acids e.g.,  

$$\text{PH}_3 + \text{HBr} \rightarrow \text{PH}_4\text{Br}$$
- (ii)  $\text{PH}_3 + \text{O}_2 \xrightarrow{150^\circ} \text{P}_2\text{O}_5 + \text{H}_2\text{O}$   
 (iii)  $\text{PH}_3 + 3\text{Cl}_2 \longrightarrow \text{PCl}_3 + 3\text{HCl}$   
 (iv)  $\text{PH}_3 + 4\text{N}_2\text{O} \xrightarrow[\text{sparking}]{\text{electrical}} \text{H}_3\text{PO}_4 + 4\text{N}_2$   
 (v)  $\text{PH}_3 + 6\text{AgNO}_3 \longrightarrow [\text{Ag}_3\text{P} \cdot 3\text{AgNO}_3 \downarrow] + \text{H}_3\text{NO}_3$   
yellow ppt.  

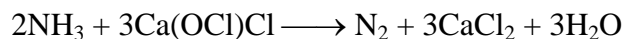
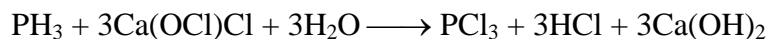
$$\text{Ag}_3\text{P} \cdot 3\text{AgNO}_3 + 3\text{H}_2\text{O} \longrightarrow 6\text{Ag} \downarrow + 3\text{HNO}_3 + \text{H}_3\text{PO}_3$$
Black ppt.
- (vi)  $\text{PH}_3 + 4\text{HCHO} + \text{HCl} \longrightarrow [\text{P}(\text{CH}_2\text{OH})_4] + \text{Cl}^-$   
white/colourless solid  
which is used for making  
fire-proof cotton fabrics

**Note :**

Like  $\text{NH}_3$ ,  $\text{PH}_3$  also can form addition product.



$\text{PH}_3$  can be absorbed by  $\text{Ca}(\text{OCl})\text{Cl}$ .



**Uses :**

- (i) The spontaneous combustion of phosphine is technically used in Holme's signals. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.
- (ii) It is also used in smoke screens.

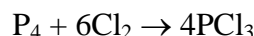
**PHOSPHORUS HALIDES**

Phosphorus forms two types of halides,  $\text{PX}_3$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) and  $\text{PX}_5$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ).

**PHOSPHORUS TRICHLORIDE**

**Preparation**

- (i) By passing dry chlorine over heated white phosphorus.

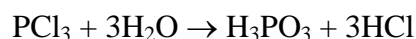


- (ii) By the action of thionyl chloride with white phosphorus.

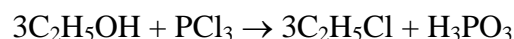
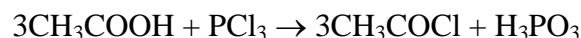


**Properties**

- (i) It is a colourless oily liquid
- (ii) Hydrolyses in the presence of moisture.



- (iii) It reacts with organic compounds containing  $-\text{OH}$  group such as  $\text{CH}_3\text{COOH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ .



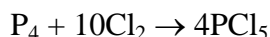
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**PHOSPHORUS PENTACHLORIDE**

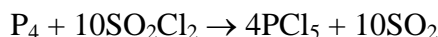
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**Preparation**

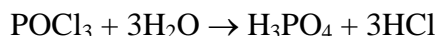
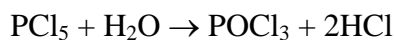
- (i) By the reaction of white phosphorus with excess of dry chlorine.



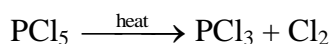
- (ii) By the action of  $\text{SO}_2\text{Cl}_2$  on phosphorus.

**Properties :**

- (i)  $\text{PCl}_5$  is a yellowish white powder  
(ii) It hydrolysis in moist air to  $\text{POCl}_3$  and finally gets converted to phosphoric acid.



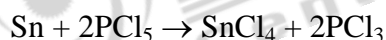
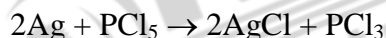
- (iii) When heated, it sublimes but decomposes on stronger heating.



- (iv) It reacts with organic compounds containing  $-\text{OH}$  group converting them to chloro derivatives.



- (v) Finely divided metals on heating with  $\text{PCl}_5$  give corresponding chlorides.

**Uses :**

It is used in the synthesis of some organic compounds, e.g.,  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{CH}_3\text{COCl}$ .

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**OXIDES OF PHOSPHORUS**

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It forms three important oxides which exist in dimeric forms.

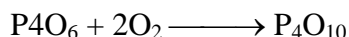
**PHOSPHORUS TRIOXIDE ( $\text{P}_4\text{O}_6$ )****Preparation**

Phosphorus trioxides is formed when phosphorus is burnt in a limited supply of air.



### Properties

- (a) **Heating in air :** On heating in air, it forms phosphorus pentoxide.



Phosphorus (V) oxide

- (b) **Action of water :** It dissolves in cold water to give phosphorus acid.



Phosphorus(V)acid

It is, therefore, considered as anhydride of phosphorus acid.

**Note:** With hot water, it gives phosphoric acid and inflammable phosphine.

### PHOSPHORUS (V) OXIDE (P<sub>4</sub>O<sub>10</sub>)

Preparation : It is prepared by heating white phosphorus in excess of air.



### Properties

- (a) It is snowy white solid.

- (b) **Action with water :** It readily dissolves in cold water forming metaphosphoric acid.



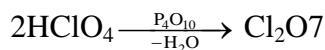
Metaphosphoric acid.

With hot water it gives phosphoric acid.

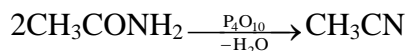


Phosphoric acid

- (c) **Dehydrating nature :** Phosphorus pentoxide has strong affinity for water and, therefore, acts as a powerful dehydrating agent. It extracts water from many inorganic and organic compounds.
- (d) P<sub>4</sub>O<sub>10</sub> is a very strong dehydrating agent and extracts water from many compounds including sulphuric acid and nitric acid.



Chlorine (VII) oxide



Acetamide

Methyl cyanide

### Structure

- (a) Its structure is similar to that of P<sub>4</sub>O<sub>6</sub>.
- (b) In addition, each phosphorus atom forms a double bond with oxygen atom.

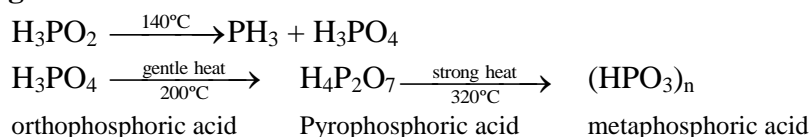
**OXOACIDS OF PHOSPHORUS :**

The important oxoacids of phosphorus with their formulae, methods of preparation and the presence of some characteristic bonds in their structures are given in a table.

**Oxoacids of Phosphorus**

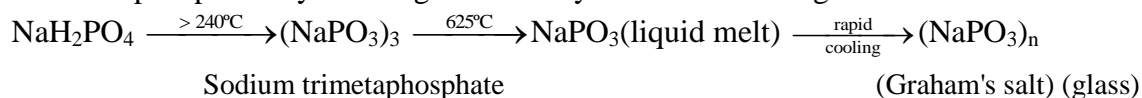
| Name                          | Formula                          | Oxidation State of Phosphorus | Characteristic Bonds and their number          | Preparation  |
|-------------------------------|----------------------------------|-------------------------------|--|--|
| Hypophosphorus (Phosphinic)   | $\text{H}_3\text{PO}_2$          | + 1                           | One P – OH<br>Two P – H<br>One P = O           | White $\text{P}_4$ + alkali                              |
| Orthophosphorous (Phosphonic) | $\text{H}_3\text{PO}_3$          | + 3                           | Two P – OH<br>One P – H<br>One P = O           | $\text{P}_2\text{O}_3 + \text{H}_2\text{O}$              |
| Pyrophosphorous               | $\text{H}_4\text{P}_2\text{O}_5$ | + 3                           | Two P – OH<br>Two P – H<br>Two P = O           | $\text{PCl}_3 + \text{H}_3\text{PO}_3$                   |
| Hypophosphoric                | $\text{H}_4\text{P}_2\text{O}_6$ | + 4                           | Four P – OH<br>Two P = O<br>One P – OH         | Red $\text{P}_4$ + alkali                                |
| Orthophosphoric               | $\text{H}_3\text{PO}_4$          | + 5                           | Three P – OH<br>One P = P                      | $\text{P}_4\text{O}_{10} + \text{H}_2\text{O}$           |
| Pyrophosphoric                | $\text{H}_4\text{P}_2\text{O}_7$ | + 5                           | Four P – OH<br>Two P = H<br>One P – O – P      | Heat phosphoric acid                                     |
| Metaphosphoric                | $(\text{HPO}_3)_n$               | + 5                           | Three P – OH<br>Three P = O<br>Three P – O – P | Phosphorous acid + $\text{Br}_2$ , heat in a sealed tube |

**Heating Effect :**



**Graham salt**

Graham's salt is the best known of these long chain polyphosphates, and is formed by quenching molten  $\text{NaPO}_3$ . Graham's salt is soluble in water. These solutions give precipitates with metal ions such as  $\text{Pb}^{2+}$  and  $\text{Ag}^+$  but not with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Graham's salt is sold commercially under the trade name Calgon. In industry it is incorrectly called sodium hexametaphosphate crystallizing. It is widely used for softening water.



**OXYGEN FAMILY**  
**GROUP 16 ELEMENTS (O, S, Se, Te, Po)**

This is sometimes known as group of chalcogens.

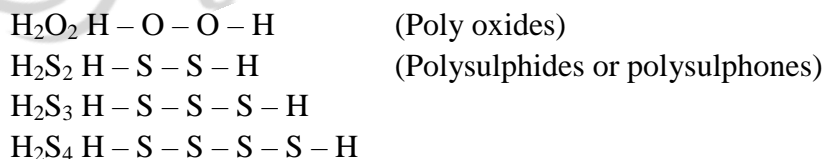
- **Occurrence**  
Oxygen is the most abundant of all the elements on earth crust. Oxygen forms about 46.6% by mass of earth's crust. Dry air contains 20.946% oxygen by volume.
- **Electronic Configuration**  
 $ns^2np^4$  is the general valence shell electronic configuration.
- **Atomic and Ionic Radii :** Covalent radius :  $O < S < Se < Te$
- **Ionisation Enthalpy :**  $O > S > Se > Te > Po$  (IE1 values)
- **Electron Gain Enthalpy :**  $S > Se > Te > Po > O$
- **Electronegativity :**  $O > S > Se > Te$
- **Metallic Character :**  $O < S < Se < Te < Po$
- **Melting and Boiling points:** M.P. :  $Te > Po > Se > S > O$   
B.P. :  $Te > Po > Se > S > O$

**Elemental State**

Oxygen exist as diatomic molecular gas in this case there is  $p\pi - p\pi$  overlap thus two O atoms form double bond  $O = O$ . The intermolecular forces in  $O_2$  are weak VB forces.  $\therefore O_2$  exist as gas. On the other hand, other elements of family do not form stable  $p\pi - p\pi$  bonds and do not exist as  $M_2$  molecules. Other atoms are linked by single bonds and form poly atomic complex molecules for eg.  
 $S - S_8$ ,  $Se - Se_8$

**Catenation**

In this group only S has a strong tendency for catenation oxygen has this tendency to a limited extent.



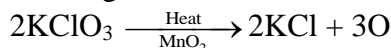
- **Physical Properties**
  - Oxygen and sulphur are non-metals, selenium and tellurium metalloids, whereas polonium is a metal.
  - Polonium is radioactive and is short lived (Half-life 13.8 days).
  - All these elements exhibit allotropy.  
Amongst tetrafluorides,  $SF_4$  is a gas,  $SeF_4$  a liquid and  $TeF_4$  a solid. These fluorides have  $sp^3d$  hybridisation and thus, have trigonal bipyramidal structures in which one of the equatorial positions is occupied by a lone pair of electrons. This geometry is also regarded as see-saw geometry. All elements except selenium form dichlorides and dibromides. These dihalides are formed by  $sp^3$  hybridisation and thus, have tetrahedral structure. The well known monohalides are dimeric in nature. Examples are  $S_2F_2$ ,  $S_2Cl_2$ ,  $S_2Br_2$ ,  $Se_2Cl_2$  and  $Se_2Br_2$ . These dimeric halides undergo disproportionation as given below :  $2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$



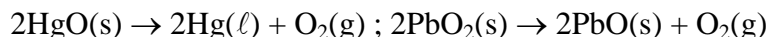
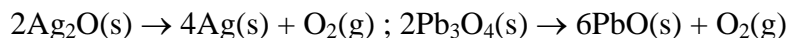
## DIOXYGEN

### (a) Laboratory method

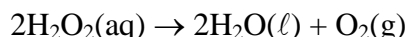
- (i) By heating oxygen containing salts such as chlorates, nitrates and permanganates.



- (ii) By the thermal decomposition of the oxides of metals low in the electrochemical series and higher oxides of some metals.



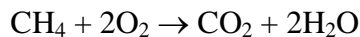
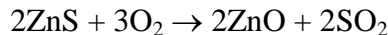
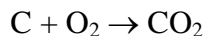
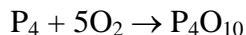
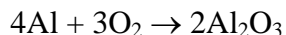
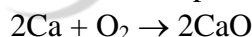
- (iii) Hydrogen peroxide is readily decomposed into water and dioxygen by catalysts such as finely divided metals and manganese dioxide.



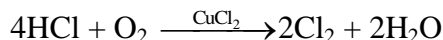
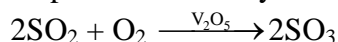
- (b) Large scale preparation : It can be prepared from water or air. Electrolysis of water leads to the release of hydrogen at the cathode and oxygen at the anode.
- (c) Industrially method : Dioxygen is obtained from air by first removing carbon dioxide and water vapour and then, the remaining gases are liquefied and fractionally distilled to give dinitrogen and dioxygen.

### Properties

- (i) Dioxygen is a colourless and odourless gas.
- (ii) Its solubility in water is to the extent of  $3.08 \text{ cm}^3$  in  $100 \text{ cm}^3$  water at 293 K which is just sufficient for the vital support of marine and aquatic life.
- (iii) It liquefies at 90 K and freezes at 55 K.
- (iv) Oxygen atom has three stable isotopes:  $^{16}\text{O}$ ,  $^{17}\text{O}$  and  $^{18}\text{O}$ . Molecular oxygen,  $\text{O}_2$  is unique in being paramagnetic inspite of having even number of electrons.
- (v) Dioxygen directly reacts with nearly all metals and non-metals except some metals ( e.g., Au, Pt) and some noble gases. Some of the reactions of dioxygen with metals, non-metals and other compounds are as follows :



Some compounds are catalytically oxidised. For example,



### Uses:

- (i) It's importance in normal respiration and combustion processes, oxygen is used in oxyacetylene welding, in the manufacture of many metals, particularly steel.
- (ii) Oxygen cylinders are widely used in hospitals, high altitude flying and in mountaineering.
- (iii) The combustion of fuels, e.g., hydrazines in liquid oxygen, provides tremendous thrust in rockets.

### SIMPLE OXIDES

A binary compound of oxygen with another element is called oxide. In many cases one element forms two or more oxides. The oxides vary widely in their nature and properties. Oxides can be simple (e.g., MgO, Al<sub>2</sub>O<sub>3</sub>) or mixed (Pb<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>).

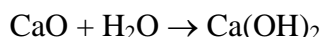
#### Types of simple oxide :

**Acidic oxide :** An oxide that combines with water to give an acid is termed acidic oxide (e.g., SO<sub>2</sub>, Cl<sub>2</sub>O<sub>7</sub>, CO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>).

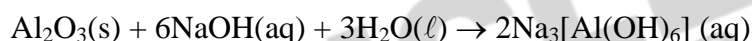
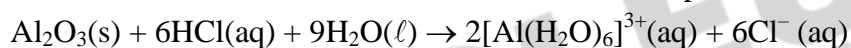


As a general rule, only non-metal oxides are acidic but oxides of some metals in high oxidation state also have acidic character (e.g., Mn<sub>2</sub>O<sub>7</sub>, CrO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>).

**Basic oxide :** The oxides which give a base with water are known as basic oxides (e.g., Na<sub>2</sub>O, CaO, BaO). In general, metallic oxides are basic. For example, CaO combines with water to give Ca(OH)<sub>2</sub>, a base.



**Amphoteric oxide :** Some metallic oxides exhibit a dual behaviour. They show characteristics of both acidic as well as basic oxides. Such oxides are known as amphoteric oxides.



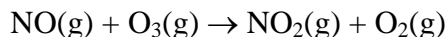
**Neutral oxide:** There are some oxides which are neither acidic nor basic. Such oxides are known as neutral oxides. Examples of neutral oxides are CO, NO and N<sub>2</sub>O.

### OZONE

Ozone is an allotropic form of oxygen.

#### Threats to ozone layer

- (i) Experiments have shown that nitrogen oxides (particularly nitric oxide) combine very rapidly with ozone and there is, thus, the possibility that nitrogen oxides emitted from the exhaust systems of supersonic jet aeroplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.



- (ii) Another threat to this ozone layer is probably posed by the use of freons which are used in aerosol sprays and as refrigerants.

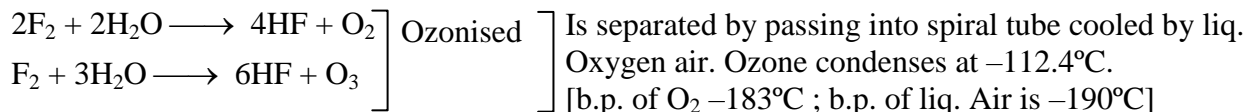
#### Preparation

When a slow dry stream of oxygen is passed through a silent electrical discharge, conversion of oxygen to ozone (10%) occurs. The product is known as ozonised oxygen.



Since the formation of ozone from oxygen is an endothermic process, it is necessary to use a silent electrical discharge in its preparation to prevent its decomposition. If concentration of ozone greater than 10 percent is required, a battery of ozonisers can be used, and pure ozone (b.p. 385 K) can be condensed in a vessel surrounded by liquid oxygen.

**Note:**



**Properties**

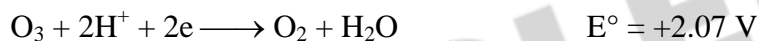
- (i) Pure ozone is a pale blue gas, dark blue liquid and violet-black solid.
- (ii) It is diamagnetic gas.
- (iii) Ozone has a characteristic fishy smell and in small concentrations it is harmless.

**Toxic effect :**

- (a) Toxic enough (more toxic than KCN). Its intense blue colour is due to the absorption of red light.
- (b) However, if the concentration rises above about 100 parts per million, breathing becomes uncomfortable resulting in headache and nausea.

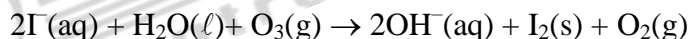
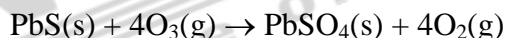
**Oxidizing properties**

It is one of best oxidising agent, in acid solution, its standard, reduction potential value is 2.07 V.

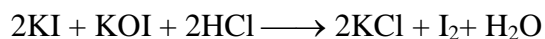
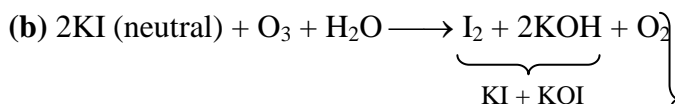
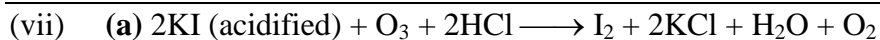


It is next to  $\text{F}_2$ . [above 2.07 V, only  $\text{F}_2$ ,  $\text{F}_2\text{O}$  are there]

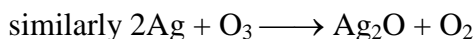
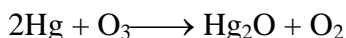
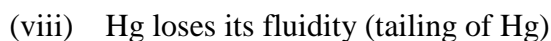
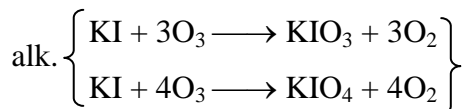
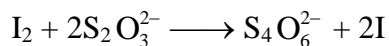
It is not really surprising, therefore, high concentrations of ozone can be dangerously explosive. Due to the ease with which it liberates atoms of nascent oxygen ( $\text{O}_3 \rightarrow \text{O}_2 + \text{O}$ ), it acts as a powerful oxidising agent. For example, it oxidises lead sulphide to lead sulphate and iodide ions to iodine.



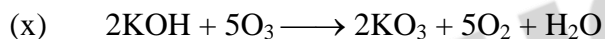
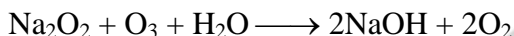
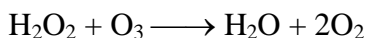
- (i) Metal Sulphides to Sulphates.  
 $\text{MS} + 4\text{O}_3 \longrightarrow \text{MSO}_4 + 4\text{O}_2$  [M = Pb, Cu, Zn, Cd]
- (ii)  $2\text{HX} + \text{O}_3 \longrightarrow \text{X}_2 + \text{H}_2\text{O} + \text{O}_2$  [X = Cl, Br, I]
- (iii)  $\text{NaNO}_2 + \text{O}_3 \longrightarrow \text{NaNO}_3 + \text{O}_2$   
 $\text{Na}_2\text{SO}_3 + \text{O}_3 \longrightarrow \text{Na}_2\text{SO}_4 + \text{O}_2$   
 $\text{Na}_2\text{AsO}_3 + \text{O}_3 \longrightarrow \text{Na}_2\text{AsO}_4 + \text{O}_2$
- (iv) Moist S, P, As +  $\text{O}_3 \Rightarrow$   
 $\text{S} + \text{H}_2\text{O} + 3\text{O}_3 \longrightarrow \text{H}_2\text{SO}_4 + 3\text{O}_2$   
 $2\text{P} + 3\text{H}_2\text{O} + 5\text{O}_3 \longrightarrow 2\text{H}_3\text{PO}_4 + 5\text{O}_2$   
 $2\text{As} + 3\text{H}_2\text{O} + 5\text{O}_3 \longrightarrow 2\text{H}_3\text{AsO}_4 + 5\text{O}_2$
- (v) Moist  $\text{I}_2 \longrightarrow \text{HIO}_3$  whereas dry iodine  $\longrightarrow \text{I}_4\text{O}_9$  (yellow)  
 $\text{I}_2 + 5\text{O}_3 + \text{H}_2\text{O} \longrightarrow 2\text{HIO}_3 + 5\text{O}_2$   
 $2\text{I}_2 + 9\text{O}_3 \longrightarrow \text{I}_4\text{O}_9 + 9\text{O}_2$
- (vi)  $2\text{KMnO}_4 + \text{O}_3 + \text{H}_2\text{O} \longrightarrow 2\text{KMnO}_4 + 2\text{KOH} + \text{O}_2$   
 $2\text{K}_4[\text{Fe}(\text{CN})_6] + \text{O}_3 + \text{H}_2\text{O} \longrightarrow 2\text{K}_3[\text{Fe}(\text{CN})_6] + 2\text{KOH} + \text{O}_2$   
 $2\text{FeSO}_4 + \text{O}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{O}_2 + \text{H}_2\text{O}$



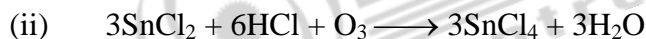
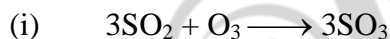
$\left. \begin{array}{l} \text{KI} + \text{KOI} \\ 2\text{KI} + \text{KOI} + 2\text{HCl} \longrightarrow 2\text{KCl} + \text{I}_2 + \text{H}_2\text{O} \end{array} \right\} \text{O}_3 \text{ is estimated by this reaction}$



Brown



**In all above reaction  $\text{O}_3$  gives up  $\text{O}_2$  but some reactions are there which consumes all O-atom.**



**Uses :**

- Sterilising water
- Detection of position of the double bond in the unsaturated compound.
- It is used as a germicide, disinfectant and for sterilising water.
- It is also used for bleaching oils, ivory, flour, starch, etc.
- It acts as an oxidising agent in the manufacture of potassium permanganate.

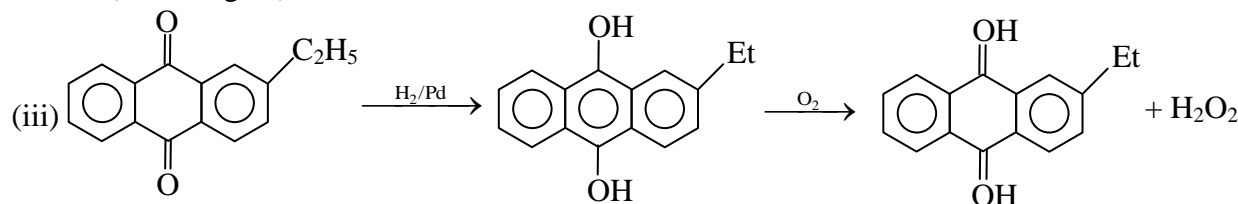
**Qus.** Ozone is thermodynamically unstable with respect to oxygen. Explain ?

**Sol.** Because its decomposition into oxygen results in the liberation of heat ( $\Delta H$  is negative) and an increase in entropy ( $\Delta S$  is positive). These two effects reinforce each other, resulting in large negative Gibbs energy change ( $\Delta G$ ) for its conversion into oxygen.

**HYDROGEN PEROXIDE (H<sub>2</sub>O<sub>2</sub>)**

**Method of preparation:**

- (i)  $\text{Na}_2\text{O}_2 + \text{H}_2\text{O (ice cold water)} \longrightarrow 2\text{NaOH} + \text{H}_2\text{O}_2$
- (ii)  $\text{BaO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2$   
Instead of H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> is added now-a-days because H<sub>2</sub>SO<sub>4</sub> catalyses the decomposition of H<sub>2</sub>O<sub>2</sub> whereas H<sub>3</sub>PO<sub>4</sub> favours to restore it.  
 $3\text{BaO}_2 + 2\text{H}_3\text{PO}_4 \rightarrow \text{Ba}_3(\text{PO}_4)_2 + 3\text{H}_2\text{O}_2$  and  $\text{Ba}_3(\text{PO}_4)_2 + 3\text{H}_2\text{SO}_4 \rightarrow 3\text{BaSO}_4 + 2\text{H}_3\text{PO}_4$  (reused again)



**Properties:**

- (i) Colourless, odourless liquid (b.p.152°)
- (ii) Acidic nature :  $\text{H}_2\text{O}_2 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{O}_2 + \text{H}_2\text{O}$   
 $\text{H}_2\text{O}_2 + \text{Na}_2\text{CO}_3 \longrightarrow \text{Na}_2\text{O}_2 + \text{CO}_2 + \text{H}_2\text{O}$
- (iii) It is oxidant as well as reductant.  
 $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e} \rightarrow 2\text{H}_2\text{O}$  [reaction in acidic medium]  
 $\text{H}_2\text{O}_2 + 2\text{e} \rightarrow 2\text{OH}^-$  [rxn<sup>n</sup> in alkali medium]

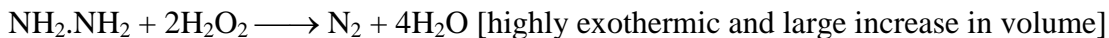
**Oxidising Properties:**

- (i)  $\text{PbS} + 4\text{H}_2\text{O}_2 \longrightarrow \text{PbSO}_4 + 4\text{H}_2\text{O}$  (Used in washing of oil painting)
- (ii)  $\text{NaNO}_2 + \text{H}_2\text{O}_2 \longrightarrow \text{NaNO}_3 + \text{H}_2\text{O}$   
 $\text{Na}_2\text{SO}_3 + \text{H}_2\text{O}_2 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$   
 $2\text{KI} + \text{H}_2\text{O}_2 \longrightarrow 2\text{KOH} + \text{I}_2$   
 $\text{H}_2\text{S} + \text{H}_2\text{O}_2 \longrightarrow \text{S} \downarrow + 2\text{H}_2\text{O}$   
 $\text{H}_2\text{SO}_4 + 2\text{FeSO}_4 + \text{H}_2\text{O}_2 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O}$   
 $2\text{K}_4[\text{Fe}(\text{CN})_6] + \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \longrightarrow 2\text{K}_3[\text{Fe}(\text{CN})_6] + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$

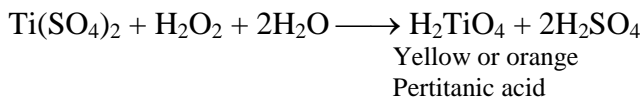
**Reducing properties:**

- (a)  $\text{Ag}_2\text{O} + \text{H}_2\text{O}_2 \longrightarrow 2\text{Ag} + \text{H}_2\text{O} + \text{O}_2$
- (b)  $\text{O}_3 + \text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + 2\text{O}_2$
- (c)  $\text{MnO}_2 + \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{O}_2$
- (d)  $\text{PbO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{PbO} + \text{H}_2\text{O} + \text{O}_2$
- (e)  $\text{Pb}_3\text{O}_4 + 4\text{HNO}_3 \longrightarrow 2\text{Pb}(\text{NO}_3)_2 + \text{PbO}_2 + 2\text{H}_2\text{O}$   
 $\text{PbO}_2 + \text{H}_2\text{O}_2 \longrightarrow \text{PbO} + \text{H}_2\text{O} + \text{O}_2$   
 $\text{PbO} + 2\text{HNO}_3 \longrightarrow \text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{O}$   
 $\text{Pb}_3\text{O}_4 + \text{H}_2\text{O}_2 + 6\text{HNO}_3 \longrightarrow 3\text{Pb}(\text{NO}_3)_2 + 4\text{H}_2\text{O} + \text{O}_2$
- (f)  $\text{X}_2 + \text{H}_2\text{O}_2 \longrightarrow 2\text{HX} + \text{O}_2$  [X = Cl, Br]
- (g)  $2[\text{Fe}(\text{CN})_6]^{3-} + 2\text{OH}^- + \text{H}_2\text{O}_2 \longrightarrow 2[\text{Fe}(\text{CN})_6]^{4-} + 2\text{H}_2\text{O} + \text{O}_2$
- (h)  $\text{NaOCl} + \text{H}_2\text{O}_2 \longrightarrow \text{NaCl} + \text{H}_2\text{O} + \text{O}_2$
- (i)  $\text{NaIO}_4 + \text{H}_2\text{O}_2 \longrightarrow \text{NaIO}_3 + \text{H}_2\text{O} + \text{O}_2$

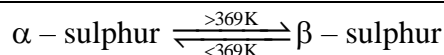
**Uses :** (i) As a rocket propellant:



(ii) In detection of  $\text{Cr}^{+3}$ ,  $\text{Ti}^{+4}$  etc.



### ALLOTROPIC FORMS OF SULPHUR



At 369 K both the forms are stable. This temperature is called transition temperature.

#### Rhombic sulphur ( $\alpha$ -sulphur)

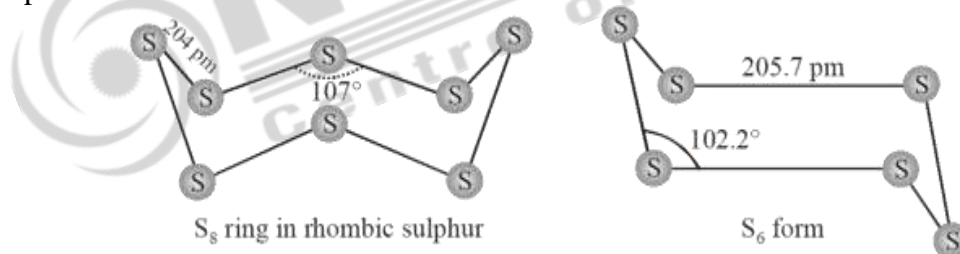
- (i) This allotrope is yellow in colour, m.p. 385.8 K and specific gravity 2.06.
- (ii) Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in  $\text{CS}_2$ .
- (iii) It is insoluble in water but dissolves to some extent in benzene, alcohol and ether.
- (iv) It is readily soluble in  $\text{CS}_2$ .

#### Monoclinic sulphur ( $\beta$ -sulphur)

- (i) Its m.p. is 393 K and specific gravity 1.98.
- (ii) It is soluble in  $\text{CS}_2$ .

#### Structure of $\alpha$ and $\beta$ sulphur

Both rhombic and monoclinic sulphur have  $\text{S}_8$  molecules. These  $\text{S}_8$  molecules are packed to give different crystal structures. The  $\text{S}_8$  ring in both the forms is puckered and has a crown shape.



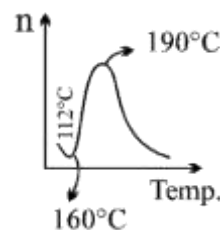
Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesized in the last two decades. In cyclo- $\text{S}_6$ , the ring adopts the chair form. At elevated temperatures ( $\sim 1000$  K),  $\text{S}_2$  is the dominant species and is paramagnetic like  $\text{O}_2$ .

#### Note: Viscosity of 'S' with temperature :

m.p. of 'S'  $\longrightarrow$  112.8°C.

> 112.8°C to 160°C  $\Rightarrow$  slow decreases due to  $\text{S}_8$  rings slip and roll over one another easily.

> 160°C, increases sharply due to breaking of  $\text{S}_8$  rings into chains and polymerises into large size chain.



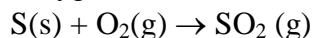
#### Amorphous forms are

- (i) Plastic sulphur                      (ii) Milk of sulphur                      (iii) Colloidal sulphur

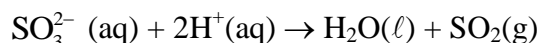
## SULPHUR DIOXIDE

### Preparation

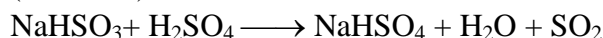
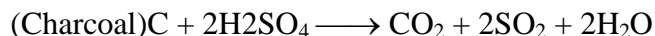
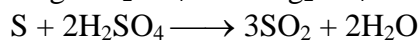
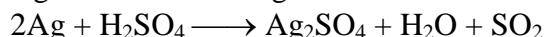
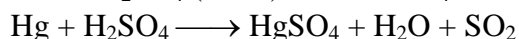
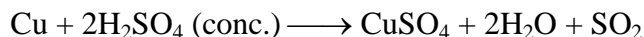
Sulphur dioxide is formed together with a little (6-8%) sulphur trioxide when sulphur is burnt in air or oxygen:



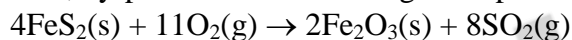
**laboratory method** by treating a sulphite with dilute sulphuric acid.



### other preparation :



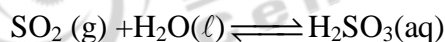
**Industrial method**, by-product of the roasting of sulphide ores.



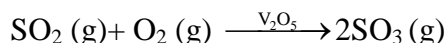
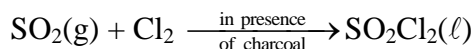
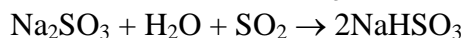
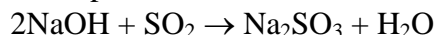
The gas after drying is liquefied under pressure and stored in steel cylinders.

### Properties

- (i) Sulphur dioxide is a colourless gas with pungent smell.
- (ii) It is highly soluble in water.
- (iii) It liquefies at room temperature under a pressure of two atmospheres and boils at 263 K.
- (iv) Acidic character sulphur dioxide, when passed through water, forms a solution of sulphurous acid.

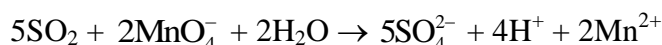
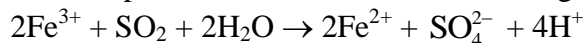


It reacts readily with sodium hydroxide solution, forming sodium sulphite, which then reacts with more sulphur dioxide to form sodium hydrogen sulphite.

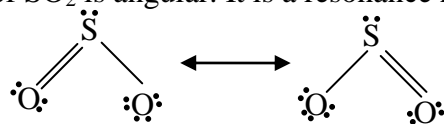


### Reducing properties

When moist, sulphur dioxide behaves as a reducing agent.



**Bonding in SO<sub>2</sub>** : The molecule of SO<sub>2</sub> is angular. It is a resonance hybrid of the two canonical forms:



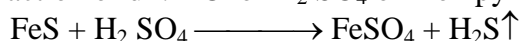
**Uses:**

- It is used refining petroleum and sugar
- It is used in bleaching wool and silk
- It is used as an anti-chlor, disinfectant and preservative. Sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite (industrial chemicals) are manufactured from sulphur dioxide. Liquid SO<sub>2</sub> is used as a solvent to dissolve a number of organic and inorganic chemicals.

**HYDROGEN SULPHIDE (H<sub>2</sub>S) SULPHURATED HYDROGEN**

**Preparation**

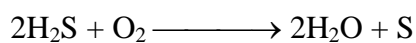
By the action of dil. HCl or H<sub>2</sub> SO<sub>4</sub> on iron pyrites.



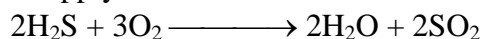
**Properties**

It is a colourless gas having an offensive smell of rotten eggs.

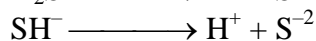
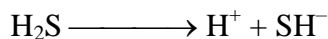
- It burn in air with blue flame



If the air supply is in excess



- It is a mild acid.



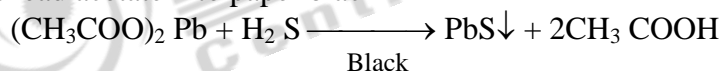
- It act as a reducing agent. It reduces halogen into corresponding hydroacid.



**Tests of H<sub>2</sub>S**

- Unpleasant odour resembling that of rotten eggs.

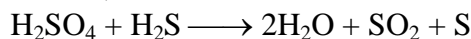
- It turns lead acetate into paper black



**Uses**

- It is mainly employed in salt analysis for the detection of cation.
- Reducing agent for H<sub>2</sub>SO<sub>4</sub>, KMnO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, FeCl<sub>3</sub>

**Note:** Drying agent for this gas : fused CaCl<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> (dehydrated) P<sub>2</sub>O<sub>5</sub> etc.  
But not H<sub>2</sub>SO<sub>4</sub>, because



**SULPHURIC ACID**

**Industrial Manufacturing** (Contact process)

Steps involved :

- Burning of sulphur or sulphide ores in air to generate SO<sub>2</sub>.**
- Conversion of SO<sub>2</sub> to SO<sub>3</sub> by the reaction with oxygen in the presence of a catalyst (V<sub>2</sub>O<sub>5</sub>):**

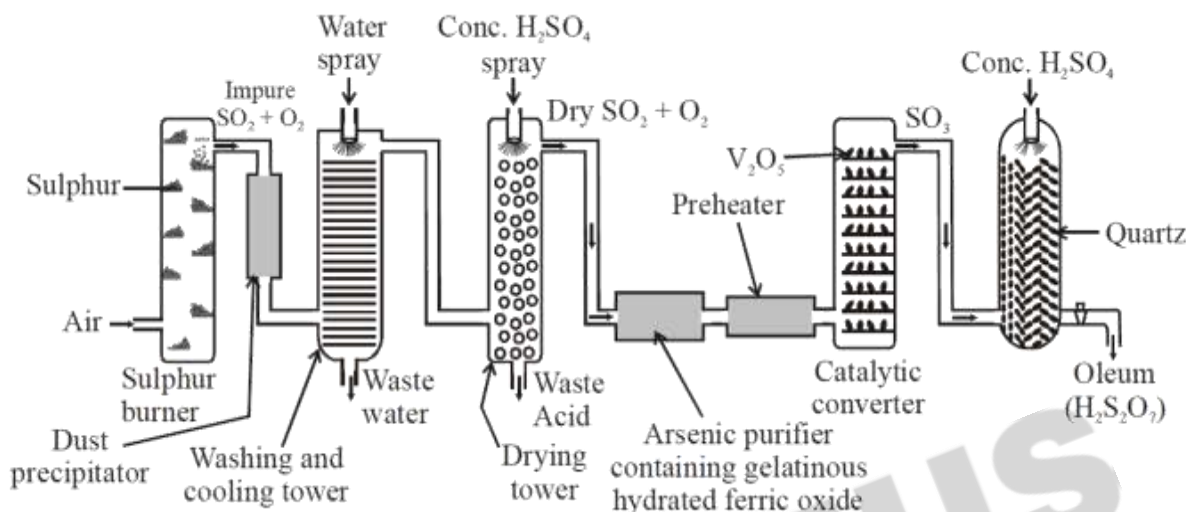
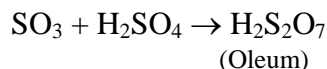
The key step in the manufacture of H<sub>2</sub>SO<sub>4</sub> is the catalytic oxidation of SO<sub>2</sub> with O<sub>2</sub> to give SO<sub>3</sub> in the presence of V<sub>2</sub>O<sub>5</sub> (catalyst).



The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume.

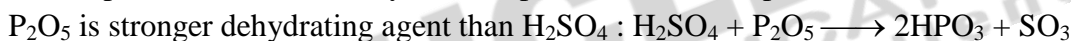


- (iii) The  $\text{SO}_3$  gas from the catalytic converter is absorbed in concentrated  $\text{H}_2\text{SO}_4$  to produce oleum. Dilution of oleum with water gives  $\text{H}_2\text{SO}_4$  of the desired concentration.



Flow diagram for the manufacture of sulphuric acid

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



### Properties

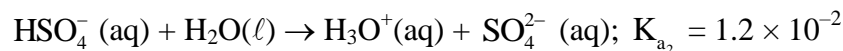
- (i) Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K.
- (ii) The acid freezes at 283 K and boils at 611 K.
- (iii) It dissolves in water.

### Chemical properties

The chemical reactions of sulphuric acid are as a result of the following characteristics:

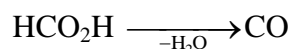
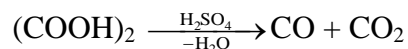
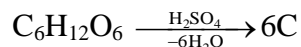
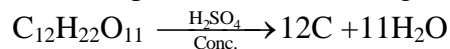
#### (1) Acidic character :

In aqueous solution, sulphuric acid ionises in two steps.



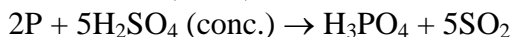
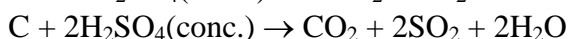
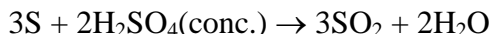
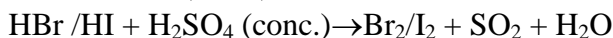
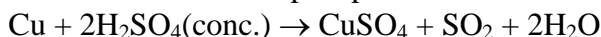
#### (2) Dehydrating Property :

Concentrated sulphuric acid is a strong dehydrating agent.



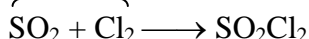
**(3) Oxidizing Nature :**

Hot concentrated sulphuric acid is a moderately strong oxidising agent. In this respect, it is intermediate between phosphoric and nitric acids.



**H<sub>2</sub>SO<sub>4</sub> & SO<sub>3</sub> :**

Both gas



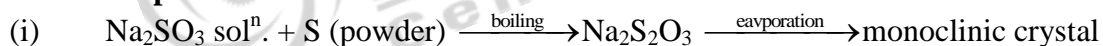
good chlorinating agent

**Uses:**

- (i) petroleum refining
- (ii) manufacture of pigments, paints and dyestuff intermediates
- (iii) detergent industry
- (iv) metallurgical applications (e.g., cleansing metals before enameling, electroplating and galvanising)
- (v) storage batteries
- (vi) in the manufacture of nitrocellulose products and
- (vii) as a laboratory reagent.

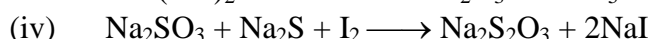
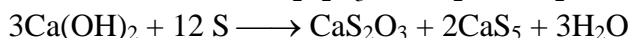
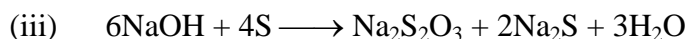
**SODIUM THIOSULPHATE**

**Prep<sup>n</sup>.:**

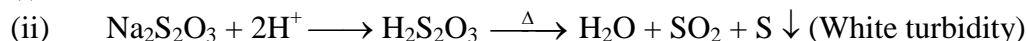
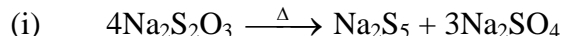


Salt cake    Coke

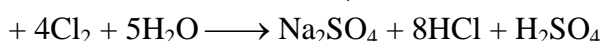
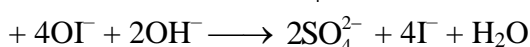
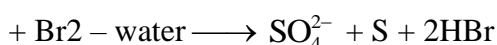
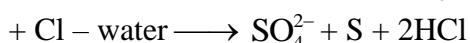
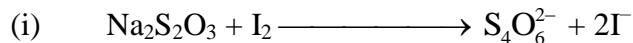
$\downarrow$  SO<sub>2</sub> passed into it



**Props:**



**Reaction:**



**HALOGEN FAMILY**  
**GROUP 17 ELEMENTS (F, Cl, Br, I, At)**

**Electronic Configuration**

The electronic configuration of outermost shell 17<sup>th</sup> group element is  $(ns^2np^5)$ .

- Atomic and ionic radii :  $F < Cl < Br < I$
- Ionisation Enthalpy :  $F > Cl > Br > I$
- Electron Gain Enthalpy:  $Cl > F > Br > I$
- Electronegativity :  $F > Cl > Br > I$

**Physical Properties**

- Their melting and boiling points steadily increase with atomic number.
- All halogens are coloured. For example,  $F_2$  has yellow gas,  $Cl_2$  greenish yellow gas,  $Br_2$  red liquid and  $I_2$  violet coloured solid.
- Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water but are soluble in various organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions.
- Bond energy order ;  $Cl_2 > Br_2 > F_2 > I_2$

**Chemical Properties**

**Oxidation states :**

- All the halogens exhibit  $-1$  oxidation state. However, chlorine, bromine and iodine exhibit  $+1$ ,  $+3$ ,  $+5$  and  $+7$  oxidation states also as explained below:

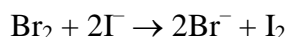
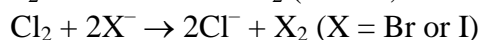
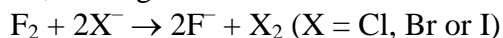
| Halogen atom                             | ns                   | ns                                   | nd                                       |   |
|--|----------------------|--------------------------------------|--|---|
| In ground state<br>(other than fluorine) | $\uparrow\downarrow$ | $\uparrow\downarrow\uparrow\uparrow$ | $\square\square\square\square\square$    | 1 unpaired electron accounts<br>For $-1$ or $+1$ oxidation states |
| First excited state                      | $\uparrow\downarrow$ | $\uparrow\downarrow\uparrow\uparrow$ | $\uparrow\square\square\square\square$   | 3 unpaired electron accounts<br>For $+3$ oxidation states         |
| Second excited state                     | $\uparrow\downarrow$ | $\uparrow\uparrow\uparrow$           | $\uparrow\uparrow\square\square\square$  | 5 unpaired electron accounts<br>For $+5$ oxidation states         |
| Third excited state                      | $\uparrow$           | $\uparrow\uparrow\uparrow$           | $\uparrow\uparrow\uparrow\square\square$ | 7 unpaired electron accounts<br>For $+7$ oxidation states         |

- The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms. e.g., in interhalogens, oxides and oxoacids.
- The oxidation states of  $+4$  and  $+6$  occur in the oxides and oxoacids of chlorine and bromine.
- The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only  $-1$  oxidation state.

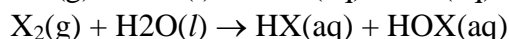
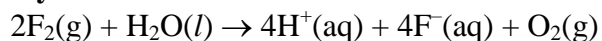
### Chemical reactivity

- (i) All the halogens are highly reactive.
- (ii) They react with metals and non-metals to form halides and the reactivity of the halogens decreases down the group. i.e. the order is  $F_2 > Cl_2 > Br_2 > I_2$
- (iii) The ready acceptance of an electron is the reason for the strong oxidising nature of halogens.  $F_2$  is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase.

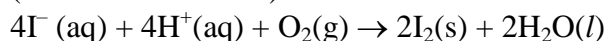
In general, a halogen oxidises halide ions of higher atomic number.



#### (1) Reactivity towards water



(where  $X = Cl \text{ or } Br$ )



- (2) **Reactivity towards hydrogen :** They all react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to iodine.

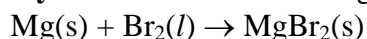
- (i) The acidic strength order :  $HF < HCl < HBr < HI$

- (ii) The stability order of these halides :  $H-F > H-Cl > H-Br > H-I$ .

#### (3) Reactivity towards oxygen :

- (i) Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides  $OF_2$  and  $O_2F_2$ . However, only  $OF_2$  is thermally stable at 298 K. These oxides are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents.  $O_2F_2$  oxidises plutonium to  $PuF_6$  and the reaction is used in removing plutonium as  $PuF_6$  from spent nuclear fuel.
- (ii) Chlorine, bromine and iodine form oxides in which the oxidation states of these halogens range from +1 to +7.
- (iii) A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens,  $I > Cl > Br$ .
- (iv) The higher oxides of halogens tend to be more stable than the lower ones.
- (v) Chlorine oxides,  $Cl_2O$ ,  $ClO_2$ ,  $Cl_2O_6$  and  $Cl_2O_7$  are highly reactive oxidising agents and tend to explode.  $ClO_2$  is used as a bleaching agent for paper pulp and textiles and in water treatment.
- (vi) The bromine oxides,  $Br_2O$ ,  $BrO_2$ ,  $BrO_3$  are the least stable halogen oxides (middle row anomaly) and exist only at low temperatures. They are very powerful oxidising agents.
- (vii) The iodine oxides,  $I_2O_4$ ,  $I_2O_5$ ,  $I_2O_7$  are insoluble solids and decompose on heating.  $I_2O_5$  is a very good oxidising agent and is used in the estimation of carbon monoxide.

#### (4) Reactivity towards metals : Halogens react with metals to form metal halides.

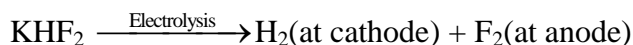
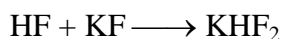
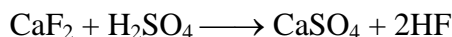


The ionic character of the halides decreases in the order  $MF > MCl > MBr > MI$  where M is monovalent metal.

## FLUORINE

### Method of Prep<sup>n</sup> :

**Moissan process** : [By electrolysis of  $\text{KHF}_2$  (which is obtained from  $\text{CaF}_2$ )]

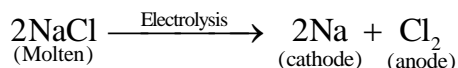
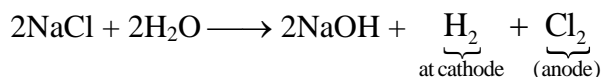


{ KF decreases the m.p. of  
the mix. depending upon  
the composition. }

## CHLORINE

### Preparation

(i) By electrolysis of aq.  $\text{NaCl}$  :



(ii) By heating manganese dioxide with concentrated hydrochloric acid.



However, a mixture of common salt and concentrated  $\text{H}_2\text{SO}_4$  is used in place of  $\text{HCl}$ .

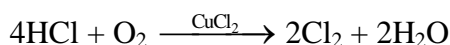


(iii) By the action of  $\text{HCl}$  on potassium permanganate.



### ❑ MANUFACTURE OF CHLORINE

(i) **Deacon's process** : By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of  $\text{CuCl}_2$  (catalyst) at 723 K.



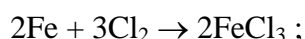
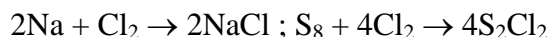
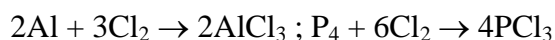
(ii) **Electrolytic process** : Chlorine is obtained by the electrolysis of brine (concentrated  $\text{NaCl}$  solution).

Chlorine is liberated at anode. It is also obtained as a by-product in many chemical industries.

### Properties

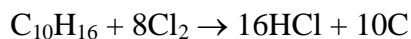
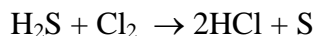
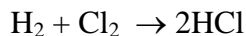
(i) It is a greenish yellow gas with pungent and suffocating odour.

(ii) It is soluble in water. Chlorine reacts with a number of metals and non-metals to form chlorides.



### Reaction with hydrogen

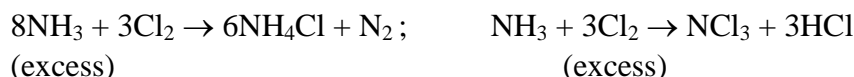
It has great affinity for hydrogen. It reacts with compounds containing hydrogen to form HCl.



### Reaction with ammonia

With excess ammonia, chlorine gives nitrogen and ammonium chloride whereas with excess chlorine,

nitrogen trichloride (explosive) is formed.



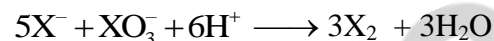
### Reaction with alkalis



(cold and dilute)



(hot and conc.)

 $[X = \text{Cl, Br, I}]$ 

## Reaction with slaked lime

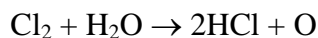
With dry slaked lime it gives bleaching powder.



The composition of bleaching powder is  $\text{Ca(OCl)}_2 \cdot \text{CaCl}_2 \cdot \text{Ca(OH)}_2 \cdot 2\text{H}_2\text{O}$ .

**Note :** Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl. Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

It is a powerful bleaching agent; bleaching action is due to oxidation.



Coloured substance + O  $\rightarrow$  Colourless substance

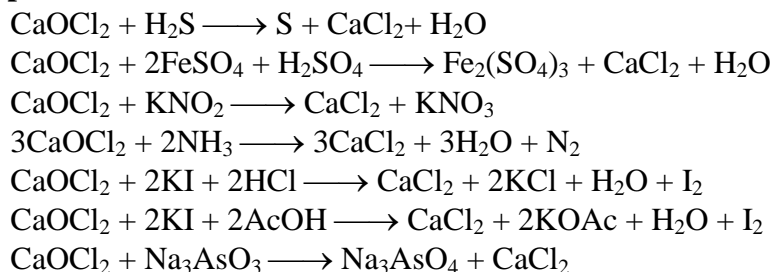
**Uses:** It is used (i) for bleaching woodpulp (required for the manufacture of paper and rayon), bleaching cotton and textiles, (ii) in the extraction of gold and platinum (iii) in the manufacture of dyes, drugs and organic compounds such as  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , DDT, refrigerants, etc. (iv) in sterilising drinking water and (v) preparation of poisonous gases such as phosgene ( $\text{COCl}_2$ ), tear gas ( $\text{CCl}_3\text{NO}_2$ ), mustard gas ( $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$ ).



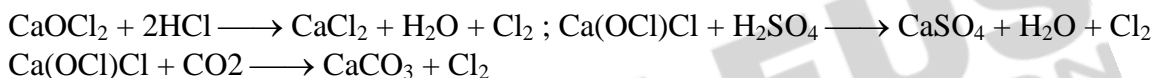


- (a) On long standing it undergoes
- auto oxidation  $6\text{Ca}(\text{OCl})\text{Cl} \longrightarrow \text{Ca}(\text{ClO}_3)_2 + 5\text{CaCl}_2$
  - $2\text{Ca}(\text{OCl})\text{Cl} \xrightarrow[\text{Cat.}]{\text{CoCl}_2} 2\text{CaCl}_2 + \text{O}_2$
  - $\text{Ca}(\text{OCl})\text{Cl} + \text{H}_2\text{O} \longrightarrow \text{Ca}(\text{OH})_2 + \text{Cl}_2$

**Oxidising Prop.:**



**Reaction with acid:**

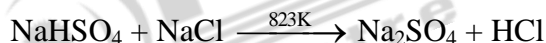


**Note:**  $\text{ClO}_2$  does not dimerise because odd e<sup>-</sup> undergoes delocalisation (in its own vacant 3d-orbital)  
 $\text{Cl}_2\text{O}_4$  ( $\text{Cl}.\text{ClO}_4$ ) is not the dimer of  $\text{ClO}_2$ . Actually it is Cl-perchlorate.

**HYDROGEN CHLORIDE**

**Preparation**

**Laboratory method :** it is prepared by heating sodium chloride with concentrated sulphuric acid.



HCl gas can be dried by passing through concentrated sulphuric acid.

**Properties**

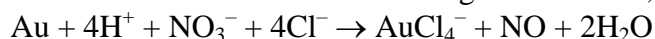
- It is a colourless and pungent smelling gas.
- It is easily liquefied to a colourless liquid (b.p. 189 K) and freezes to a white crystalline solid (f.p. 159 K).
- It is extremely soluble in water
- Acidic character :** It ionises as follows  
 $\text{HCl}(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \quad K_a = 10^7$

Its aqueous solution is called hydrochloric acid. High value of dissociation constant ( $K_a$ ) indicates that it is a strong acid in water. It reacts with  $\text{NH}_3$  and gives white fumes of  $\text{NH}_4\text{Cl}$ .



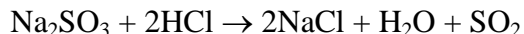
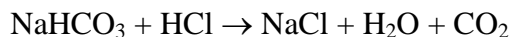
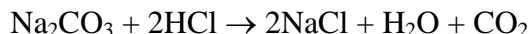
**Note : Aqua regia**

When three parts of concentrated HCl and one part of concentrated  $\text{HNO}_3$  are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.



### Reaction with salts

Hydrochloric acid decomposes salts of weaker acids, e.g., carbonates, hydrogencarbonates, sulphites, etc.



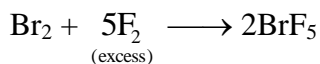
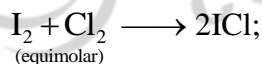
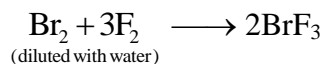
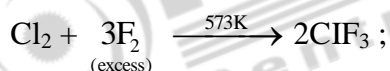
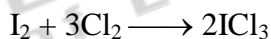
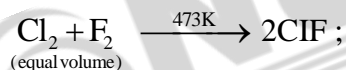
- Uses:**
- (i) It is used in the manufacture of chlorine,  $\text{NH}_4\text{Cl}$  and glucose (from corn starch)
  - (ii) It is used for extracting glue from bones and purifying bone black
  - (iii) It is used in medicine and as a laboratory reagent.
  - (iv) It bleaches vegetable or organic matter in the presence of moisture. Bleaching effect of chlorine is permanent.

### INTERHALOGEN COMPOUNDS

When two different halogens react with each other, interhalogen compounds are formed. They can be assigned general compositions as  $\text{XX}'$ ,  $\text{XX}_3'$ ,  $\text{XX}_5'$  and  $\text{XX}_7'$  where X is halogen of larger size and  $\text{X}'$  of smaller size and X is more electropositive than  $\text{X}'$ .

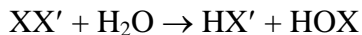
### Preparation

The interhalogen compounds can be prepared by the direct combination or by the action of halogen on lower interhalogen compounds. The product formed depends upon some specific conditions, For e.g.,



### Properties

- (i) These are all covalent molecules and are diamagnetic in nature.
- (ii) They are volatile solids or liquids at 298 K except  $\text{ClF}$  which is a gas.
- (iii) Their physical properties are intermediate between those of constituent halogens except that their m.p. and b.p. are a little higher than expected.
- (iv) Their chemical reactions can be compared with the individual halogens. In general, interhalogen compounds are more reactive than halogens (except fluorine). This is because  
 $\text{X-X}'$  bond in interhalogens is weaker than  $\text{X-X}$  bond in halogens except  $\text{F-F}$  bond.
- (v) All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when  $\text{XX}'$ ), halite (when  $\text{XX}_3'$ ), halate (when  $\text{XX}_5'$ ) and perhalate (when  $\text{XX}_7'$ ) anion derived from the larger halogen.





**PSEUDO HALOGEN**

There are univalent ion consisting of two or more atoms of which at least one is N, that have properties similar to those of the halide ions. E.g.

- (i) Na-salts are soluble in water but Ag-salts are insoluble in water.
- (ii) H-compounds are acids like HX.
- (iii) Some anions can be oxidised to give molecules  $X_2$ .

| <b>Anions :</b>       | <b>Acids</b>            | <b>Dimer</b>  |
|-----------------------|-------------------------|---------------|
| $CN^-$                | HCN                     | $(CN)_2$      |
| $SCN^-$               | HSCN(thiocyanic acid)   | $(SCN)_2$     |
| $SeCN^-$              |                         | $(SeCN)_2$    |
| $OCN^-$               | HOCN                    | (cyanic acid) |
| $NCN^{2-}$ (Bivalent) | $H_2NCN$ (cyanamide)    |               |
| $ONC^-$               | HONC (Fulminic acid)    |               |
| $N_3^-$               | $HN_3$ (Hydrazoic acid) |               |

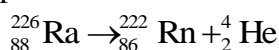
$CN^\ominus$  shows maximum similarities with  $Cl^-$ ,  $Br^-$ ,  $I^-$

- (i) forms HCN    (ii) forms  $(CN)_2$     (iii) AgCN,  $Pb(CN)_2$ , are insoluble
- (iv) Interpseudo halogen compounds ClCN, BrCN, ICN can be formed
- (v) AgCN is insoluble in  $H_2O$  but soluble in  $NH_3$
- (vi) forms large no. of complex. e.g.  $[Cu(CN)_4]^{3-}$  &  $[CuCl_4]^{3-}$   
 $[Co(CN)_6]^{3-}$  &  $[CoCl_6]^{3-}$

**NOBLE GASES FAMILY**  
**GROUP 18 ELEMENTS (He, Ne, Ar, Kr, Xe, Rn)**

**Occurrence**

- (i) All the noble gases except radon occur in the atmosphere.  
Relative abundance : Ar is highest (Ne, Kr, He, Rn)
- (ii) Their atmospheric abundance in dry air is ~ 1% by volume of which argon is the major constituent.
- (iii) Helium and sometimes neon are found in minerals of radioactive origin e.g., pitchblende, monazite, cleveite.
- (iv) The main commercial source of helium is natural gas.
- (v) Xenon and radon are the rarest elements of the group.
- (vi) Radon is obtained as a decay product of  $^{226}\text{Ra}$ .



- (vii) He liquid can exist in two forms. I-form when changes to II-form at  $\lambda$ -point temperature many physical properties change abruptly.

e.g.

- (i) Sp. heat changes by a factor of 10
- (ii) Thermal conductivity increases by  $10^6$  and it becomes 800 times faster than Cu
- (iii) It shows zero resistance
- (iv) It can flow up the sides of the vessel

☐ **Electronic Configuration**

General electronic configuration of 18 group element is  $ns^2np^6$  except helium which has  $1s^2$ .

☐ **Ionisation Enthalpy**

$\text{He} > \text{Ne} > \text{Ar} > \text{Kr} > \text{Xe} > \text{Rn}$  (I.E. order)

☐ **Atomic Radii**

$\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe} < \text{Rn}$  (atomic radius order)

☐ **Electron Gain Enthalpy**

They have large positive values of electron gain enthalpy due to stable electronic configurations, and there for have no tendency to accept the electron

☐ **Melting point and boiling point**

$\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe} < \text{Rn}$  (Melting point order)

↓

( $-269^\circ\text{C}$ )

**B.P. order :**  $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe} < \text{Rn}$  (Boiling point order)

☐ **Density order :**

$\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe} < \text{Rn}$  (Density order)

**Physical properties :**

- (i) All the noble gases are monoatomic.
- (ii) They are colourless, odourless and tasteless.
- (iii) They are sparingly soluble in water.
- (iv) They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces.
- (v) Helium has the lowest boiling point (4.2 K) of any known substance.
- (vi) It has an unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

**❑ Chemical Properties**

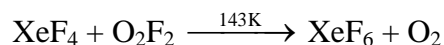
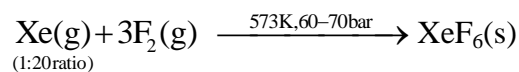
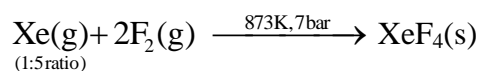
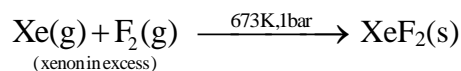
In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

- (i) The noble gases except helium ( $1s^2$ ) have completely filled  $ns^2np^6$  electronic configuration in their valence shell.
- (ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

**Note :** The reactivity of noble gases has been investigated occasionally, In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as  $O_2^+ PtF_6^-$ . He, then realised that the first ionisation enthalpy of molecular oxygen ( $1175 \text{ kJmol}^{-1}$ ) was almost identical with that of xenon ( $1170 \text{ kJ mol}^{-1}$ ). He made efforts to prepare same type of compound with Xe and was successful in preparing another red colour compound  $Xe^+PtF_6^-$  by mixing  $PtF_6$  and xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised. The compounds of krypton are fewer. Only the difluoride ( $KrF_2$ ) has been studied in detail. Compounds of radon have not been isolated but only identified (e.g.,  $RnF_2$ ) by radiotracer technique. No true compounds of Ar, Ne or He are yet known.

**FLUORINEDES OF XENON**

**Preparation**

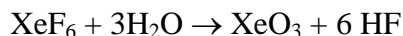
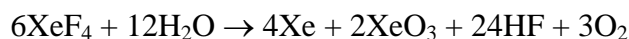
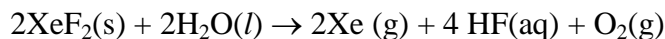


### Physical properties

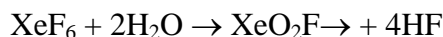
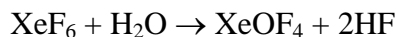
XeF<sub>2</sub>, XeF<sub>4</sub> and XeF<sub>6</sub> are colourless crystalline solids and sublime readily at 298 K.

### Chemical properties

#### (i) Hydrolysis :



Partial hydrolysis of XeF<sub>6</sub> gives oxyfluorides, XeOF<sub>4</sub> and XeO<sub>2</sub>F<sub>2</sub>.



#### Note : Hydrolysis in alkaline medium



Xenate ion



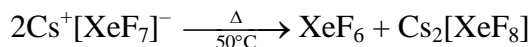
#### (ii) As fluorinating agents : They are powerful fluorinating agents.



#### (iii) As fluoride donar



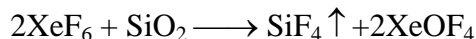
#### (iv) As Fluoride acceptor



(alkali metals fluoride)

#### (v) Reaction with SiO<sub>2</sub>

SiO<sub>2</sub> also converts XeF<sub>6</sub> into XeOF<sub>4</sub>



violet

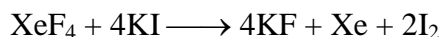
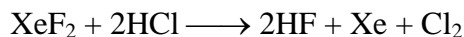
Similarly, XeO<sub>3</sub> + XeOF<sub>4</sub>  $\longrightarrow$  2XeO<sub>2</sub>F<sub>2</sub> | XeO<sub>3</sub> + 2XeF<sub>6</sub>  $\longrightarrow$  3XeOF<sub>4</sub>

**(vi) Oxidizing properties**

H<sub>2</sub> reduces Xe – fluorides to Xe



Xe – fluorides oxidise Cl<sup>-</sup> to Cl<sub>2</sub> and I<sup>-</sup> to I<sub>2</sub>

**Uses of helium :**

- (i) He a non-inflammable and light gas. Hence, it is used in filling balloons for meteorological observations.
- (ii) It is also used in gas-cooled nuclear reactors.
- (iii) It is used in cryoscopy to obtain the very low temperature required for superconductor and laser  
(b.p. 4.2 K) finds use as cryogenic agent for carrying out various experiments at low temperatures.
- (iv) It is used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems for clinical diagnosis.
- (v) It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood. He is used in preference to N<sub>2</sub> to dil. O<sub>2</sub> in the gas cylinders used by divers. This is because N<sub>2</sub> is quite soluble in blood, so a sudden change in pressure causes degassing and gives bubbles of N<sub>2</sub> in the blood. This causes the painful condition called bends. He is slightly soluble so the risk of bends is reduced.

**USES OF NEON :**

- (i) Ne is used in discharge tubes and fluorescent bulbs for advertisement display purposes.
- (ii) Neon bulbs are used in botanical gardens and in green houses.

**USES OF ARGON :**

- (i) Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys) and for filling electric bulbs.
- (ii) It is also used in the laboratory for handling substances that are air-sensitive.

**USES OF XENON AND KRYPTON :**

There are no significant uses of Xenon and Krypton. They are used in light bulbs designed for special purposes.

### SOLVED EXAMPLE

**1.** Though nitrogen exhibits +5 oxidation state, it does not form pentahalide. Give reason.

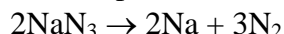
**Sol.** Nitrogen with  $n = 2$ , has s and p orbitals only. It does not have d orbitals to expand its covalency beyond four. That is why it does not form pentahalide.

2.  $\text{PH}_3$  has lower boiling point than  $\text{NH}_3$ . Why?

**Sol.** Unlike  $\text{NH}_3$ ,  $\text{PH}_3$  molecules are not associated through hydrogen bonding in liquid state. That is why the boiling point of  $\text{PH}_3$  is lower than  $\text{NH}_3$ .

**3.** Write the reaction of thermal decomposition of sodium azide.

**Sol.** Thermal decomposition of sodium azide gives dinitrogen gas.

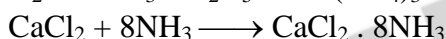
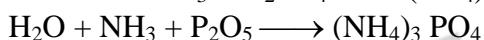


**4.** Why does  $\text{NH}_3$  act as a Lewis base ?

**Sol.** Nitrogen atom in  $\text{NH}_3$  has one lone pair of electrons which is available for donation. Therefore, it acts as a Lewis base.

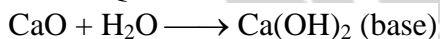
**5.**  $\text{NH}_3$  can't be dried by  $\text{H}_2\text{SO}_4$ ,  $\text{P}_2\text{O}_5$  and anh.  $\text{CaCl}_2$

**Sol.** because :  $2\text{NH}_3 + \text{H}_2\text{SO}_4 \longrightarrow (\text{NH}_4)_2 \text{SO}_4$



forms adduct

Quick lime is used for this purpose



NH<sub>3</sub> (base)

Hence no  
interaction

**6. Why does  $\text{NO}_2$  dimerise ?**

**Sol.**  $\text{NO}_2$  contains odd number of valence electrons. It behaves as a typical odd molecule. On dimerisation, it is converted to stable  $\text{N}_2\text{O}_4$  molecule with even number of electrons.

**7.** In what way can it be proved that  $\text{PH}_3$  is basic in nature?

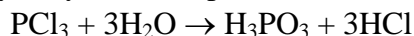
**Sol.**  $\text{PH}_3$  reacts with acids like HI to form  $\text{PH}_4\text{I}$  which shows that it is basic in nature.



Due to lone pair on phosphorus atom,  $\text{PH}_3$  is acting as a Lewis base in the above reaction.

8. Why does  $\text{PCl}_3$  fume in moisture ?

**Sol.**  $\text{PCl}_3$  hydrolyses in the presence of moisture giving fumes of  $\text{HCl}$ .



9. Are all the five bonds in  $\text{PCl}_5$  molecule equivalent? Justify your answer.

**Sol.**  $\text{PCl}_5$  has a trigonal bipyramidal structure and the three equatorial P-Cl bonds are equivalent, while the two axial bonds are different and longer than equatorial bonds.

- 10.** How do you account for the reducing behaviour of  $\text{H}_3\text{PO}_2$  on the basis of its structure?
- Sol.** In  $\text{H}_3\text{PO}_2$ , two H atoms are bonded directly to P atom which imparts reducing character to the acid.
- 11.** Elements of Group 16 generally show lower value of first ionisation enthalpy compared to the corresponding periods of group 15. Why?
- Sol.** Due to extra stable half-filled p orbitals electronic configurations of Group 15 elements, larger amount of energy is required to remove electrons compared to Group 16 elements.
- 12.**  $\text{H}_2\text{S}$  is less acidic than  $\text{H}_2\text{Te}$ . Why?
- Sol.** Due to the decrease in bond (E–H) dissociation enthalpy down the group, acidic character increases.
- 13.** Which form of sulphur shows paramagnetic behaviour ?
- Sol.** In vapour state sulphur partly exists as  $\text{S}_2$  molecule which has two unpaired electrons in the antibonding  $\pi^*$  orbitals like  $\text{O}_2$  and, hence, exhibits paramagnetism.
- 14.** What happens when  
(i) Concentrated  $\text{H}_2\text{SO}_4$  is added to calcium fluoride  
(ii)  $\text{SO}_3$  is passed through water?
- Sol.** (i) It forms hydrogen fluoride  

$$\text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + 2\text{HF}$$
  
(ii) It dissolves  $\text{SO}_3$  to give  $\text{H}_2\text{SO}_4$ .  

$$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$$
- 15.** Halogens have maximum negative electron gain enthalpy in the respective periods of the periodic table. Why?
- Sol.** Halogens have the smallest size in their respective periods and therefore high effective nuclear charge.  
As a consequence, they readily accept one electron to acquire noble gas electronic configuration.
- 16.** Although electron gain enthalpy of fluorine is less negative as compared to chlorine, fluorine is a stronger oxidising agent than chlorine. Why?
- Sol.** It is due to  
(i) low enthalpy of dissociation of F–F bond  
(ii) high hydration enthalpy of  $\text{F}^-$
- 17.** Fluorine exhibits only –1 oxidation state whereas other halogens exhibit + 1, + 3, + 5 and + 7 oxidation states also. Explain.
- Sol.** Fluorine is the most electronegative element and cannot exhibit any positive oxidation state. Other halogens have d orbitals and therefore, can expand their octets and show + 1, + 3, + 5 and + 7 oxidation states also.

18. Write the balanced chemical equation for the reaction of  $\text{Cl}_2$  with hot and concentrated  $\text{NaOH}$ . Is this reaction a disproportionation reaction? Justify.

**Sol.**  $3\text{Cl}_2 + 6\text{NaOH} \rightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$   
Yes, chlorine from zero oxidation state is changed to  $-1$  and  $+5$  oxidation states.

19.  $\text{CaF}_2$  used in HF prep<sup>n</sup>. must be free from  $\text{SiO}_2$ . Explain.

**Ans.**  $\text{CaF}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + \text{HF}$   
If  $\text{SiO}_2$  present as impurity  
 $4\text{HF} + \text{SiO}_2 \longrightarrow \text{SiF}_4 + 2\text{H}_2\text{O}$   
 $\text{SiF}_4 + 2\text{HF} \longrightarrow \text{H}_2[\text{SiF}_6]$

Hence presence of one molecule  $\text{SiO}_2$   
Consume 6 molecule of HF

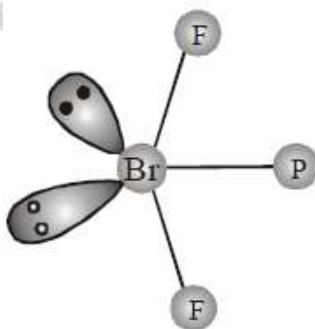
HF can not be stored in glass vessel due to same reason.

20. When  $\text{HCl}$  reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride. Why?

**Sol.** Its reaction with iron produces  $\text{H}_2$ .  
 $\text{Fe} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2$   
 Liberation of hydrogen prevents the formation of ferric chloride.

21. Discuss the molecular shape of  $\text{BrF}_3$  on the basis of VSEPR theory.

**Sol.** The central atom Br has seven electrons in the valence shell. Three of these will form electronpair bonds with three fluorine atoms leaving behind four electrons. Thus, there are three bond pairs and two lone pairs. According to VSEPR theory, these will occupy the corners of a trigonal bipyramid.  
 The two lone pairs will occupy the equatorial positions to minimise lone pair-lone pair and the bond pair-lone pair repulsions which are greater than the bond pair-bond pair repulsions. In addition, the axial fluorine atoms will be bent towards the equatorial fluorine in order to minimize the lone-pair-lone pair repulsions. The shape would be that of a slightly bent 'T'.



22. Why are the elements of Group 18 known as noble gases ?

**Sol.** The elements present in Group 18 have their valence shell orbitals completely filled and, therefore, react with a few elements only under certain conditions. Therefore, they are now known as noble gases.

23. Noble gases have very low boiling points. Why?

**Sol.** Noble gases being monoatomic have no interatomic forces except weak dispersion forces and therefore, they are liquefied at very low temperatures. Hence, they have low boiling points.



**24.** Does the hydrolysis of  $\text{XeF}_6$  lead to a redox reaction?

**Sol.** No, the products of hydrolysis are  $\text{XeOF}_4$  and  $\text{XeO}_2\text{F}_2$  where the oxidation states of all the elements remain the same as it was in the reacting state.

25. Standard electrode potential values,  $E^\ominus$  for  $\text{Al}^{3+}/\text{Al}$  is  $-1.66\text{ V}$  and that of  $\text{Tl}^{3+}/\text{Tl}$  is  $+1.26\text{ V}$ . Predict about the formation of  $\text{M}^{3+}$  ion in solution and compare the electropositive character of the two metals.

**Sol.** Standard electrode potential values for two half cell reactions suggest that aluminium has high tendency to make  $\text{Al}^{3+}(\text{aq})$  ions, whereas  $\text{Tl}^{3+}$  is not only unstable in solution but is a powerful oxidizing agent also. Thus  $\text{Tl}^{+}$  is more stable in solution than  $\text{Tl}^{3+}$ . Aluminium being able to form +3 ions easily, is more electropositive than thallium.

**26.** White fumes appear around the bottle of anhydrous aluminium chloride. Give reason.

**Sol.** Anhydrous aluminium chloride is partially hydrolysed with atmospheric moisture to liberate HCl gas. Moist HCl appears white in colour.

**27.** Boron is unable to form  $\text{BF}_6^{3-}$  ion. Explain.

**Sol.** Due to non-availability of d orbitals, boron is unable to expand its octet. Therefore, the maximum covalence of boron cannot exceed 4.

**28.** Why is boric acid considered as a weak acid ?

**Sol.** Because it is not able to release  $\text{H}^+$  ions on its own. It receives  $\text{OH}^-$  ions from water molecule to complete its octet and in turn releases  $\text{H}^+$  ions.

**29.** Select the member(s) of group 14 that (i) forms the most acidic dioxide, (ii) is commonly found in +2 oxidation state, (iii) used as semiconductor.

**Sol.** (i) carbon (ii) lead (iii) silicon and germanium

**30.**  $[\text{SiF}_6]^{2-}$  is known whereas  $[\text{SiCl}_6]^{2-}$  not. Give possible reasons.

**Sol.** The main reasons are :

- (i) six large chloride ions cannot be accommodated around  $\text{Si}^{4+}$  due to limitation of its size.
- (ii) interaction between lone pair of chloride ion and  $\text{Si}^{4+}$  is not very strong.

**31.** Diamond is covalent, yet it has high melting point. Why ?

**Sol.** Diamond has a three-dimensional network involving strong C—C bonds, which are very difficult to break and, in turn has high melting point.

**32.**  $\text{SiH}_4$  is more reactive than  $\text{CH}_4$ . Explain

## Reasons

(i)  $\overline{\text{Si}^{\delta+} - \text{H}^{\delta-}}$  in  $\text{C}^{\delta-} - \text{H}^{\delta+}$

C – more electronegative than H  
Si less electronegative than H

So bond polarity is reversed when  $\text{Nu}^-$  attacks, it faces repulsion in C but not in Si

(ii) Silicon is having vacant d orbital which is not in case of carbon

(iii) Silicon is larger in size compared to C. By which the incoming  $\text{Nu}^-$  doesn't face any steric hindrance to attack at Si whereas  $\text{CH}_4$  is tightly held from all sides.

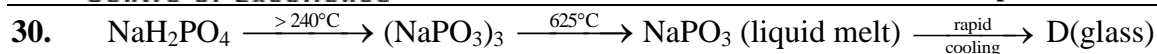
**EXERCISE-I**

Only one option is correct :

- PH<sub>3</sub>(Phosphine) when passed in aqueous solution of CuSO<sub>4</sub> it produce -  
 (A) Blue precipitate of Cu(OH)<sub>2</sub> (B) dark blue solution of [Cu(PH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub>  
 (C) Black precipitate of Cu<sub>3</sub>P<sub>2</sub> (D) Colorless solution of [Cu(H<sub>2</sub>O)<sub>4</sub>]<sup>+</sup>
- H<sub>3</sub>PO<sub>2</sub>  $\xrightarrow{\Delta}$  (X) + PH<sub>3</sub> ; is  
 (A) Dehydration reaction (B) Oxidation reaction  
 (C) Disproportionation reaction (D) Dephosphorelation reaction
- Which of the following species is not a pseudohalide?  
 (A) CNO<sup>-</sup> (B) RCOO<sup>-</sup> (C) OCN<sup>-</sup> (D) N<sub>3</sub><sup>-</sup>
- An orange solid (X) on heating, gives a colourless gas (Y) and a only green residue (Z). Gas (Y) on treatment with Mg, produces a white solid substance .....  
 (A) Mg<sub>3</sub>N<sub>2</sub> (B) MgO (C) Mg<sub>2</sub>O<sub>3</sub> (D) MgCl<sub>2</sub>
- Conc. HNO<sub>3</sub> is yellow coloured liquid due to  
 (A) dissolution of NO in conc. HNO<sub>3</sub> (B) dissolution of NO<sub>2</sub> in conc. HNO<sub>3</sub>  
 (C) dissolution of N<sub>2</sub>O in conc. HNO<sub>3</sub> (D) dissolution of N<sub>2</sub>O<sub>3</sub> in conc. HNO<sub>3</sub>
- A gas at low temperature does not react with the most of compounds. It is almost inert and is used to create inert atmosphere in bulbs. The combustion of this gas is exceptionally an endothermic reaction. Based on the given information, we can conclude that the gas is  
 (A) oxygen (B) nitrogen  
 (C) carbon mono-oxide (D) hydrogen
- When chlorine gas is passed through an aqueous solution of a potassium halide in the presence of chloroform, a violet colouration is obtained. On passing more of chlorine water, the violet colour is disappeared and solution becomes colourless. This test confirms the presence of ..... in aqueous solution.  
 (A) chlorine (B) fluorine (C) bromine (D) iodine
- H<sub>3</sub>PO<sub>2</sub>  $\xrightarrow{140^{\circ}\text{C}}$  A  $\xrightarrow{220^{\circ}\text{C}}$  B  $\xrightarrow{320^{\circ}\text{C}}$  C  
 Compound (C) is  
 (A) H<sub>2</sub>PO<sub>3</sub> (B) H<sub>3</sub>PO<sub>3</sub> (C) (HPO<sub>3</sub>)<sub>n</sub> (D) H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>
- An explosive compound (A) reacts with water to produce NH<sub>4</sub>OH and HOCl. Then, the compound (A), is  
 (A) TNG (B) NCl<sub>3</sub> (C) PCl<sub>3</sub> (D) HNO<sub>3</sub>

10. An inorganic compound (A) made of two most occurring elements into the earth crust, having a polymeric tetra-headral network structure. With carbon, compound (A) produces a poisonous gas (B) which is the most stable diatomic molecule. Compounds (A) and (B) will be  
(A)  $\text{SiO}_2$ ,  $\text{CO}_2$       (B)  $\text{SiO}_2$ , CO      (C) SiC, CO      (D)  $\text{SiO}_2$ ,  $\text{N}_2$
11. A sulphate of a metal (A) on heating evolves two gases (B) and (C) and an oxide (D). Gas (B) turns  $\text{K}_2\text{Cr}_2\text{O}_7$  paper green while gas (C) forms a trimer in which there is no S-S bond. Compound (D) with HCl, forms a Lewis acid (E) which exists as a dimer. Compounds (A), (B), (C), (D) and (E) are respectively  
(A)  $\text{FeSO}_4$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeCl}_3$       (B)  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeCl}_3$   
(C)  $\text{FeS}$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{FeSO}_4$ ,  $\text{FeCl}_3$       (D)  $\text{FeS}$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{Fe}_2(\text{PO}_4)_3$ ,  $\text{FeCl}_2$
12. A tetra-atomic molecule (A) on reaction with nitrogen(I)oxide, produces two substances (B) and (C). (B) is a dehydrating agent in its monomeric form while substance (C) is a diatomic gas which shows almost inert behaviour. The substances (A) and (B) and (C) respectively will be  
(A)  $\text{P}_4$ ,  $\text{P}_4\text{O}_{10}$ ,  $\text{N}_2$       (B)  $\text{P}_4$ ,  $\text{N}_2\text{O}_5$ ,  $\text{N}_2$       (C)  $\text{P}_4$ ,  $\text{P}_2\text{O}_3$ , Ar      (D)  $\text{P}_4$ ,  $\text{P}_2\text{O}_3$ ,  $\text{H}_2$
13. First compound of inert gases was prepared by scientist Neil Barthlete in 1962. This compound is  
(A)  $\text{XePtF}_6$       (B)  $\text{XeO}_3$       (C)  $\text{XeF}_6$       (D)  $\text{XeOF}_4$
14. Carbongene has X% of  $\text{CO}_2$  and is used as an antidote for poisoning of Y. Then, X and Y are  
(A) X = 95% and Y = lead poisoning      (B) X = 5% and Y = CO poisoning  
(C) X = 30% and Y =  $\text{CO}_2$  poisoning      (D) X = 45% and Y = CO poisoning
15. The correct order of acidic strength of oxides of nitrogen is  
(A)  $\text{NO} < \text{NO}_2 < \text{N}_2\text{O} < \text{N}_2\text{O}_3 < \text{N}_2\text{O}_5$       (B)  $\text{N}_2\text{O} < \text{NO} < \text{N}_2\text{O}_3 < \text{N}_2\text{O}_4 < \text{N}_2\text{O}_5$   
(C)  $\text{NO} < \text{N}_2\text{O} < \text{N}_2\text{O}_3 < \text{N}_2\text{O}_5 < \text{N}_2\text{O}_4$       (D)  $\text{NO} < \text{N}_2\text{O} < \text{N}_2\text{O}_5 < \text{N}_2\text{O}_3 < \text{N}_2\text{O}_4$
16.  $\text{H}_3\text{BO}_3 \xrightarrow{\text{T}_1} \text{X} \xrightarrow{\text{T}_2} \text{Y} \xrightarrow{\text{redhot}} \text{B}_2\text{O}_3$   
If  $\text{T}_1 < \text{T}_2$  then X and Y respectively are  
(A) X = Metaboric acid and Y = Tetraboric acid  
(B) X = Tetraboric acid and Y = Metaboric acid  
(C) X = Borax and Y = Metaboric acid  
(D) X = Tetraboric acid and Y = Borax
17. When conc.  $\text{H}_2\text{SO}_4$  was treated with  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , CO gas was evolved. By mistake, somebody used dilute  $\text{H}_2\text{SO}_4$  instead of conc.  $\text{H}_2\text{SO}_4$  then the gas evolved was  
(A) CO      (B) HCN      (C)  $\text{N}_2$       (D)  $\text{CO}_2$
18. An inorganic white crystalline compound (A) has a rock salt structure. (A) on reaction with conc.  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$ , evolves a pungent smelling, greenish-yellow gas (B). Compound (A) gives white ppt. of (C) with  $\text{AgNO}_3$  solution. Compounds (A), (B) and (C) will be respectively  
(A) NaCl,  $\text{Cl}_2$ , Agcl      (B) NaBr,  $\text{Br}_2$ , NaBr  
(C) NaCl,  $\text{Cl}_2$ ,  $\text{Ag}_2\text{SO}_4$       (D)  $\text{Na}_2\text{CO}_3$ ,  $\text{CO}_2$ ,  $\text{Ag}_2\text{CO}_3$

19.  $\text{RCl} \xrightarrow[\text{Si}]{\text{Cu-powder}} \text{R}_2\text{SiCl}_2 \xrightarrow{\text{H}_2\text{O}} \text{R}_2\text{Si(OH)}_2 \xrightarrow{\text{condensation}} \text{A}$   
Compound (A) is  
(A) a linear silicone (B) a chlorosilane (C) a linear silane (D) a network silane
20. When oxalic acid reacts with cone.  $\text{H}_2\text{SO}_4$ , two gases produced are of neutral and acidic in nature respectively. Potassium hydroxide absorbs one of the two gases. The product formed during this absorption and the gas which gets absorbed are respectively  
(A)  $\text{K}_2\text{CO}_3$  and  $\text{CO}_2$  (B)  $\text{KHCO}_3$  and  $\text{CO}_2$  (C)  $\text{K}_2\text{CO}_3$  and  $\text{CO}$  (D)  $\text{KHCO}_3$  and  $\text{CO}$
21. Conc.  $\text{H}_2\text{SO}_4$  cannot be used to prepare  $\text{HBr}$  from  $\text{NaBr}$  because it  
(A) reacts slowly with  $\text{NaBr}$  (B) oxidises  $\text{HBr}$   
(C) reduces  $\text{HBr}$  (D) disproportionates  $\text{HBr}$
22. Ammonia can be dried by  
(A) conc.  $\text{H}_2\text{SO}_4$  (B)  $\text{P}_4\text{O}_{10}$  (C)  $\text{CaO}$  (D) anhydrous  $\text{CaCl}_2$
23. When chlorine reacts with a gas X, an explosive inorganic compound Y is formed. Then X and Y will be  
(A)  $\text{X} = \text{O}_2$  and  $\text{Y} = \text{NCl}_3$  (B)  $\text{X} = \text{NH}_3$  and  $\text{Y} = \text{NCl}_3$   
(C)  $\text{X} = \text{O}_2$  and  $\text{Y} = \text{NH}_4\text{Cl}$  (D)  $\text{X} = \text{NH}_3$  and  $\text{Y} = \text{NH}_4\text{Cl}$
24.  $\text{HNO}_3 + \text{P}_4\text{O}_{10} \longrightarrow \text{HPO}_3 + \text{A}$ ; the product A is  
(A)  $\text{N}_2\text{O}$  (B)  $\text{N}_2\text{O}_3$  (C)  $\text{NO}_2$  (D)  $\text{N}_2\text{O}_5$
25. Which of the following is the correct order of acidic strength?  
(A)  $\text{Cl}_2\text{O}_7 > \text{SO}_3 > \text{P}_4\text{O}_{10}$  (B)  $\text{CO}_2 > \text{N}_2\text{O}_5 > \text{SO}_3$   
(C)  $\text{Na}_2\text{O} > \text{MgO} > \text{Al}_2\text{O}_3$  (D)  $\text{K}_2\text{O} > \text{CaO} > \text{MgO}$
26.  $\text{Ca} + \text{C}_2 \longrightarrow \text{CaC}_2 \xrightarrow{\text{N}_2} \text{A}$   
Compound (A) is used as a/an  
(A) fertilizer (B) dehydrating agent (C) oxidising agent (D) reducing agent
27. A gas which exists in three allotropic forms a, b and g is  
(A)  $\text{SO}_2$  (B)  $\text{SO}_3$  (C)  $\text{CO}_2$  (D)  $\text{NH}_3$
28. A red coloured mixed oxide (X) on treatment with cone.  $\text{HNO}_3$  gives a compound (Y). (Y) with  $\text{HCl}$ , produces a chloride compound (Z) which can also be produced by treating (X) with cone.  $\text{HCl}$ .  
Compounds (X), (Y), and (Z) will be  
(A)  $\text{Mn}_3\text{O}_4$ ,  $\text{MnO}_2$ ,  $\text{MnCl}_2$  (B)  $\text{Pb}_3\text{O}_4$ ,  $\text{PbO}_2$ ,  $\text{PbCl}_2$   
(C)  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeCl}_2$  (D)  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeCl}_3$
29. One mole of calcium phosphide on reaction with excess of water gives  
(A) one mole of phosphine  
(B) two moles of phosphoric acid  
(C) two moles of phosphine  
(D) one mole of phosphorus penta-oxide

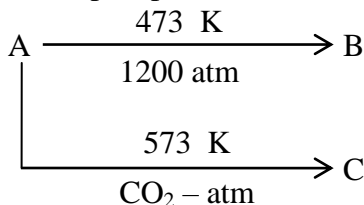


Sodium trimetaphosphate

Compound (D) is known as

- (A) Microcosmic salt (B) Graham's salt (C) Reimann's salt (D) Switzer's Salt

31. Three allotropes (A), (B) and (C) of phosphorous in the following change are respectively



(A) white, b-black, red

(B) b-black, white, red

(C) red, b-black, white

(D) red, violet, b-black

32. When an inorganic compound reacts with  $\text{SO}_2$  in aqueous medium, produces (A). (A) on reaction with  $\text{Na}_2\text{CO}_3$ , gives compound (B) which with sulphur, gives a substance (C) used in photography.

Compound (C) is

(A)  $\text{Na}_2\text{S}$

(B)  $\text{Na}_2\text{S}_2\text{O}_7$

(C)  $\text{Na}_2\text{SO}_4$

(D)  $\text{Na}_2\text{S}_2\text{O}_3$

33.  $\text{B(OH)}_3 + \text{NaOH} \rightleftharpoons \text{NaBO}_2 + \text{Na[B(OH)}_4] + \text{H}_2\text{O}$

How can this reaction is made to proceed in forward direction?

(A) addition of cis 1,2 diol

(B) addititon of borax

(C) addition of trans 1,2 diol

(D) addition of  $\text{Na}_2\text{HPO}_4$

34. Which is the compound responsible for the flickering light called **will-o-the-wisp**, some times seen in the Marsh.

(A)  $\text{PH}_3$

(B)  $\text{P}_2\text{H}_4$

(C)  $\text{H}_2\text{S}$

(D)  $\text{PH}_3 + \text{H}_2\text{S}$

35. The gun powder is consisting of '\_\_\_\_\_' + sulphur + Charcoal what is the missing substance for gun powder

(A)  $\text{LiNO}_3$

(B)  $\text{NH}_4\text{NO}_2$

(C)  $\text{KNO}_3$

(D) (A) and (B) mixture

36. An aqueous solution of borax is

(A) Neutral

(B) Amphoteric

(C) Basic

(D) Acidic

37. Boric acid is polymeric due to

(A) Its acidic nature

(B) The presence of hydrogen bonds

(C) Its monobasic nature

(D) Its geometry

38. The type of hybridisation of boron in diborane is

(A) sp

(B)  $\text{sp}^2$

(C)  $\text{sp}^3$

(D)  $\text{dsp}^2$

39. Thermodynamically the most stable form of carbon is

(A) Diamond

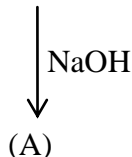
(B) Graphite

(C) Fullerenes

(D) Coal

40. Elements of group 14  
 (A) Exhibit oxidation state of + 4 only (B) Exhibit oxidation state of +2 and +4 only  
 (C) Form  $M^{2-}$  and  $M^{4+}$  ions (D) Form  $M^{2+}$  and  $M^{4+}$  ions

41.  $A + Br_2 \rightarrow N_2 + (B)$



if A is a basic gas then identified (A) and (B)

- (A)  $NH_3$ ,  $NH_4Br$  (B)  $NH_3$ ,  $N_2O$  (C)  $NH_3$ ,  $N_2O_5$  (D) None of these

**Question No. 50 to 55 (6 questions)**

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:

- (A) if both (A) and (R) are true and (R) is the correct explanation of (A)  
 (B) if both (A) and (R) are true but (R) is not correct explanation of (A)  
 (C) if (A) is true but (R) is false  
 (D) if (A) is false and (R) is true

42. **Assertion :** Borax bead test is applicable only to coloured salt.  
**Reason :** In borax bead test, coloured salts are decomposed to give coloured metal meta borates.
43. **Assertion :** Aluminium and zinc metal evolve  $H_2$  gas from NaOH solution  
**Reason :** Several non-metals such as P, S, Cl, etc. yield a hydride instead of  $H_2$  gas from NaOH
44. **Assertion :** Conc.  $H_2SO_4$  can not be used to prepare pure HBr from NaBr  
**Reason :** It reacts slowly with NaBr.
45. **Assertion :** Oxygen is more electronegative than sulphur, yet  $H_2S$  is acidic, while  $H_2O$  is neutral.  
**Reason :** H–S bond is weaker than O–H bond.
46. **Assertion :** Chlorine gas disproportionates in hot & conc. NaOH solution.  
**Reason :** NaCl and NaOCl are formed in the above reaction.
47. **Assertion :** Liquid  $IF_5$  conducts electricity.  
**Reason :** Liquid  $IF_5$  self ionizes as,  $2IF_5 \rightleftharpoons IF_4^+ + IF_6^-$

**EXERCISE-II**

*One or more than one option may be correct :*

- When a compound X reacts with ozone in aqueous medium, a compound Y is produced. Ozone also reacts with Y and produces compound Z. Z acts as an oxidising agent, then X, Y and Z will be  
 (A)  $X = \text{HI}$ ,  $Y = \text{I}_2$  and  $Z = \text{HIO}_3$   
 (B)  $X = \text{KI}$ ,  $Y = \text{I}_2$  and  $Z = \text{HIO}_3$   
 (C)  $X = \text{KI}$ ,  $Y = \text{I}_2$  and  $Z = \text{HIO}_4$   
 (D)  $X = \text{HI}$ ,  $Y = \text{I}_2$  and  $Z = \text{HIO}_4$
- Which of the following statements is/are correct regarding  $\text{B}_2\text{H}_6$ ?  
 (A) banana bonds are longer but stronger than normal B–H bonds  
 (B)  $\text{B}_2\text{H}_6$  is also known as 3c–2e compound  
 (C) the hybrid state of B in  $\text{B}_2\text{H}_6$  is  $\text{sp}^3$  while that of  $\text{sp}^2$  in  $\text{BH}_3$   
 (D) it cannot be prepared by reacting  $\text{BF}_3$  with  $\text{LiBH}_3$  in the presence of dry ether
- Which of the following statements is/are correct regarding inter-halogen compounds of  $\text{AB}_x$  types?  
 (A) x may be 1,3,5 and 7  
 (B) A is a more electronegative halogen than B  
 (C)  $\text{FBr}_3$  cannot exist  
 (D) The interhalogens are generally more reactive than the halogens (except  $\text{F}_2$ ) due to weaker A–X bonds compared to X–X bond.
- When an inorganic compound (X) having 3e-2e as well as 2e-2e bonds reacts with ammonia gas at a certain temperature, gives a compound (Y) iso-structural with benzene. Compound (X) with ammonia at a high temperature, produces a hard substance (Z). Then  
 (A) (X) is  $\text{B}_2\text{H}_6$   
 (B) (Z) is known as inorganic graphite  
 (C) (Z) having structure similar to graphite  
 (D) (Z) having structure similar to (X)
- Boric acid  
 (A) exists in polymeric form due to inter-molecular hydrogen bonding.  
 (B) is used in manufacturing of optical glasses.  
 (C) is a tri-basic acid  
 (D) with borax, it is used in the preparation of a buffer solution.

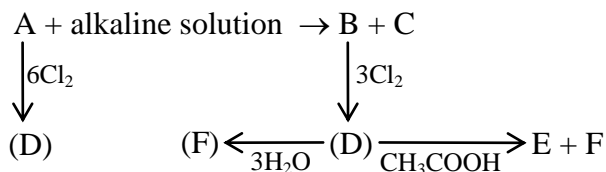
6. The correct statement(s) related to allotropes of carbon is/are  
 (A) graphite is the thermodynamically most stable allotrope of carbon and having a two dimensional sheet like structure of hexagonal rings of carbon ( $sp^2$ )  
 (B) diamond is the hardest allotrope of carbon and having a three dimensional network structure of  $C(sp^3)$   
 (C) fullerene ( $C_{60}$ ) is recently discovered non-crystalline allotrope of carbon having a football-like structure.  
 (D) Vander Waal's force of attraction acts between the layers of graphite  $6.14 \text{ \AA}$  away from each other
7.  $Al_2(SO_4)_3 + NH_4OH \longrightarrow X$ , then  
 (A) X is a white coloured compound (B) X is insoluble in excess of  $NH_4OH$   
 (C) X is soluble in NaOH (D) X cannot be used as an antacid
8. The species that undergo(es) disproportionation in an alkaline medium is/are  
 (A)  $Cl_2$  (B)  $MnO_4^{2-}$  (C)  $P_4$  (D)  $ClO_4^-$
9. Select correct statement(s):  
 (A) Borax is used as a buffer  
 (B) 1 M borax solution reacts with equal volumes of 2 M HCl solution  
 (C) Titration of borax can be made using methyl orange as the indicator  
 (D) Coloured bead obtained in borax-bead test contains metaborate
10. Which of the following is / are correct for group 14 elements?  
 (A) The stability of dihalides are in the order  $CX_2 < SiX_2 < GeX_2 < SnX_2 < PbX_2$   
 (B) The ability to form pp–pp multiple bonds among themselves increases down the group  
 (C) The tendency for catenation decreases down the group  
 (D) They all form oxides with the formula  $MO_2$ .
11. Zeolite is used in which of the following cases :  
 (A) Conversion of alcohols into gasoline (B) Cracking of hydrocarbon  
 (C) Isomerisation of hydrocarbons (D) Softning of hard water
12. Which of the following oxides are mixed oxide :  
 (A)  $PbO_2$  (B)  $SnO_2$  (C)  $Pb_2O_3$  (D)  $Pb_3O_4$
13. Which of the following oxide(s) gives brown ppt on reaction with conc.  $HNO_3$  :  
 (A)  $PbO$  (B)  $SnO$  (C)  $Pb_2O_3$  (D)  $Pb_3O_4$



14. Which of the following reaction produces  $\text{PH}_3$  :  
 (A)  $\text{Ca}_3\text{P}_2 + \text{H}_2\text{O} \rightarrow$  (B)  $\text{P}_4 + \text{NaOH} \rightarrow$  (C)  $\text{PH}_4\text{I} + \text{KOH} \rightarrow$  (D)  $\text{H}_3\text{PO}_2 \xrightarrow{\Delta}$
15. Which of the following element of chalcogen group can form  $\text{MX}_2$  type of compound where  $\text{X} = \text{Cl}$  and  $\text{Br}$  :  
 (A) O (B) S (C) Se (D) Te
16.  $\text{Ca}_2\text{B}_6\text{O}_{11} + \text{Na}_2\text{CO}_3 \xrightarrow{\Delta} [\text{X}] + \text{CaCO}_3 + \text{NaBO}_2$  (Unbalanced equation)  
 Correct statement for [X]  
 (A) Structure of anion of crystalline (X) has one boron atom  $\text{sp}^3$  hybridised and other three boron atoms  $\text{sp}^2$  hybridised  
 (B) (X) with  $\text{NaOH(aq.)}$  gives a compound which on reaction with  $\text{H}_2\text{O}_2$  in alkaline medium yields a compound used as brightner in soaps  
 (C) Hydrolysis of (X) with  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  yields a compound which on reaction with  $\text{HF}$  gives fluoroboric acid  
 (D) [X] on heating with cobalt salt in oxidising flame gives blue coloured bead
17. (A)  $+ 2\text{C} \xrightarrow[2500^\circ\text{C}]{2000^\circ\text{C to}} (\text{B}) + 2\text{CO} \uparrow$   
 (B)  $+ \text{Carbon} \xrightarrow[2500^\circ\text{C}]{2000^\circ\text{C to}} (\text{C})$   
 If A is an example of 3-d silicate then select the correct statements about (C)  
 (A) Central atom of C is  $\text{sp}^3$  hybridised  
 (B) (C) is non planar and all atoms are  $\text{sp}^3$  hybridised  
 (C) C has diamond like structure, and it is colourless when impurity is present but yellow solid at room temperature  
 (D) (C) is silicon carbide ( $\text{SiC}$ ) and it is not being affected by any acid except  $\text{H}_3\text{PO}_4$

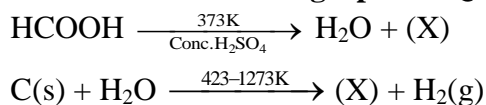
**EXERCISE-III**

**Paragraph for Question No. 1 & 2**



- When D react with  $\text{C}_2\text{H}_5\text{OH}$  then product will be  
 (A)  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{H}_3\text{PO}_4$  (B)  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{H}_3\text{PO}_3$   
 (C)  $\text{CH}_3\text{COCl}$ ,  $\text{H}_3\text{PO}_3$  (D) Only  $\text{H}_3\text{PO}_3$
- B can be absorbed by :  
 (A)  $\text{Ca}(\text{OCl})\text{Cl}$  (B)  $\text{H}_2\text{S}$  (C) Both (D) None

**Paragraph for Question No. 3 to 6**



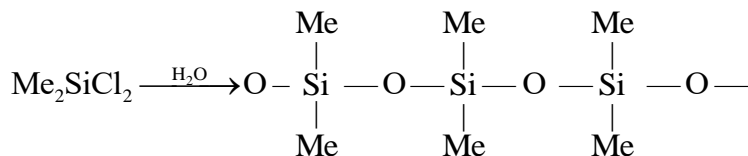
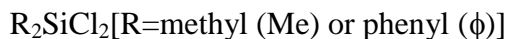
- Select the correct statement about (X)  
 (A) (X) is a colourless, odourless and almost water insoluble gas  
 (B) X is highly poisonous and burns with blue flame  
 (C) When (X) gas is passed through  $\text{PdCl}_2$  solution giving rise to black ppt  
 (D) All of these
- Mixture of (X) gas +  $\text{H}_2$  is called  
 (A) Water gas or synthesis gas (B) Producer gas  
 (C) Methane gas (D) None of these
- In second reaction when air is used instead of steam a mixed of (X) gas and  $\text{N}_2$  is produced which is called  
 (A) Water gas (B) Synthesis gas (C) Producer gas (D) Carbon dioxide gas
- Select the correct statement about (X)  
 (A) (X) gas is estimated by  $\text{I}_2\text{O}_5$   
 (C) (X) gas is the purifying agent for Ni  
 (B)  $\text{Cu}_2\text{Cl}_2$  is absorber of (X) gas  
 (D) All of these

**Paragraph for Question No. 7 & 8**

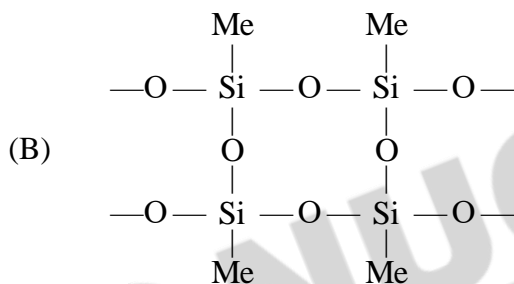
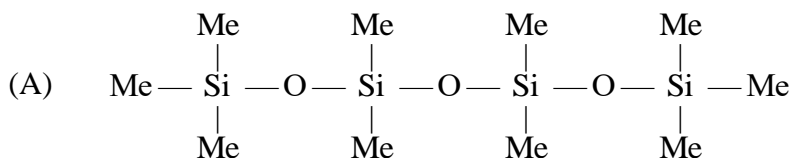
Read the following write-ups and answer the questions at the end of it.

Silicones are synthetic polymers containing repeated  $\text{R}_2\text{SiO}$  units. Since, the empirical formula is that of a ketone ( $\text{R}_2\text{CO}$ ), the name silicone has been given to these materials. Silicones can be made into oils, rubbery elastomers and resins. They find a variety of applications because of their chemical inertness, water repelling nature, heat-resistance and good electrical insulating property.

Commercial silicon polymers are usually methyl derivatives and to a lesser extent phenyl derivatives and are synthesised by the hydrolysis of

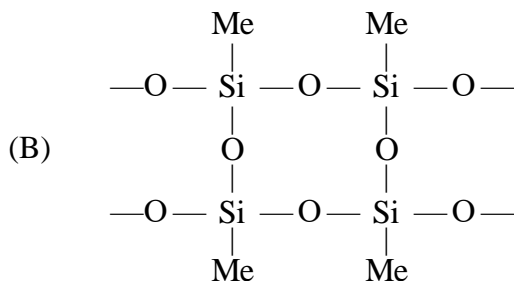
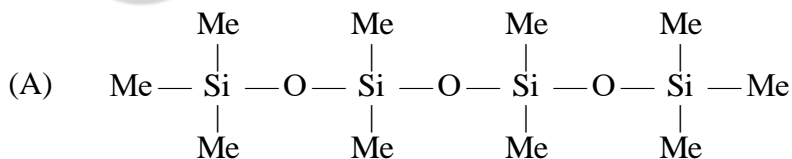


7. If we mix  $Me_3SiCl$  with  $Me_2SiCl_2$ , we get silicones of the type:



- (C) both of the above  
(D) none of the above

8. If we start with  $MeSiCl_3$  as the starting material, silicones formed is:



- (C) Both of the above  
(D) None of the above

**Paragraph for Question No. 9 & 10**

CO gas is absorbed by aqueous suspension of cuprous chloride forming the complex like  $[\text{CuCl}(\text{CO})(\text{H}_2\text{O})_2]$ .

9. Comment on the shape of the above complex.  
(A) Tetrahedral (B) TBP (C) Square planar (D) Can not be predicted
10. Choose the correct statement regarding the above molecule  
(A) Cl-atom is separated by equal angle from both of the water molecule  
(B) Magnetic moment of the above complex is 1.73 B.M.  
(C) There are two stereo isomer for the above complex.  
(D) Both (A) and (C)

**Paragraph for Question No. 11 to 12**

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of  $\text{NH}_3$  and  $\text{PH}_3$ . Phosphine is a flammable gas and is prepared from white phosphorous.

11. Among the following, the correct statement is  
(A) Phosphates have no biological significance in humans  
(B) Between nitrates and phosphates, phosphates are less abundant in earth's crust  
(C) Between nitrates and phosphates, nitrates are less abundant in earth's crust  
(D) Oxidation of nitrates is possible in soil
12. White phosphorus on reaction with NaOH gives  $\text{PH}_3$  as one of the products. This is a  
(A) dimerization reaction (B) disproportionation reaction  
(C) condensation reaction (D) precipitation reaction

13. Match List-I with List-II

**List-I (Chemical reaction)**

- (I)  $4\text{NH}_3 + 5\text{O}_2 \xrightarrow{800^\circ\text{C}/\text{Pt}} 4\text{NO} + 6\text{H}_2\text{O}$   
(II)  $4\text{HCl} + \text{O}_2 \xrightarrow{230^\circ\text{C}/\text{CuCl}_2} 2\text{Cl}_2 + 2\text{H}_2\text{O}$   
(III)  $2\text{SO}_2 + \text{O}_2 \xrightarrow{450-500^\circ/\text{V}_2\text{O}_5} 2\text{SO}_3$   
(IV)  $2\text{N}_2 + 3\text{H}_2 \xrightarrow{\text{Fe}+\text{Mo}} 2\text{NH}_3$   
(A) I-a, II-b, III-d, IV-c  
(C) I-a, II-d, III-c, IV-b

**List-II (Name of process)**

- (a) Contact process  
(b) Ostwald's process  
(c) Deacon's process  
(d) Haber's process  
(B) I-b, II-c, III-a, IV-d  
(D) I-a, II-c, III-b, IV-d

- 14.**
- | Column-I        | Column-II                             |
|-----------------|---------------------------------------|
| (P) Dry ice     | (1) Used as antidote for CO-poisoning |
| (Q) Carbongene  | (2) Used as nonstick coating          |
| (R) Carborundum | (3) Used as refrigerant               |
| (S) Teflon      | (4) Used as abrasive                  |
- Code :**
- |     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 4 | 1 | 3 | 2 |
| (C) | 3 | 1 | 4 | 2 |
- 
- 15.**
- | Column-I<br>Compound | Column-II<br>Correct statement for compounds given    |
|----------------------|---|
| (P) $\text{SnCl}_2$  | (1) Used in printing technology                       |
| (Q) Butter of tin    | (2) Used for gilding purpose (in joining gold pieces) |
| (R) Mosaic gold      | (3) Reducing agent                                    |
| (S) Pink salt        | (4) Mordant   |
- Code :**
- |     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 4 | 3 | 2 | 1 |
| (C) | 2 | 1 | 3 | 4 |
- 
- 16.**
- | Column-I (Metal) | Column-II (Correct statements)                                |
|------------------|---|
| (P) Fe           | (1) Produces NO with 20% $\text{HNO}_3$                       |
| (Q) Cu           | (2) Produces $\text{NH}_4\text{NO}_3$ with 6% $\text{HNO}_3$  |
| (R) Pb           | (3) Produces $\text{NO}_2$ with 70% $\text{HNO}_3$            |
| (S) Sn           | (4) Produces $\text{NH}_4\text{NO}_3$ with 20% $\text{HNO}_3$ |
- Code :**
- |     | P    | Q    | R    | S       |
|-----|------|------|------|---------|
| (A) | 2, 1 | 1    | 3, 4 | 2, 3    |
| (B) | 2, 3 | 1, 3 | 1, 3 | 2, 3, 4 |
| (C) | 1, 3 | 1, 2 | 3, 4 | 2       |
| (D) | 1, 4 | 2, 3 | 1, 3 | 1, 4    |

**17. Column-I (Reactions)**

- (P)  $\text{XeF}_2 + \text{PF}_5 \rightarrow$   
(Q)  $\text{XeF}_4 + \text{Pt} \rightarrow$   
(R)  $\text{XeF}_4 + \text{H}_2\text{O} \rightarrow$   
(S)  $\text{XeF}_6 + \text{CsF} \rightarrow$

**Code :**

- |     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 4 | 2 | 3 | 1 |
| (C) | 4 | 3 | 2 | 1 |

**Column-II (Correct statements)**

- (1) Fluoride of Xe acts as fluoride acceptor  
(2) Fluoride of Xe undergoes disproportion  
(3) Fluoride of Xe acts as fluorinating agent  
(4) Fluoride of Xe act as fluoride donor

- |     | P | Q | R | S |
|-----|---|---|---|---|
| (B) | 3 | 2 | 1 | 4 |
| (D) | 3 | 4 | 2 | 1 |

**18. Column-I (Substances)**

- (P)  $\text{O}_3$   
(Q) Bleaching powder  
(R)  $\text{H}_2\text{O}_2$   
(S)  $\text{HNO}_3$

**Code :**

- |     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 3 | 4 | 1 | 2 |
| (C) | 2 | 1 | 3 | 4 |

**Column-II (Can be prepared by)**

- (1) Acidification of  $\text{BaO}_2$  with  $\text{H}_3\text{PO}_4$   
(2) Birkeland Eyde process  
(3) Dry  $\text{O}_2$  is passed through a silent electrical discharge  
(4)  $\text{Cl}_2$  gas is passed through slaked lime

- |     | P | Q | R | S |
|-----|---|---|---|---|
| (B) | 1 | 3 | 4 | 2 |
| (D) | 4 | 1 | 2 | 3 |

**EXERCISE-IV (JEE-MAINS)**

- Which products are expected from the disproportionation of hypochlorous acid:  
[AIEEE-2002]  
(1)  $\text{HClO}_3$  and  $\text{Cl}_2\text{O}$  (2)  $\text{HClO}_2$  and  $\text{HClO}$   
(3)  $\text{HCl}$  and  $\text{Cl}_2\text{O}$  (4)  $\text{HCl}$  and  $\text{HClO}_3$
- Identify the incorrect statement among the following : [AIEEE-2002]  
(1) Ozone reacts with  $\text{SO}_2$  to give  $\text{SO}_3$   
(2) Silicon reacts with  $\text{NaOH(aq.)}$  in the presence of air to give  $\text{Na}_2\text{SiO}_3$  and  $\text{H}_2\text{O}$   
(3)  $\text{Cl}_2$  reacts with excess of  $\text{NH}_3$  to give  $\text{N}_2$  and  $\text{HCl}$   
(4)  $\text{Br}_2$  reacts with hot and strong  $\text{NaOH}$  solution to give  $\text{NaBr}$ ,  $\text{NaBrO}_4$  and  $\text{H}_2\text{O}$
- Aluminium is industrially prepared by: [AIEEE-2002]  
(1) Fused cryolite (2) Bauxite ore (3) Alunite (4) Borax
- For making good quality mirrors, plates of float glass are used. These are obtained by floating molten glass over a liquid metal which does not solidify before glass. The metal used can be : [AIEEE-2003]  
(1) Sodium (2) Magnesium (3) Mercury (4) Tin
- What may be expected when phosphine gas is mixed with chlorine gas: [AIEEE-2003]  
(1)  $\text{PCl}_5$  and  $\text{HCl}$  are formed and mixture cools down  
(2)  $\text{PH}_3\cdot\text{Cl}_2$  is formed with warming up  
(3) The mixture only cools down  
(4)  $\text{PCl}_3$  and  $\text{HCl}$  are formed and the mixture warms up
- Graphite is a soft solid lubricant extremely difficult to melt. The reason for this anomalous behaviour is that graphite : [AIEEE-2003]  
(1) Has molecules of variable molecular masses like polymers  
(2) Has carbon atoms arranged in large plates of rings of strongly bonded carbon atoms with weak interplate bonds  
(3) Is a non crystalline substance  
(4) Is an allotropic form of diamond
- Concentrated hydrochloric acid when kept in open air sometimes produces a cloud of white fumes. This is due to : [AIEEE-2003]  
(1) Strong affinity of  $\text{HCl}$  gas for moisture in air results in forming of droplets of liquid solution which appears like a cloudy smoke  
(2) Due to strong affinity for water, conc.  $\text{HCl}$  pulls moisture of air towards self. The moisture forms droplets of water and hence the cloud  
(3) Conc.  $\text{HCl}$  emits strongly smelling  $\text{HCl}$  gas all the time  
(4) Oxygen in air reacts with emitted  $\text{HCl}$  gas to form a cloud of  $\text{Cl}_2$  gas
- Aluminium chloride exists as dimer,  $\text{Al}_2\text{Cl}_6$  in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives- [AIEEE-2004]  
(1)  $\text{Al}^{3+} + 3\text{Cl}^-$  (2)  $[\text{Al}(\text{H}_2\text{O})_6]^{3+} + 3\text{Cl}^-$   
(3)  $[\text{Al}(\text{OH})_6]^{3-} + 3\text{HCl}$  (4)  $\text{Al}_2\text{O}_3 + 6\text{HCl}$

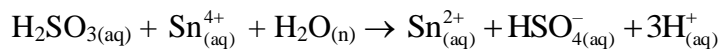
9. The soldiers of Napoleon army while at Alps during freezing winter suffered a serious problem as regards to the tin buttons of their uniforms. White Metallic tin buttons get converted to grey powder.  
This transformation is related to:- [AIEEE-2004]  
(1) An interaction with water vapour contained in humid air  
(2) A change in crystalline structure of tin  
(3) A change in the partial pressure of  $O_2$  in air  
(4) An interaction with  $N_2$  of air at low temperature
10. Which one of the following statements regarding helium is incorrect [AIEEE-2004]  
(1) It is used to produce and sustain powerful superconducting magnets  
(2) It is used as a cryogenic agent for carrying out experiments at low temperatures  
(3) It is used to fill gas balloons instead of hydrogen because it is lighter than hydrogen and noninflammable  
(4) It is used in gas-cooled nuclear reactors
11. The number of hydrogen atoms attached to phosphorus atom in hypophosphorous acid is : [AIEEE-2005]  
(1) Zero (2) Two (3) One (4) Three
12. Heating an aqueous solution of aluminium chloride to dryness will give :- [AIEEE-2005]  
(1)  $AlCl_3$  (2)  $Al_2Cl_6$  (3)  $Al_2O_3$  (4)  $Al(OH)Cl_2$
13. Which one of the following is the correct statement [AIEEE-2005]  
(1) Boric acid is a protonic acid  
(2) Beryllium exhibits coordination number of six  
(3) Chlorides of both beryllium and aluminium have bridged chloride structures in solid phase  
(4)  $B_2H_6 \cdot 2NH_3$  is known as "inorganic benzene"
14. In silicon dioxide : [AIEEE-2005]  
(1) Each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms  
(2) Each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms  
(3) Silicon atom is bonded to two oxygen atoms  
(4) There are double bonds between silicon and oxygen atoms
15. Regular use of which of the following fertilizer increases the acidity of soil : [AIEEE-2007]  
(1) Potassium nitrate (2) Urea  
(3) Superphosphate of lime (4) Ammonium sulphate
16. The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence: [AIEEE-2007]  
(1)  $GeX_2 \ll SiX_2 \ll SnX_2 \ll PbX_2$  (2)  $SiX_2 \ll GeX_2 \ll PbX_2 \ll SnX_2$   
(3)  $SiX_2 \ll GeX_2 \ll SnX_2 \ll PbX_2$  (4)  $PbX_2 \ll SnX_2 \ll GeX_2 \ll SiX_2$



17. Among the following substituted silanes the one which will give rise to cross linked silicone polymer on hydrolysis is [AIEEE-2008]  
(1)  $R_4Si$  (2)  $RSiCl_3$  (3)  $R_2SiCl_2$  (4)  $R_3SiCl$
18. Which one of the following reactions of Xenon compounds is not feasible ? [AIEEE-2009]  
(1)  $2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$   
(3)  $XeO_3 + 6HF \rightarrow XeF_6 + 3H_2O$   
(2)  $XeF_6 + RbF \rightarrow Rb[XeF_7]$   
(4)  $3XeF_4 + 6H_2O \rightarrow 2Xe + XeO_3 + 12HF + 1.5O_2$
19. Which of the following statement is wrong ? [AIEEE-2011]  
(1) Single N–N bond is weaker than the single P–P bond  
(2)  $N_2O_4$  has two resonance structures  
(3) The stability of hydrides increases from  $NH_3$  to  $BiH_3$  in group 15 of the periodic table  
(4) Nitrogen cannot form dp-pp bond
20. Which of the following statements regarding sulphur is incorrect ? [AIEEE-2011]  
(1) At  $600^\circ C$  the gas mainly consists of  $S_2$  molecules  
(2) The oxidation state of sulphur is never less than +4 in its compounds  
(3)  $S_2$  molecule is paramagnetic  
(4) The vapour at  $200^\circ C$  consists mostly of  $S_8$  rings
21. Boron cannot form which one of the following anions ? [AIEEE-2011]  
(1)  $B(OH)_4^-$  (2)  $BO_2^-$  (3)  $BF_6^{3-}$  (4)  $BH_4^-$
22. In view of the signs of  $\Delta_r G^\circ$  for the following reactions  
 $PbO_2 + Pb \rightarrow 2 PbO, \Delta_r G^\circ < 0$   
 $SnO_2 + Sn \rightarrow 2 SnO, \Delta_r G^\circ > 0$ ,  
Which oxidation states are more characteristic for lead and tin ? [AIEEE-2011]  
(1) For lead + 4, for tin + 2 (2) For lead + 2, for tin + 2  
(3) For lead + 4, for tin + 4 (4) For lead + 2, for tin + 4
23. The number of S–S bonds in  $SO_3$ ,  $S_2O_3^{2-}$ ,  $S_2O_6^{2-}$  and  $S_2O_8^{2-}$  respectively are :- [Jee Main(Online)-2012]  
(1) 1, 0, 1, 0 (2) 0, 1, 1, 0 (3) 1, 0, 0, 1 (4) 0, 1, 0, 1
24. Which one of the following depletes ozone layer ? [Jee Main(Online)-2012]  
(1) NO and freons (2)  $SO_2$  (3) CO (4)  $CO_2$
25. In which of the following arrangements, the sequence is not strictly according to the property written against it ? [Jee Main(Online)-2012]  
(1)  $CO_2 < SiO_2 < SnO_2 < PbO_2$  : increasing oxidising power  
(2)  $B < C < O < N$  : increasing first ionisation enthalpy  
(3)  $NH_3 < PH_3 < AsH_3 < SbH_3$  : increasing basic strength  
(4)  $HF < HCl < HBr < HI$  : increasing acid strength

26. The formation of molecular complex  $\text{BF}_3 - \text{NH}_3$  results in a change in hybridisation of boron :-  
[JEE(Main) Online-2012]  
(1) from  $\text{sp}_3$  to  $\text{sp}_3\text{d}$  (2) from  $\text{sp}_2$  to  $\text{dsp}_2$   
(3) from  $\text{sp}_3$  to  $\text{sp}_2$  (4) from  $\text{sp}_2$  to  $\text{sp}_3$
27. The catenation tendency of C, Si and Ge is in the order  $\text{Ge} < \text{Si} < \text{C}$ . The bond energies (in  $\text{kJ mol}^{-1}$ ) of C—C, Si—Si and Ge—Ge bonds are respectively :  
[JEE(Main) Online-2013]  
(1) 348, 260, 297 (2) 348, 297, 260 (3) 297, 348, 260 (4) 260, 297, 348
28. The gas evolved on heating  $\text{CaF}_2$  and  $\text{SiO}_2$  with concentrated  $\text{H}_2\text{SO}_4$ , on hydrolysis gives a white gelatinous precipitate. The precipitate is:  
[Jee Main(Online)-2014]  
(1) silica gel (2) silicic acid  
(3) hydrofluosilicic acid (4) calciumfluorosilicate
29. Which of the following series correctly represents relations between the elements from X to Y?  
[Jee Main(Online)-2014]  
 $\text{X} \rightarrow \text{Y}$   
(1)  $_{18}\text{Ar} \rightarrow _{54}\text{Xe}$  Noble character increases  
(2)  $_3\text{Li} \rightarrow _{19}\text{K}$  Ionization enthalpy increases  
(3)  $_6\text{C} \rightarrow _{32}\text{Ge}$  Atomic radii increases  
(4)  $_9\text{F} \rightarrow _{35}\text{Br}$  Electron gain enthalpy with negative sign increases
30. Which of the following statements about the depletion of ozone layer is correct?  
[Jee Main(Online)-2014]  
(1) The problem of ozone depletion is more serious at poles because ice crystals in the clouds over poles act as catalyst for photochemical reactions involving the decomposition of ozone by  $\text{Cl}^\bullet$  and  $\text{ClO}^\bullet$  radicals  
(2) The problem of ozone depletion is less serious at poles because  $\text{NO}_2$  solidifies and is not available for consuming  $\text{ClO}^\bullet$  radicals  
(3) Oxides of nitrogen also do not react with ozone in stratosphere  
(4) Freons, chlorofluorocarbons, are inert chemically, they do not react with ozone in stratosphere
31. Which of the following xenon-OXO compounds may not be obtained by hydrolysis of xenon fluorides ?  
[Jee Main(Online)-2014]  
(1)  $\text{XeO}_2\text{F}_2$  (2)  $\text{XeO}_3$  (3)  $\text{XeO}_4$  (4)  $\text{XeOF}_4$
32. Hydrogen peroxide acts both as an oxidising and as a reducing agent depending upon the nature of the reacting species. In which of the following cases  $\text{H}_2\text{O}_2$  acts as a reducing agent in acid medium ?  
[Jee Main(Online)-2014]  
(1)  $\text{MnO}_4^-$  (2)  $\text{SO}_3^{2-}$  (3)  $\text{KI}$  (4)  $\text{Cr}_2\text{O}_7^{2-}$

33. Consider the reaction



Which of the following statements is correct?

- (1)  $\text{H}_2\text{SO}_3$  is the reducing agent because it undergoes oxidation
- (2)  $\text{H}_2\text{SO}_3$  is the reducing agent because it undergoes reduction
- (3)  $\text{Sn}^{4+}$  is the reducing agent because it undergoes oxidation
- (4)  $\text{Sn}^{4+}$  is the oxidizing agent because it undergoes oxidation

34. In the following sets of reactants which two sets best exhibit the amphoteric character of  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  ? **[JEE(Main) Online-2014]**

**Set-1 :**  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s})$  and  $\text{OH}^{-}(\text{aq})$

**Set-2 :**  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s})$  and  $\text{H}_2\text{O}(\ell)$

**Set-3 :**  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s})$  and  $\text{H}^{+}(\text{aq})$

**Set-4 :**  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s})$  and  $\text{NH}_3(\text{aq})$

- (1) 1 and 2                      (2) 2 and 4                      (3) 1 and 3                      (4) 3 and 4

35. Which of the following compounds has a P-P bond :- [Jee Main(Online)-2015]

- (1)  $\text{H}_4\text{P}_2\text{O}_5$                       (2)  $(\text{HPO}_3)_3$                       (3)  $\text{H}_4\text{P}_2\text{O}_7$                       (4)  $\text{H}_4\text{P}_2\text{O}_6$

36. Chlorine water on standing loses its colour and forms :- **[Jee Main(Online)-2015]**

- (1)  $\text{HCl}$  and  $\text{HClO}_2$                       (2)  $\text{HCl}$  only  
(3)  $\text{HOCl}$  and  $\text{HOCl}_2$                       (4)  $\text{HCl}$  and  $\text{HOCl}$

37. Which among the following is the most reactive ? **[Jee Main-2015]**

- (1)  $\text{I}_2$                       (2)  $\text{ICl}$                       (3)  $\text{Cl}_2$                       (4)  $\text{Br}_2$

38. Which one has the highest boiling point ? **[Jee Main-2015]**

- (1) Kr                      (2) Xe                      (3) He                      (4) Ne

39. From the following statements regarding  $\text{H}_2\text{O}_2$ , choose the incorrect statement :

**[Jee Main-2015]**

- (1) It has to be stored in plastic or wax lined glass bottles in dark
- (2) It has to be kept away from dust
- (3) It can act only as an oxidizing agent
- (4) It decomposes on exposure to light

40. The reaction of zinc with dilute and concentrated nitric acid, respectively produces :

**[JEE (Main) 2016]**

- (1)  $\text{NO}_2$  and  $\text{N}_2\text{O}$                       (2)  $\text{N}_2\text{O}$  and  $\text{NO}_2$                       (3)  $\text{NO}_2$  and  $\text{NO}$                       (4)  $\text{NO}$  and  $\text{N}_2\text{O}$

41. The non-metal that does not exhibit positive oxidation state is : [JEE (Main) 2016]  
(1) Oxygen (2) Fluorine (3) Iodine (4) Chlorine
42. Which intermolecular force is most responsible in allowing xenon gas to liquefy? [JEE (Main) Online 2016]  
(1) Ionic (2) Instantaneous dipole- induced dipole  
(3) Dipole – dipole (4) Ion - dipole
43. The following statements concern elements in the periodic table. Which of the following is true ? [JEE (Main) Online 2016]  
(1) The group 13 elements are all metals.  
(2) For group 15 elements, the stability of +5 oxidation state increases down the group.  
(3) All the elements in Group 17 are gases.  
(4) Elements of group 16 have lower ionization enthalpy values compared to those of group 15 in the corresponding periods.
44. **Assertion :** Among the carbon allotropes, diamond is an insulator, whereas, graphite is a good conductor of electricity. [JEE (Main) Online 2016]  
**Reason :** Hybridization of carbon in diamond and graphite are  $sp^3$  and  $sp^2$ , respectively.  
(1) Assertion is incorrect statement, but the reason is correct.  
(2) Both assertion and reason are correct, and the reason is the correct explanation for the assertion.  
(3) Both assertion and reason are incorrect.  
(4) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion.
45. Identify the incorrect statement : [JEE (Main) Online 2016]  
(1)  $S_8$  ring has a crown shape.  
(2) The S–S–S bond angles in the  $S_8$  and  $S_6$  rings are the same  
(3)  $S_2$  is paramagnetic like oxygen  
(4) Rhombic and monoclinic sulphur have  $S_8$  molecules.
46. The product obtained when chlorine reacts with cold and dilute aqueous NaOH are : [JEE-Main 2017]  
(1)  $ClO^-$  and  $ClO_3^-$  (2)  $ClO_2^-$  and  $ClO_3^-$  (3)  $Cl^-$  and  $ClO^-$  (4)  $Cl^-$  and  $ClO_2^-$
47. In graphite and diamond, the percentage of p-characters of the hybrid orbitals in hybridisation are respectively : [Main-2018(Online)]  
(1) 33 and 25 (2) 33 and 75 (3) 50 and 75 (4) 67 and 75
48. In the following sets of reactants which two sets best exhibit the amphoteric character of  $Al_2O_3 \cdot xH_2O$  ? [Main-2018(Online)]  
Set-1 :  $Al_2O_3 \cdot xH_2O(s)$  and  $OH^-(aq)$  Set-2 :  $Al_2O_3 \cdot xH_2O(s)$  and  $H_2O(l)$   
Set-3 :  $Al_2O_3 \cdot xH_2O(s)$  and  $H^+(aq)$  Set-4 :  $Al_2O_3 \cdot xH_2O(s)$  and  $NH_3(aq)$   
(1) 1 and 2 (2) 2 and 4 (3) 1 and 3 (4) 3 and 4

49. The compound that does not produce nitrogen gas by the thermal decomposition is [Main-2018(Online)]  
(1)  $(\text{NH}_4)_2\text{SO}_4$  (2)  $\text{Ba}(\text{N}_3)_2$  (3)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (4)  $\text{NH}_4\text{NO}_2$
50. Good reducing nature of  $\text{H}_3\text{PO}_2$  is attributed to the presence of : [Main-2019(Online)]  
(1) Two P–H bonds (2) One P–OH bond (3) One P–H bond (4) Two P–OH bonds
51. Among the following reactions of hydrogen with halogens, the one that requires a catalyst is : [Main-2019(Online)]  
(1)  $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$  (2)  $\text{H}_2 + \text{F}_2 \rightarrow 2\text{HF}$  (3)  $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$  (4)  $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$
52. The pair that contains two P–H bonds in each of the oxoacids is: [Main-2019(Online)]  
(1)  $\text{H}_4\text{P}_2\text{O}_5$  and  $\text{H}_3\text{PO}_3$  (2)  $\text{H}_4\text{P}_2\text{O}_5$  and  $\text{H}_4\text{P}_2\text{O}_6$   
(3)  $\text{H}_3\text{PO}_2$  and  $\text{H}_4\text{P}_2\text{O}_5$  (4)  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_2$
53. Iodine reacts with concentrated  $\text{HNO}_3$  to yield Y along with other products. The oxidation state of iodine in Y is : [Main-2019(Online)]  
(1) 5 (2) 1 (3) 3 (4) 7
54. The element that does NOT show catenation is: [Main-2019(Online)]  
(1) Si (2) Ge (3) Pb (4) Sn
55. Chlorine on reaction with hot and concentrated sodium hydroxide gives : [Main-2019(Online)]  
(1)  $\text{ClO}_3^-$  and  $\text{ClO}_2^-$  (2)  $\text{Cl}^-$  and  $\text{ClO}_2^-$  (3)  $\text{Cl}^-$  and  $\text{ClO}^-$  (4)  $\text{Cl}^-$  and  $\text{ClO}_3^-$
56. The element that shows greater ability to form p– $\pi$ p $\pi$  multiple bond, is : [Main-2019(Online)]  
(1) Si (2) C (3) Sn (4) Ge

**EXERCISE-V (JEE-ADVANCED)**

**(IIT JEE ASKED QUESTIONS)**

**Fill in the blanks**

1. The hydrolysis of alkyl substituted chlorosilanes given..... [1991]
2. The hydrolysis of trialkylchlorosilane  $R_3SiCl$ , yields ..... [1994]
3. One recently discovered allotrope of carbon (e.g.,  $C_{60}$ ) is commonly known as .... [1994]

**True/False**

4. Carbon tetrachloride burns in air when lighted to give phosgene. [1983]
5. Graphite is a better lubricant on the moon than on the earth. [1987]
6. All the Al—Cl bonds in  $Al_2Cl_6$  are equivalent. [1989]
7. Diamond is harder than graphite. [1993]
8. The basic nature of the hydroxides of group 13 (Gr. IIIB) decreases progressively down the group. [1993]
9. The tendency for catenation is much higher for C than for Si. [1993]
10. Complete and balance the following chemical equations – [IIT-1998, 2 M]  
 (i)  $P_4O_{10} + PCl_5 \longrightarrow$  (ii)  $SnCl_4 + C_2H_5Cl + Na \longrightarrow$
11. Work out the following using chemical equations [IIT- 1998, 2M]  
 "Chlorination of calcium hydroxide produces bleaching powder"
12. Hydrogen peroxide acts both as an oxidizing and as a reducing agent in alkaline solution towards certain first row transition metal ion. Illustrate both these properties of  $H_2O_2$  using chemical equations – [IIT- 1998, 4 M]
13. In the contact process for industrial manufacture of sulphuric acid, some amount of sulphuric acid is used as a starting material. Explain briefly. What is the catalyst used in the oxidation of  $SO_2$ ? [IIT- 1998, 4 M]
14. Give reasons in one or two sentences for each of the following : [1985]  
 (i) Graphite is used as a solid lubricant,  
 (ii) Fluorine cannot be prepared from fluorides by chemical oxidation.
15. Write balanced equations for : [1990]  
 (i) The preparation of crystalline silicon from  $SiCl_4$   
 (ii) The preparation of phosphine from  $CaO$  and white phosphorus  
 (iii) The preparation of ammonium sulphate from gypsum, ammonia and carbon dioxide.
16. Anhydrous  $AlCl_3$  is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution. [1997]  
 Ionisation energy for Al =  $5137 \text{ kJ mol}^{-1}$   
 $\Delta H_{\text{hydration}}$  for  $Al^{3+} = -4665 \text{ kJ mol}^{-1}$   
 $\Delta H_{\text{hydration}}$  for  $Cl^- = -381 \text{ kJ mol}^{-1}$
17. Aluminium sulphide gives a foul odour when it becomes damp. Write a balanced chemical equation for the reaction. [1997]
18. Draw the structure of a cyclic silicate,  $(Si_3O_9)^{6-}$  with proper labelling – [IIT-1998]

19. Give reasons for the following in one or two sentences only. [IIT- 1999]  
"BeCl<sub>2</sub> can be easily hydrolysed."
20. Give reason : [IIT- 2000]  
Why elemental nitrogen exists as a diatomic molecule whereas elemental phosphorus is a tetra atomic molecule.
21. Give an example of oxidation of one halide by another halogen. Explain the feasibility of the reaction. [IIT- 2000]
22. Compounds X on reduction with LiAlH<sub>4</sub> gives a hydride Y containing 21.72% hydrogen alongwith other products. The compound Y reacts with air explosively resulting in boron trioxide. Identify X and Y. Give balanced reactions involved in the formation of Y and its reaction with air Draw the structure of Y. [IIT- 2001]
23. Starting from SiCl<sub>4</sub>, prepare the following in steps not exceeding the number given in parenthesis (reactions only) [IIT- 2001]  
(i) Silicon (1)  
(ii) Linear silicon containing methyl group only (4)  
(iii) Na<sub>2</sub>SiO<sub>3</sub> (3)
24. Write the balanced chemical equation for developing photographic films. [IIT- 2001]
25. Identify (X) in the following synthetic scheme and write their structures. [IIT- 2001]  
$$\text{BaCO}_3^* + \text{H}_2\text{SO}_4 \longrightarrow \text{X (gas)} \quad (\text{C denotes C}^{14})$$
26. Write the balanced equations for the reactions of the following compounds with water [2002]  
(i) Al<sub>4</sub>C<sub>3</sub>      (ii) CaNCN      (iii) BF<sub>3</sub>      (iv) NCl<sub>3</sub>      (v) XeF<sub>4</sub>
27. Write the balanced equations for the reactions of the following compounds with water: [IIT- 2002]  
(i) Al<sub>4</sub>C<sub>3</sub>      (ii) CaNCN      (iii) BF<sub>3</sub>      (iv) NCl<sub>3</sub>      (v) XeF<sub>4</sub>
28. Identify the following: [IIT- 2003]  
$$\text{Na}_2\text{CO}_3 \xrightarrow[\text{(aq)}]{\text{SO}_2} \text{A} \xrightarrow{\text{Na}_2\text{CO}_3} \text{B} \xrightarrow[\Delta]{\text{elemental S}} \text{C} \xrightarrow{\text{I}_2} \text{D}$$
  
Also mention the oxidation state of S in all the compounds.
29. Arrange the following oxides in the increasing order of Bronsted basicity. [IIT- 2004]  
Cl<sub>2</sub>O<sub>7</sub>, BaO, SO<sub>3</sub>, CO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>
30. When zeolite, which is hydrated sodium aluminium silicate, is treated with hard water, the sodium ions are exchanged with : [1990]  
(A) H<sup>+</sup> ions      (B) Ca<sup>2+</sup> ions      (C) SO<sub>4</sub><sup>2-</sup> ions      (D) Mg<sup>2+</sup> ions

31. Which of the following halides is least stable and has doubtful existence ? [1996]  
(A)  $\text{CCl}_4$  (B)  $\text{GeI}_4$  (C)  $\text{SnI}_4$  (D)  $\text{PbI}_4$
32. The number of P—O—P bonds in cyclic tetrametaphosphoric acid is – [IIT-2000]  
(A) Zero (B) Two (C) Three (D) Four
33. The correct order of acidic strength is – [IIT-2000]  
(A)  $\text{Cl}_2\text{O}_7 > \text{SO}_2 < \text{P}_4\text{O}_{10}$  (B)  $\text{CO}_2 > \text{N}_2\text{O}_5 > \text{SO}_3$   
(C)  $\text{Na}_2\text{O} > \text{MgO} > \text{Al}_2\text{O}_3$  (D)  $\text{K}_2\text{O} > \text{CaO} > \text{MgO}$
34. Amongst  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$ , the one with the highest boiling point is – [IIT-2000]  
(A)  $\text{H}_2\text{O}$  because of hydrogen bonding (B)  $\text{H}_2\text{Te}$  because of higher molecular weight  
(C)  $\text{H}_2\text{S}$  because of hydrogen bonding (D)  $\text{H}_2\text{Se}$  because of lower molecular weight.
35. Ammonia can be dried by – [IIT-2000]  
(A) Conc.  $\text{H}_2\text{SO}_4$  (B)  $\text{P}_4\text{O}_{10}$  (C)  $\text{CaO}$  (D) Anhydrous  $\text{CaCl}_2$
36. Which of the following are hydrolysed – [REE 2000]  
(A)  $\text{NCl}_3$  (B)  $\text{BCl}_3$  (C)  $\text{CCl}_4$  (D)  $\text{SiCl}_4$
37. The set with correct order of acidity is – [IIT-2001]  
(A)  $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$  (B)  $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$   
(C)  $\text{HClO} < \text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2$  (D)  $\text{HClO}_4 < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}$
38. – The reaction,  $3\text{ClO}^- (\text{aq}) \longrightarrow \text{ClO}_3^- (\text{aq}) + 2\text{Cl}^- (\text{aq})$  is an example of – [IIT-2001]  
(A) Oxidation reaction (B) reduction reaction  
(C) Disproportionation reaction (D) Decomposition reaction
39. The number of S—S bonds in sulphur trioxide trimer,  $(\text{S}_3\text{O}_9)$  is – [IIT-2001]  
(A) Three (B) Two (C) One (D) Zero
40. **Statement-I :** Between  $\text{SiCl}_4$  and  $\text{CCl}_4$ , only  $\text{SiCl}_4$  reacts with water [IIT-2001]  
**Because :**  
**Statement-II :**  $\text{SiCl}_4$  is ionic and  $\text{CCl}_4$  is covalent  
(A) If both assertion and reason are correct and reason is the correct explanation of the assertion  
(B) If both assertion and reason are correct, but reason is not the correct explanation of the assertion  
(C) If assertion is correct, but reason is incorrect  
(D) If assertion is incorrect, but reason is correct.



41. Polyphosphates are used as water softening agents because they – [IIT- 2002]  
(A) Form soluble complexes with anionic species  
(B) Precipitate anionic species  
(C) Form soluble complexes with cationic species  
(D) Precipitate cationic species
42. Identify the correct order of solubility of  $\text{Na}_2\text{S}$ ,  $\text{CuS}$ , and  $\text{ZnS}$  in aqueous medium – [IIT- 2002]  
(A)  $\text{CuS} > \text{ZnS} > \text{Na}_2\text{S}$  (B)  $\text{ZnS} > \text{Na}_2\text{S} > \text{CuS}$   
(C)  $\text{Na}_2\text{S} > \text{CuS} > \text{ZnS}$  (D)  $\text{Na}_2\text{S} > \text{ZnS} > \text{CuS}$
43. Identify, the correct order of acidic strength of  $\text{CO}_2$ ,  $\text{CuO}$ ,  $\text{CaO}$ ,  $\text{H}_2\text{O}$  – [IIT- 2002]  
(A)  $\text{CaO} < \text{CuO} < \text{H}_2\text{O} < \text{CO}_2$  (B)  $\text{H}_2\text{O} < \text{CuO} < \text{CaO} < \text{CO}_2$   
(C)  $\text{CaO} < \text{H}_2\text{O} < \text{CuO} < \text{CO}_2$  (D)  $\text{H}_2\text{O} < \text{CO}_2 < \text{CaO} < \text{CuO}$
44.  $\text{H}_3\text{BO}_3$  is – [IIT- 2002, 3]  
(A) Monobasic acid and weak Lewis acid (B) Monobasic and weak Bronsted acid  
(C) Monobasic and strong Lewis acid (D) Tribasic and weak Bronsted acid
45. When  $\text{I}^-$  is oxidised by  $\text{MnO}_4^-$  in alkaline medium,  $\text{I}^-$  converts into – [IIT- 2003]  
(A)  $\text{IO}_3^-$  (B)  $\text{I}_2$  (C)  $\text{IO}_4^-$  (D)  $\text{IO}^-$
46. **Column-I (Change)** **Column-II (Given change is done by)** [IIT- 2003]  
(A)  $\text{Bi}^{3+} \longrightarrow (\text{BiO})^+$  (p) Heat  
(B)  $[\text{AlO}_2]^- \longrightarrow \text{Al}(\text{OH})_3$  (q) Hydrolysis  
(C)  $\text{SiO}_4^{4-} \longrightarrow \text{Si}_2\text{O}_7^{6-}$  (r) Acidification  
(D)  $(\text{B}_4\text{O}_7^{2-}) \longrightarrow [\text{B}(\text{OH})_3]$  (s) Dilution by water
47.  $(\text{Me})_2\text{SiCl}_2$  on hydrolysis will produce – [IIT- 2003]  
(A)  $(\text{Me})_2\text{Si}(\text{OH})_2$  (B)  $(\text{Me})_2\text{Si} = \text{O}$   
(C)  $[\text{—O—}(\text{Me})_2\text{Si—O—}]_n$  (D)  $\text{Me}_2\text{SiCl}(\text{OH})$
48. Which is the most thermodynamically stable allotropic form of phosphorus? [IIT- 2004]  
(A) Red (B) White (C) Black (D) Yellow
49. When  $\text{PbO}_2$  reacts with conc.  $\text{HNO}_3$  the gas evolved may be : [IIT- 2004]  
(A)  $\text{NO}_2$  (B)  $\text{O}_2$  (C)  $\text{N}_2$  (D)  $\text{N}_2\text{O}$
50. Which of the following is not oxidised by  $\text{O}_3$ ? [IIT- 2005]  
(A)  $\text{KI}$  (B)  $\text{FeSO}_4$  (C)  $\text{KMnO}_4$  (D)  $\text{K}_2\text{MnO}_4$

51. Which blue-liquid is obtained on reacting equimolar amounts of two gases at  $-30^{\circ}\text{C}$  ? [IIT- 2005]  
(A)  $\text{N}_2\text{O}$  (B)  $\text{N}_2\text{O}_3$  (C)  $\text{N}_2\text{O}_4$  (D)  $\text{N}_2\text{O}_5$
52.  $\text{B}(\text{OH})_3 + \text{NaOH} \rightleftharpoons \text{NaBO}_2 + \text{Na}[\text{B}(\text{OH})_4] + \text{H}_2\text{O}$  how can this reaction is made to proceed in forward direction ? [IIT- 2006]  
(A) Addition of cis 1, 2 diol (B) Addition of borax  
(C) Addition of trans 1, 2 diol (D) Addition of  $\text{Na}_2\text{HPO}_4$
53. Among the following, the paramagnetic compound is – [IIT- 2007]  
(A)  $\text{Na}_2\text{O}_2$  (B)  $\text{O}_3$  (C)  $\text{N}_2\text{O}$  (D)  $\text{KO}_2$
54. **Statement-I :** Boron always forms covalent bond [IIT-2007]  
**Because :**  
**Statement-II :** The small size of  $\text{B}^{3+}$  favours formation of covalent bond.  
(A) Statement-I is True, Statement-II is Ture, Statement-II is a correct explanation for Statement-I  
(B) Statement-I is Ture, Statement-II is Ture, Statement-II is not a correct explanation for Statement-II  
(C) Statement-I is Ture, Statement-II is False  
(D) Statement-I is False, Statement-II is Ture
55. **Statement-I :** In water, orthoboric acid behaves as a weak monobasic acid. [IIT-2007]  
**Statement-II :** In water, orthoboric acid acts as a proton donor.  
(A) Statement-I is True, Statement-II is Ture, Statement-II is a correct explanation for Statement-I  
(B) Statement-I is Ture, Statement-II is Ture, Statement-II is not a correct explanation for Statement-II  
(C) Statement-I is Ture, Statement-II is False  
(D) Statement-I is False, Statement-II is Ture

### Comprehension # 1 (Q. 56 to 58)

The noble gases have closed-shell electronic configuration and are monoatomic gases under normal conditions. The low boiling point of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions. The direct reaction of xenon with fluorine leads to a series of compounds with oxidation number + 2, + 4 and + 6.  $\text{XeF}_4$  reacts violently with water to give  $\text{XeO}_3$ . The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell. [IIT- 2007]

56. Argon is used in arc welding because of its –  
(A) Low reactivity with metal (B) Ability to lower the melting point of metal  
(C) Flammability (D) High calorific value
57. The structure of  $\text{XeO}_3$  is –  
(A) Linear (B) Planar (C) Pyramidal (D) T-shaped
58.  $\text{XeF}_4$  and  $\text{XeF}_6$  are expected to be –  
(A) Oxidising agent (B) Reducing agent (C) Unreactive (D) Strongly basic

**Comprehension # 2 (Q.59 to 61)**

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of  $\text{NH}_3$  and  $\text{PH}_3$ . Phosphine is a flammable gas and is prepared from white phosphorous. **[IIT- 2008]**

- 59.** Among the following, the correct statement is :-  
 (A) Phosphates have no biological significance in humans  
 (B) Between nitrates and phosphates, phosphates are less abundant in earth's crust  
 (C) Between nitrates and phosphates, nitrates are less abundant in earth's crust  
 (D) Oxidation of nitrates is possible in soil
- 60.** Among the following, the correct statement is :-  
 (A) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{NH}_3$  is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional  
 (B) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{PH}_3$  is a better electron donor because the lone pair of electrons occupies  $\text{sp}^3$  orbital and is more directional  
 (C) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{NH}_3$  is a better electron donor because the lone pair of electrons occupies  $\text{sp}^3$  orbital and is more directional  
 (D) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{PH}_3$  is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional.
- 61.** White phosphorus on reaction with  $\text{NaOH}$  gives  $\text{PH}_3$  as one of the products. This is a :-  
 (A) dimerization reaction (B) disproportionation reaction  
 (C) condensation reaction (D) precipitation reaction
- 62.** The reaction of  $\text{P}_4$  with X leads selectively to  $\text{P}_4\text{O}_6$ . The X is **[JEE 2009]**  
 (A) Dry  $\text{O}_2$  (B) A mixture of  $\text{O}_2$ , and  $\text{N}_2$   
 (C) Moist  $\text{O}_2$  (D)  $\text{O}_2$  in the presence of aqueous  $\text{NaOH}$
- 63.** The reaction of white phosphorus with aqueous  $\text{NaOH}$  gives phosphine along with another phosphorus containing compound. The reaction type ; the oxidation states of phosphorus in phosphine and the other product are respectively **[JEE 2012]**  
 (A) redox reaction ; -3 and -5 (B) redox reaction ; +3 and +5  
 (C) disproportionation reaction ; -3 and +1 (D) disproportionation reaction ; -3 and +3
- 64.** Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is : **[JEE 2012]**  
 (A)  $\text{Cl}_2\text{O}$  (B)  $\text{Cl}_2\text{O}_7$  (C)  $\text{ClO}_2$  (D)  $\text{Cl}_2\text{O}_6$

65. With respect to graphite and diamond, which of the statement(s) given below is (are) correct ?  
(A) Graphite is harder than diamond. [JEE 2012]  
(B) Graphite has higher electrical conductivity than diamond.  
(C) Graphite has higher thermal conductivity than diamond.  
(D) Graphite has higher C–C bond order than diamond.
66. Concentrated nitric acid, upon long standing, turns yellow-brown due to the formation of -  
(A) NO (B) NO<sub>2</sub> (C) N<sub>2</sub>O (D) N<sub>2</sub>O<sub>4</sub> [JEE 2013]
67. The correct statement(s) about O<sub>3</sub> is(are) [JEE 2013]  
(A) O–O bond lengths are equal (B) Thermal decomposition of O<sub>3</sub> is endothermic  
(C) O<sub>3</sub> is diamagnetic in nature (D) O<sub>3</sub> has a bent structure

**Comprehension # 3 (Q. 68 and 69)**

The reaction of Cl<sub>2</sub> gas with cold dilute and hot concentrated NaOH in water give sodium salt of two (different) oxoacids of chlorine P and Q respectively. The Cl<sub>2</sub> gas reacts with SO<sub>2</sub> gas, in presence of charcoal to give a product R. R reacts with white phosphorous to give a compound S. On hydrolysis, S gives as oxoacid of phosphorous T.

68. R, S and T, respectively are - [JEE 2013]  
(A) SO<sub>2</sub>Cl<sub>2</sub>, PCl<sub>5</sub> and H<sub>3</sub>PO<sub>4</sub> (B) SO<sub>2</sub>Cl<sub>2</sub>, PCl<sub>3</sub> and H<sub>3</sub>PO<sub>3</sub>  
(C) SOCl<sub>2</sub>, PCl<sub>3</sub> and H<sub>3</sub>PO<sub>2</sub> (D) SO<sub>2</sub>Cl<sub>2</sub>, PCl<sub>5</sub> and H<sub>3</sub>PO<sub>4</sub>
69. P and Q, respectively, are the sodium salts of -  
(A) Hypochlorous and chloric acid (B) Hypochlorous and chlorous acid  
(C) Chloric and perchloric acids (D) Chloric and hypochlorous acids
70. The unbalanced chemical reactions given in List-I show missing reagent or condition (?) which are provided in List-II. Match List-I with List-II and select the correct answer using the code given below the lists :A [JEE 2013]

**List-I**

- (P)  $\text{PbO}_2 + \text{H}_2\text{SO}_4 \xrightarrow{?} \text{PbSO}_4 + \text{O}_2 + \text{other product}$  (1)  
(Q)  $\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \xrightarrow{?} \text{NaHSO}_4 + \text{other product}$  (2)  
(R)  $\text{N}_2\text{H}_4 \xrightarrow{?} \overset{\circ}{\text{N}}_2 + \text{other product}$  (3)  
(S)  $\text{XeF}_2 \xrightarrow{?} \text{Xe} + \text{Other product}$  (4)

**List-II**

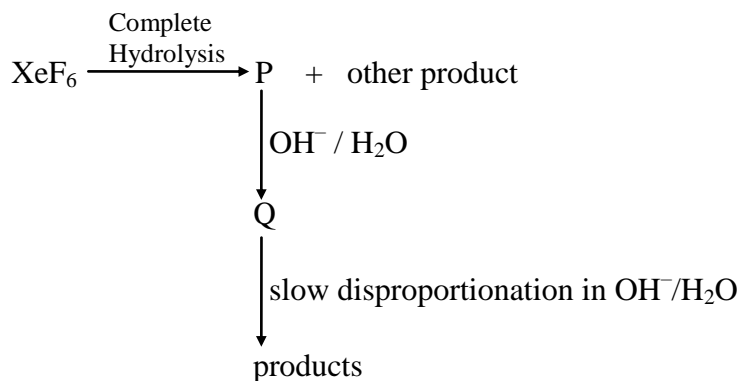
- (1) NO  
(2) I<sub>2</sub>  
(3) Warm  
(4) Cl<sub>2</sub>

**Codes :**

|     | P | Q | R | S   |
|-----|---|---|---|-----|
| (A) |   | 4 | 2 | 3 1 |
| (C) |   | 1 | 4 | 2 3 |

|     | P | Q | R | S   |
|-----|---|---|---|-----|
| (B) |   | 3 | 2 | 1 4 |
| (D) |   | 3 | 4 | 2 1 |

71. Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is [JEE Adv. 2014]



- (A) 0 (B) 1 (C) 2 (D) 3

72. The product formed in the reaction of  $\text{SOCl}_2$  with white phosphorous is [JEE Adv. 2014]  
(A)  $\text{PCl}_3$  (B)  $\text{SO}_2\text{Cl}_2$  (C)  $\text{SCl}_2$  (D)  $\text{POCl}_3$

73. The correct statement(s) for orthoboric acid is / are - [JEE Adv. 2014]  
(A) It behaves as a weak acid in water due to self ionization  
(B) Acidity of its aqueous solution increases upon addition of ethylene glycol  
(C) It has a three dimensional structure due to hydrogen bonding.  
(D) It is a weak electrolyte in water

74. The correct statement(s) regarding, (i)  $\text{HClO}$ , (ii)  $\text{HClO}_2$ , (iii)  $\text{HClO}_3$  and (iv)  $\text{HClO}_4$ , is(are) [JEE Adv. 2015]  
(A) The number of  $\text{Cl}=\text{O}$  bonds in (ii) and (iii) together is two  
(B) The number of lone pairs of electrons on Cl in (ii) and (iii) together is three  
(C) The hybridization of Cl in (iv) is  $\text{sp}^3$   
(D) Amongst (i) to (iv), the strongest acid is (i)

75. When  $\text{O}_2$  is adsorbed on a metallic surface, electron transfer occurs from the metal to  $\text{O}_2$ . The **TRUE**, statement (s) regarding this adsorption is (are) [JEE Adv. 2015]  
(A)  $\text{O}_2$  is physisorbed (B) heat is released  
(C) occupancy of  $\pi_{2p}^*$  of  $\text{O}_2$  is increased (D) bond length of  $\text{O}_2$  is increased

76. Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are [JEE (Adv.) 2015]  
(A)  $\text{CH}_3\text{SiCl}_3$  and  $\text{Si}(\text{CH}_3)_4$  (B)  $(\text{CH}_3)_2\text{SiCl}_2$  and  $(\text{CH}_3)_3\text{SiCl}$   
(C)  $(\text{CH}_3)_2\text{SiCl}_2$  and  $\text{CH}_3\text{SiCl}_3$  (D)  $\text{SiCl}_4$  and  $(\text{CH}_3)_3\text{SiCl}$

77. Three moles of  $\text{B}_2\text{H}_6$  are completely reacted with methanol. The number of moles of boron containing product formed is - [JEE (Adv.) 2015]

78. The increasing order of atomic radii of the following group 13 elements is : [JEE Adv. 2016]  
 (A)  $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$  (B)  $\text{Ga} < \text{Al} < \text{In} < \text{Tl}$   
 (C)  $\text{Al} < \text{In} < \text{Ga} < \text{Tl}$  (D)  $\text{Al} < \text{Ga} < \text{Tl} < \text{In}$
79. The crystalline form of borax has [JEE Adv. 2016]  
 (A) Tetranuclear  $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$  unit  
 (B) All boron atoms in the same plane  
 (C) Equal number of  $\text{sp}^2$  and  $\text{sp}^3$  hybridized boron atoms  
 (D) One terminal hydroxide per boron atom
80. The nitrogen containing compound produced in the reaction of  $\text{HNO}_3$  with  $\text{P}_4\text{O}_{10}$  [JEE Adv. 2016]  
 (A) can also be prepared by reaction of  $\text{P}_4$  and  $\text{HNO}_3$   
 (B) is diamagnetic  
 (C) contains one N-N bond  
 (D) reacts with Na metal producing a brown gas

**PARAGRAPH Q.81 to 82**

Upon heating  $\text{KClO}_3$  in the presence of catalytic amount of  $\text{MnO}_2$ , a gas W is formed. Excess amount of W reacts with white phosphorus to give X. The reaction of X with pure  $\text{HNO}_3$  gives Y and Z. [JEE(Advanced) 2017]

81. W and X are, respectively  
 (A)  $\text{O}_2$  and  $\text{P}_4\text{O}_6$  (B)  $\text{O}_3$  and  $\text{P}_4\text{O}_{10}$  (C)  $\text{O}_3$  and  $\text{P}_4\text{O}_6$  (D)  $\text{O}_2$  and  $\text{P}_4\text{O}_{10}$
82. Y and Z are, respectively  
 (A)  $\text{N}_2\text{O}_4$  and  $\text{HPO}_3$  (B)  $\text{N}_2\text{O}_3$  and  $\text{H}_3\text{PO}_4$  (C)  $\text{N}_2\text{O}_5$  and  $\text{HPO}_3$  (D)  $\text{N}_2\text{O}_4$  and  $\text{H}_3\text{PO}_3$
83. The compound(s) which generate(s)  $\text{N}_2$  gas upon thermal decomposition below  $300^\circ\text{C}$  is (are) [JEE(Advanced) 2018]  
 (A)  $\text{NH}_4\text{NO}_3$  (B)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (C)  $\text{Ba}(\text{N}_3)_2$  (D)  $\text{Mg}_3\text{N}_2$
84. A tin chloride Q undergoes the following reactions (not balanced) [JEE(Advanced) 2019]  
 $\text{Q} + \text{Cl}^- \rightarrow \text{X}$   
 $\text{Q} + \text{Me}_3\text{N} \rightarrow \text{Y}$   
 $\text{Q} + \text{CuCl}_2 \rightarrow \text{Z} + \text{CuCl}$   
 X is a monoanion having pyramidal geometry. Both Y and Z are neutral compounds.

Choose the correct option(s)

- (A) There is a coordinate bond in Y
- (B) The central atom in Z has one lone pair of electrons
- (C) The central atom in X is  $sp^3$  hybridized
- (D) The oxidation state of the central atom in Z is +2

85. With reference to aqua regia, choose the correct options(s) [JEE(Advanced) 2019]

- (A) Reaction of gold with aqua regia produces  $NO_2$  in the absence of air
- (B) Reaction of gold with aqua regia produces an anion having Au in +3 oxidation state
- (C) Aqua regia is prepared by mixing conc. HCl and conc.  $HNO_3$  in 3 : 1 (v/v) ratio
- (D) The yellow colour of aqua regia is due to the presence of  $NOCl$  and  $Cl_2$



**ANSWER KEY**

**EXERCISE-I**

|     |   |     |   |     |   |     |   |     |   |     |   |     |   |
|-----|---|-----|---|-----|---|-----|---|-----|---|-----|---|-----|---|
| 1.  | C | 2.  | C | 3.  | B | 4.  | A | 5.  | B | 6.  | B | 7.  | D |
| 8.  | C | 9.  | B | 10. | B | 11. | A | 12. | A | 13. | A | 14. | B |
| 15. | B | 16. | A | 17. | B | 18. | A | 19. | A | 20. | A | 21. | B |
| 22. | C | 23. | B | 24. | D | 25. | A | 26. | A | 27. | B | 28. | B |
| 29. | C | 30. | B | 31. | A | 32. | D | 33. | A | 34. | B | 35. | C |
| 36. | C | 37. | B | 38. | C | 39. | B | 40. | D | 41. | A | 42. | A |
| 43. | B | 44. | C | 45. | A | 46. | C | 47. | A |     |   |     |   |

**EXERCISE-II**

|     |         |     |         |     |       |     |         |     |       |
|-----|---------|-----|---------|-----|-------|-----|---------|-----|-------|
| 1.  | A,B     | 2.  | A,B,C   | 3.  | A,C,D | 4.  | A,B,C   | 5.  | A,B,D |
| 6.  | A,B     | 7.  | A,B,C   | 8.  | A,B,C | 9.  | A,B,C,D | 10. | A, C, |
| 11. | A,B,C,D | 12. | C,D     | 13. | C,D   | 14. | A,B,C,D | 15. | A,B,D |
| 16. | B,C,D   | 17. | A,B,C,D |     |       |     |         |     |       |

**EXERCISE-III**

|     |   |     |   |     |   |     |   |     |   |     |   |     |   |
|-----|---|-----|---|-----|---|-----|---|-----|---|-----|---|-----|---|
| 1.  | B | 2.  | A | 3.  | D | 4.  | A | 5.  | C | 6.  | D | 7.  | A |
| 8.  | B | 9.  | A | 10. | A | 11. | C | 12. | B | 13. | B | 14. | C |
| 15. | B | 16. | B | 17. | C | 18. | A |     |   |     |   |     |   |

**EXERCISE-IV(JEE-MAIN)**

|     |   |     |   |     |   |     |   |     |   |     |   |     |   |
|-----|---|-----|---|-----|---|-----|---|-----|---|-----|---|-----|---|
| 1.  | 4 | 2.  | 4 | 3.  | 2 | 4.  | 3 | 5.  | 4 | 6.  | 2 | 7.  | 3 |
| 8.  | 2 | 9.  | 2 | 10. | 3 | 11. | 2 | 12. | 3 | 13. | 3 | 14. | 1 |
| 15. | 4 | 16. | 3 | 17. | 2 | 18. | 3 | 19. | 3 | 20. | 2 | 21. | 3 |
| 22. | 4 | 23. | 2 | 24. | 1 | 25. | 3 | 26. | 4 | 27. | 2 | 28. | 2 |
| 29. | 3 | 30. | 1 | 31. | 3 | 32. | 1 | 33. | 1 | 34. | 3 | 35. | 4 |
| 36. | 4 | 37. | 2 | 38. | 2 | 39. | 3 | 40. | 2 | 41. | 2 | 42. | 2 |
| 43. | 4 | 44. | 4 | 45. | 2 | 46. | 3 | 47. | 4 | 48. | 3 | 49. | 1 |
| 50. | 1 | 51. | 3 | 52. | 3 | 53. | 1 | 54. | 3 | 55. | 4 | 56. | 2 |



**EXERCISE-V(JEE-ADVANCED)**

**Fill in the blanks**

1. Silicones                      2.  $R_3Si(OH)$                       3. Buckminstre fullerene

**True/False**

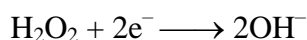
4. F                      5. T                      6. F                      7. T                      8. F                      9. T

**Subjective**

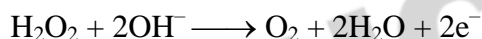
10. (i)  $P_4O_{10} + 6PCl_3 \longrightarrow 10POCl_3$                       (ii)  $SnCl_4 + 2C_2H_5Cl + 2Na \longrightarrow Na_2SnCl_6 + C_4H_{10}$

11.  $3Ca(OH)_2 + 2Cl_2 \longrightarrow \underbrace{Ca(OCl)_2 + Ca(OH)_2}_{\text{Bleaching powder is a mixture of } CaOCl_2 \text{ And hydrated basic calcium chloride.}} + 2H_2O$

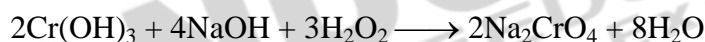
12. When  $H_2O_2$  acts as oxidizing agent, therefore, following reaction takes place:



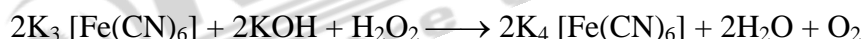
while, regarding is action on reducing agent, the following reaction takes place :



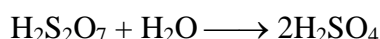
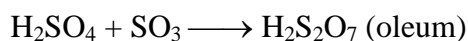
**Oxidizing character :**



**Reducing character:**



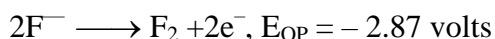
13. In  $SO_3 + H_2O \longrightarrow H_2SO_4$  reaction,  $H_2SO_4$  is obtained in misty form and reaction is explosive (highly exothermic). By adding  $H_2SO_4$  the above reaction is prevented.



The catalyst used is  $V_2O_5$  and  $K_2O$  is used as promotor for the oxidation of  $SO_2$  into  $SO_3$ .

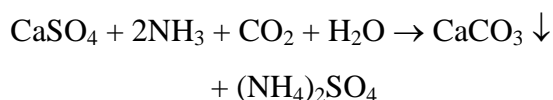
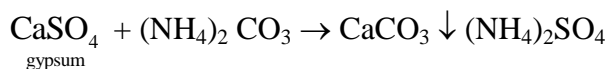
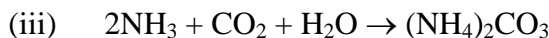
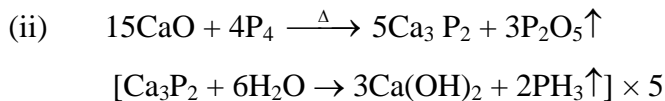
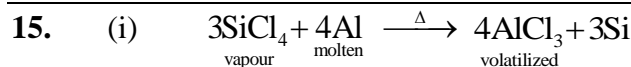
14. (i) Graphite, hexagonal planes are held by weak van der Waals forces. Since these forces are overcome, one plane slides over the other. This explains the lubricating properties of graphite.

- (ii) Fluoride has negative oxidation potential



Hence, fluoride is the poorest reducing agent.

Hence,  $F_2$  can't be prepared by oxidation of HF by even strong oxidising agents such as  $KMnO_4$ ,  $MnO_2$  etc.



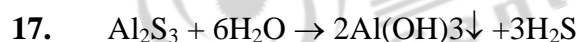
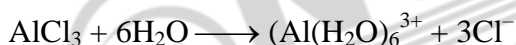
16. Total hydration energy of  $\text{Al}^{3+}$  and  $3\text{Cl}^-$  ions of  $\text{AlCl}_3$

$(\Delta H_{\text{hydration}})$

$= (\text{Hydration energy of } \text{Al}^{3+} + 3 \times \text{hydration energy of } \text{Cl}^-)$

$= [-4665 + 3(-381)] \text{ kJ mol}^{-1} = 5808 \text{ kJ mol}^{-1}$

This amount of energy is more than that required for the ionisation of Al into  $\text{Al}^{3+}$  (Ionisation energy of Al to  $\text{Al}^{3+}$ ). Due to this reason,  $\text{AlCl}_3$  becomes ionic in aqueous solution. In aqueous solution, it exists in ionic form as below :

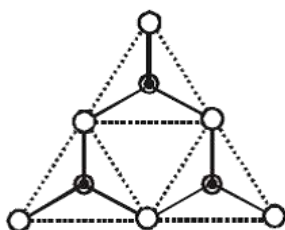


foul odour

Foul odour, on damping of  $\text{Al}_2\text{S}_3$  is due to formation of  $\text{H}_2\text{S}$  gas.

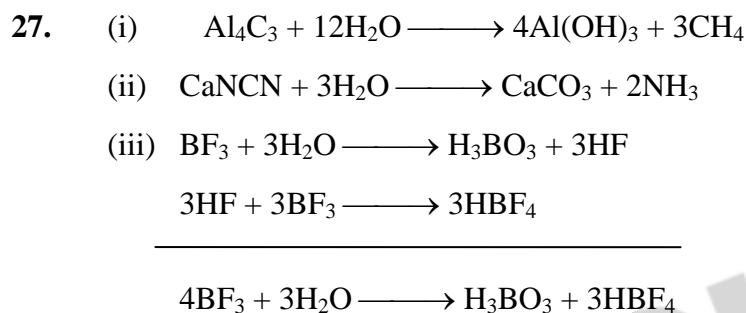
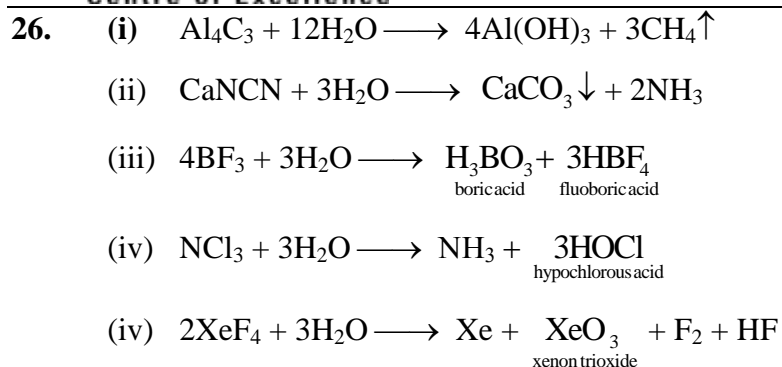
18. In cyclic  $(\text{Si}_3\text{O}_9)^{6-}$ , three tetrahedral of  $\text{SiO}_4$  are joined together by sharing of two oxygen atoms per tetrahedral.

Structure of  $(\text{Si}_3\text{O}_9)^{6-}$

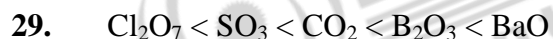


In it dark circles (·) represent Si and open circles (O) represent oxygen atom or iron.

19.  $\text{BeCl}_2$  is hydrolysed due to high polarising power and presence of vacant p-orbitals in Be atom.  
(Be =  $1s^2, 2s^2, 2p_x^1, 2p_y^0, 2p_z^0$ )
20. In nitrogen, d-orbitals are not present, so in it the possibility of intramolecular multiplicity exists which leads to the completion of octet through  $\pi$ -bond between two nitrogen atoms.  
In phosphorus, d-orbitals are present, so in it due to large size of P, the P-P bonds are longer and hence intramolecular multiplicity is ruled out. So, for the completion of octet, it forms the bonds with three other 'P' atoms. Hence due to this reason it shows molecular formula as  $\text{P}_4$ .
21.  $2\text{I}^- (\text{aqueous}) + \text{Cl}_2 \longrightarrow \text{I}_2 + 2\text{Cl}^- (\text{aqueous})$   
(i)  $2\text{I}^- (\text{aqueous}) \longrightarrow \text{I}_2 (\text{s}) + 2\text{e}^-$   
(ii)  $\text{Cl}_2 (\text{g}) + 2\text{e}^- \longrightarrow 2\text{Cl}^- (\text{aq})$   
Thus,  $\text{I}^-$  is oxidised into  $\text{I}_2$  by  $\text{Cl}_2$  due to higher oxidised potential of  $\text{Cl}_2$  than  $\text{I}_2$
22. X :  $\text{BCl}_3$   
Y :  $\text{B}_2\text{H}_6$   
 $4\text{BCl}_3 + 3\text{LiAlH}_4 \longrightarrow 3\text{AlCl}_3 + 3\text{LiCl} + 2\text{B}_2\text{H}_6$   
X  
 $\text{B}_2\text{H}_6 + 3\text{O}_2 \longrightarrow \text{B}_2\text{O}_3 + 3\text{H}_2\text{O}$  (exothermic)  
Y
23. (i)  $3\text{SiCl}_4 + 4\text{Al} \longrightarrow 3\text{Si} + 4\text{AlCl}_3$  (in one step)  
(ii)  $\text{SiCl}_4 + 2\text{Mg} \longrightarrow 2\text{MgCl}_2 + \text{Si}$   
 $\text{Si} + \text{Cu} \longrightarrow \text{Si}-\text{Cu}$   
 $2\text{CH}_3\text{Cl} + \text{Si}-\text{Cu} \longrightarrow (\text{CH}_3)_2\text{SiCl}_2 + \text{Cu}$   
 $(\text{CH}_3)_2\text{SiCl}_2 + 2\text{H}_2\text{O} \longrightarrow (\text{CH}_3)_2\text{Si}(\text{OH})_2 + 2\text{HCl}$   
$$2(\text{CH}_3)_2\text{Si}(\text{OH})_2 \xrightarrow[-\text{H}_2\text{O}]{\Delta} \text{H}-\text{O}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{Si}}}-\text{O}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{Si}}}-\text{OH}$$
  
(iii)  $\text{SiCl}_4 + 4\text{H}_2\text{O} \longrightarrow \text{Si}(\text{OH})_4 + 4\text{HCl}$   
 $\text{Si}(\text{OH})_4 \longrightarrow \text{SiO}_2 + 2\text{H}_2\text{O}$   
 $\text{SiO}_2 + \text{Na}_2\text{CO}_3 \xrightarrow[1673\text{K}]{\Delta} \text{Na}_2\text{SiO}_3 + \text{CO}_2$
24. Unreacted AgBr is removed by hypo ( $\text{Na}_2\text{S}_2\text{O}_3$ )  
 $\text{AgBr} + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2] + \text{NaBr}$
25.  $14\text{CO}_2$



28. Oxidation state



- |        |         |                               |         |         |         |         |
|--------|---------|-------------------------------|---------|---------|---------|---------|
| 30. BD | 31. D   | 32. D                         | 33. A   | 34. A   | 35. C   | 36. ABD |
| 37. A  | 38. C   | 39. D                         | 40. C   | 41. C   | 42. D   | 43. A   |
| 44. A  | 45. A   | 46. A- QS ,B- RS ,C- P, D- QR | 47. C   | 48. C   |         |         |
| 49. B  | 50. C   | 51. B                         | 52. A   | 53. D   | 54. A   | 55. C   |
| 56. A  | 57. C   | 58. A                         | 59. C   | 60. C   | 61. B   | 62. B   |
| 63. C  | 64. A   | 65. B, D                      | 66. B   | 67. ACD | 68. A   | 69. A   |
| 70. D  | 71. C   | 72. A                         | 73. B,D | 74. B,C | 75. BCD | 76. B   |
| 77. 6  | 78. B   | 79. ACD                       | 80. BD  | 81. D   | 82. C   | 83. BC  |
| 84. AC | 85. BCD |                               |         |         |         |         |

