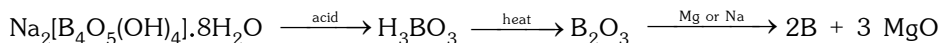


P-BLOCK ELEMENTS

BORON FAMILY

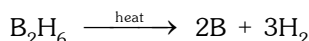
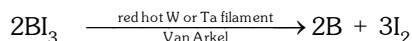
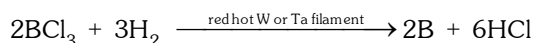
1. EXTRACTION OF BORON

Amorphous boron of low purity (called moissan boron) is obtained by reducing B_2O_3 with Mg or Na at a high temperature. It is 95–98% pure (being contaminated with metal borides), and is black in colour.



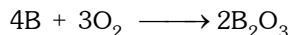
It is difficult to obtain pure crystalline boron, as it has a very high melting point (2180°C) and the liquid is corrosive. Small amounts of crystalline boron may be obtained :

- (a) By reducing BCl_3 with H_2 . This is done on the kilogram scale.
- (b) Pyrolysis of BI_3 (Van Arkel method).
- (c) Thermal decomposition of diborane or other boron hydrides.

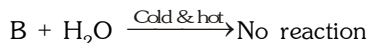


Property of Boron

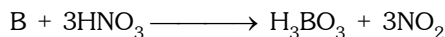
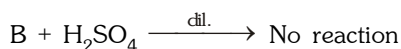
- (a) Burning in air



- (b) Reaction with water

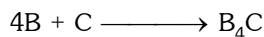


- (c) $B + HCl \longrightarrow$ No reaction



- (d) $2B + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2$

- (e) $2B + N_2 \longrightarrow 2NB$



- (f) $3Mg + 2B \longrightarrow Mg_3B_2$

2. BORANES

Boranes are boron hydrogen compounds with general molecular formula B_nH_{n+4} or B_nH_{n+6} . They are electron deficient compounds. The lighter boranes (upto B_5) spontaneously react with air whereas remaining compound are air stable. The physical properties of boranes are given as under :

| Formula | Name | Melting point (°C) | Boiling point (°C) |
|---------------------------------|-----------------|-----------------------|-----------------------|
| B ₂ H ₆ | Diborane | - 165.6 | - 92.5 |
| B ₄ H ₁₀ | Tetraborane | - 120 | 18 |
| B ₅ H ₉ | Pentaborane -9 | - 46.6 | 48 |
| B ₅ H ₁₁ | Pentaborane -11 | - 123 | 63 |
| B ₆ H ₁₀ | Hexaborane -10 | - 62.5 | 110 |
| B ₆ H ₁₂ | Hexaborane -12 | - 82.3 | 80-90 |
| B ₈ H ₁₂ | Octaborane -12 | - 20 | — |
| B ₈ H ₁₄ | Octaborane -14 | - 20 | — |
| B ₉ H ₁₅ | Enneborane | 2.6 | — |
| B ₁₀ H ₁₄ | Decaborane | 99.7 | 213 |
| B ₂₀ H ₁₆ | Isosaborane-16 | 196.2 | — |

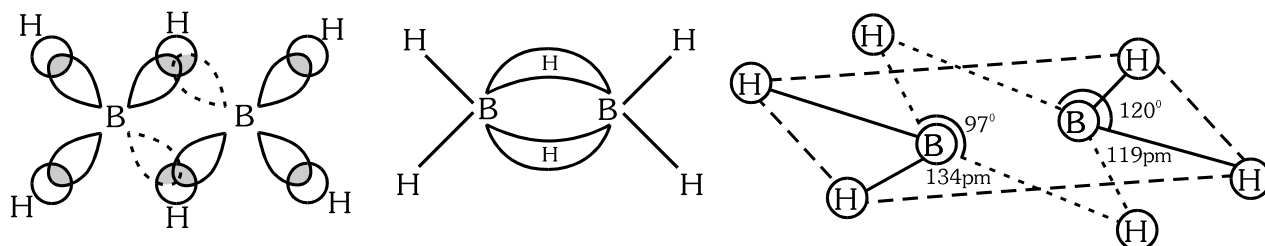
Preparation of Diborane

- (a) $\text{Mg}_3\text{B}_2 + \text{HCl} \longrightarrow \text{B}_2\text{H}_6 + \text{B}_4\text{H}_{10} + \text{B}_5\text{H}_9 \text{ etc.}$
(10%)
- (b) $\text{B}_4\text{H}_{10} \xrightarrow[100^\circ\text{C}]{\Delta} \text{B}_2\text{H}_6 + \text{H}_2 + \text{higher borane}$
- (c) $2 \text{BCl}_3 \text{ (or B Br}_3\text{)} + 6 \text{H}_2 \xrightarrow[\text{discharge at low pressure}]{\text{Electric}} \text{B}_2\text{H}_6 + 6\text{HCl}$
- (d) $3\text{LiAlH}_4 / \text{LiBH}_4 + 4\text{BF}_3 \longrightarrow 3\text{LiF}/3\text{BF}_3 + 3\text{AlF}_3 + 2 \text{B}_2\text{H}_6$

Chemical properties

- (a) $\text{B}_2\text{H}_6 + \text{O}_2 \xrightarrow[\text{air spontaneously}]{\text{burns in}} \text{B}_2\text{O}_3 + \text{H}_2\text{O}$
- (b) $\text{B}_2\text{H}_6 + \text{H}_2\text{O} \xrightarrow{\text{Cold is enough}} \text{H}_3\text{BO}_3 + 6\text{H}_2$
- (c) $\text{B}_2\text{H}_6 + 2\text{KOH} \longrightarrow 2\text{KOBH}_2 + 2\text{H}_2$
- (d) $\text{B}_2\text{H}_6 + \text{HCl} \xrightarrow[\text{dry}]{\text{anh. AlCl}_3} \text{B}_2\text{H}_5\text{Cl} + \text{H}_2$

Structure of diborane



The structure of diborane B₂H₆

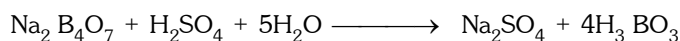
The structure of diborane is shown in fig. The four terminal hydrogen atoms and the two boron atoms lie in one plane. Above and below this plane, there are two bridging hydrogen atoms. The four terminal B-H bonds are regular two centre-two electron bonds while the two bridge (B-H-B) bonds are different and can be described in terms of three centre - two e^- bonds.

Bonding in diborane :- Each B atom uses sp^3 hybrids for bonding. Out of the four sp^3 hybrids on each B atom, one is without an electron shown in broken lines. The terminal B-H bonds are normal 2c-2e bonds but the two bridge bonds are 3c-2e bonds. The 3c-2e bridge bonds are also referred to as **banana bonds or tau bonds**.

3. BORIC ACID

Preparation

It is prepared by borax reacting with sulphuric acid.

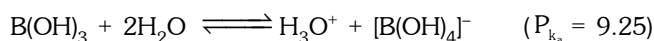


Physical properties

- Its crystals are soft, white, needle like having a soapy touch.
- It is steam volatile.

Chemical properties

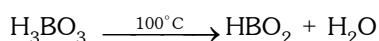
- Ortho boric acid does not donate proton, like most of the acids but rather it accepts OH^- , therefore it is a lewis acid and is represented by $B(OH)_3$.



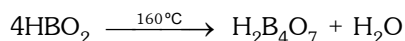
- $B(OH)_3$ partially reacts with water to form $H_3 O^+$ and $[B(OH)_4]^-$ and behaves as a weak acid. Thus $B(OH)_3$ can not be titrated satisfactorily with NaOH because a sharp end point is not obtained. If polyhydroxy compound like glycerol, mannitol or sugar are added to titration mixture than it can be titrated with NaOH.



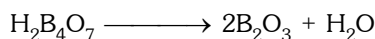
- Effect of temperature at 100 C $H_3 BO_3$ losses water and convert into metaboric acid.



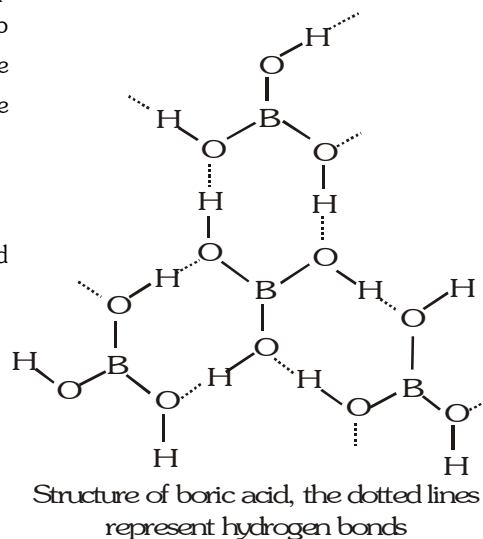
metaboric acid form tetraboric acid on heating at 160 C.



On strong heating $B_2 O_3$ is produced



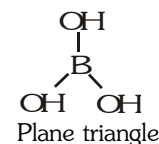
- Boric acid react with ethyl alcohol to form ethyl borate which



burns with green edged flame.

Structure of orthoboric acid

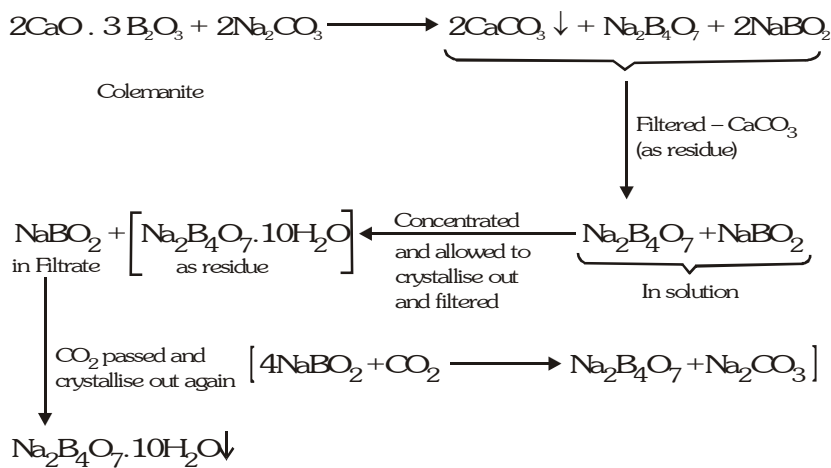
At lower concentration, its structure is a plane triangle.



4. BORAX

Preparation

- (a) In making glass, enamel and glaze of pottery.
 (b) As antiseptic in medicinal soaps preparation.



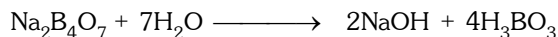
- (c) Orthoboric acid on neutralization with Na_2CO_3 gives borax.

$$\text{Na}_2\text{CO}_3 + 4\text{H}_3\text{BO}_3 \longrightarrow \text{Na}_2\text{B}_4\text{O}_7 + 6\text{H}_2\text{O} + \text{CO}_2$$
- (d) Colemanite is converted into borax by boiling it with concentrated solution of Na_2CO_3 .

$$\text{Ca}_2\text{B}_6\text{O}_{11} + 2\text{Na}_2\text{CO}_3 \longrightarrow \text{Na}_2\text{B}_4\text{O}_7 + 2\text{CaCO}_3 + 2\text{NaBO}_2$$

Chemical properties

The solution of borax is alkaline in nature due to hydrolysis.

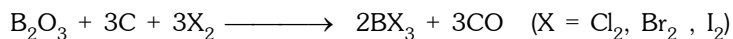


5. BORON TRIHALIDES

Boron combines with halogens and forms the halides of type BX_3 , ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$)

Preparation

Except BF_3 , other trihalides can be prepared by the treatment of halogens on a mixture of B_2O_3 and carbon at high temperature.



Properties

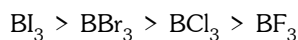
- (a) Due to small size and high charge density of B^{3+} ion, halides are covalent in nature.
 (b) These are non-electrolytes, as in liquid state they do not conduct electricity.
 (c) The boiling point are very low. The boiling point increases as the atomic number of halogen increases.
 (d) BF_3 is gas, BCl_3 (B.P. 13°C), BBr_3 (B.P. 90°C) are fuming liquids while BI_3 (M.P. 310°C) is a fusible solid.
 (e) The trihalides are electron deficient compounds. Boron atom acquires six electrons on account of three B – X bonds, i.e., 2 electrons, short to complete an octet. Thus the boron atom in BX_3 molecule can accept two more electron. i.e., an electron pair from the donor atoms like N, P, O, S, F, etc., in NH_3 , PH_3 , H_2O , H_2S , HF , F^- etc., respectively to form addition compounds (donor-acceptor compounds).



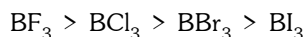
Donor Acceptor

(Lewis base) (Lewis acid)

- (f) The relative lewis acid character of boron trihalides is found to follow the following order.



but the expected order on the basis of electronegativity of the halogens (electronegativity of halogens decreases from F to I) should be –

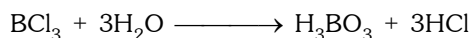


This anomaly is explained on the basis of the relative tendency of the halogen atom to back donate its unutilised electrons to vacant p-orbital of boron atom forming $p\pi - p\pi$ bond.

Extent of back bonding decrease from BF_3 to BI_3 with increase in size p-orbital of halogen.

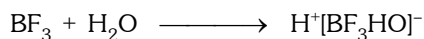
$p\pi - p\pi$ back bonding is maximum in BF_3 due same energy and same size of 2p orbital of boron and filled 2p-orbital of F.

- (g) All boron trihalides, except boron trifluoride, are hydrolysed to boric acid.



The degree of hydrolysis increases from BCl_3 to BI_3 because covalent character increases. Due to resistance of BF_3 to hydrolysis and its tendency to act as lewis acid BF_3 is used as a catalyst in organic reactions.

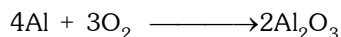
BF_3 form addition product with water as B – F bond is very strong



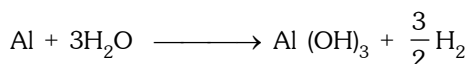
6. ALUMINIUM

Properties

- (a) Burning in air



- (b) Reaction with water

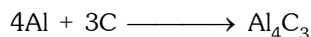


- (c) $2\text{Al} + 6\text{H}_2\text{SO}_4 \longrightarrow \text{Al}_2(\text{SO}_4)_3 + 3\text{SO}_2 + 6\text{H}_2\text{O}$

$\text{Al} + \text{HNO}_3 \longrightarrow \text{Al}_2\text{O}_3$ (passive layer) and does not react further.

- (d) $2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaAlO}_2 + 3\text{H}_2$

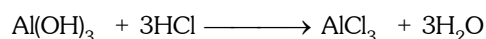
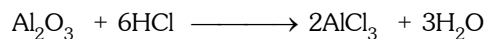
- (e) $2\text{Al} + \text{N}_2 \longrightarrow 2\text{AlN}$



7. ALUMINIUM CHLORIDE (AlCl_3)

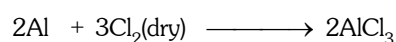
- (a) **Hydrated $\text{AlCl}_3 \rightarrow \text{AlCl}_3 \cdot 6\text{H}_2\text{O}$**

- (i) AlCl_3 is prepared by dissolving aluminium oxide or its hydroxide in dilute HCl.

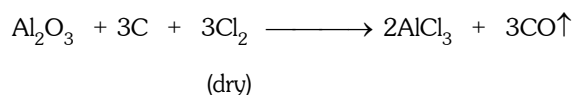


- (b) **Anhydrous AlCl_3**

- (i) Anhydrous aluminium chloride can be obtained by passing dry chlorine gas and dry HCl gas over heated aluminium in vacuum.

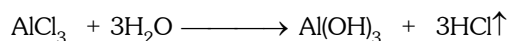


- (ii) **Macaffé's process** - The anhydrous salt is prepared by heating alumina with coke and chlorine.



Properties

- (a) Aluminium chloride is a white crystalline substance which fumes in moist air. It fumes in moist air due to its hydrolysis.



- (b) On heating it sublimes at 180°C .
- (c) At sublimation point its vapour density corresponds to formula Al_2Cl_6 i.e, it exists as a dimer. At higher temperatures i.e, above 750°C it exists as a monomer AlCl_3 .
- (d) It is largely covalent hence it does not conduct current in fused state.

Uses of AlCl_3

Anhydrous AlCl_3 is employed as a catalyst in organic reactions i.e, Friedal crafts reaction.

8. ALUM

- (a) Alums are double sulphates with their general formula $\text{R}_2\text{SO}_4 \cdot \text{M}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ where R = monovalent radical like Na^+ , K^+ , NH_4^+ and M = Trivalent radical like Al^{+3} , Cr^{+3} , Fe^{+3} .
- (b) The different alums are -
- Potash alum - $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
 - Chrome alum - $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
 - Iron alum - $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
 - Ammonium alum - $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
- (c) In alums each metal ion is surrounded by six water molecules.
- (d) Lithium does not form alum because Li ion is too small to have a coordination number of six.

Properties

- (a) It is a white crystalline solid highly soluble in water.
- (b) On heating it undergoes dehydration and swells up.
- (c) It is highly acidic in aqueous solution due to the hydrolysis of aluminium sulphate to sulphuric acid
- (d) It is a double salt and its aqueous solution gives reaction of all the constituents ions K^+ , Al^{+3} , SO_4^{-2} .

Uses

- (a) Alum is used to stop bleeding.
- (b) It is used for purification of water.
- (c) It is used as a mordant in dyeing industry.
- (d) Alum is used for tanning of leather.

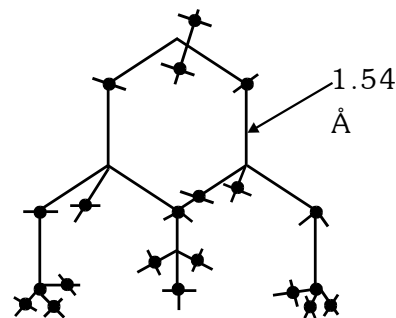
CARBON FAMILY

1. ALLOTROPIC FORM OF CARBON

(A) CRYSTALLINE

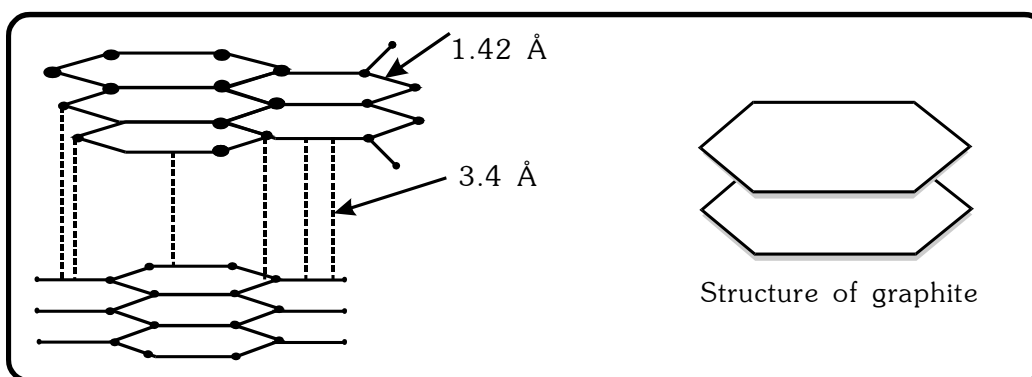
(a) **Diamond**

- (i) Three dimensional polymeric structure.
- (ii) In diamond each carbon is in sp^3 hybridized state and is linked to four other neighbouring carbon atoms held at the corners of a regular tetrahedron by covalent bonds.
- (iii) In this structure C-C distance is 1.54 \AA with a bond angle of 109.5° .
- (iv) Due to these strong covalent bonds, diamond is the hardest substance having abnormally high melting point (3600°C) and is extremely inert, chemically.
- (v) It has very high refractive index (2.5), i.e. light rays are slowed down by the tightly bound electron.
- (vi) Due to unavailability of mobile electrons it is non-conductor of electricity.

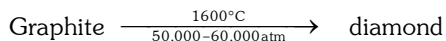


(b) **Graphite**

- (i) Unlike diamond, it has a two dimensional **laminar** structure.
- (ii) The adjacent layers of sheet are held together by weak vander Waal forces.
- (iii) Here each carbon atom is in sp^2 hybridised state and is thus attached to three other carbon atoms by three σ bonds forming a hexagonal planar structure.
- (iv) The fourth electron present in an unhybridised p-orbital of each carbon atom of a hexagonal unit then overlap with each other to form a pi bond.
- (v) The C—C bond length in graphite is shorter (1.42 \AA) than that of diamond (1.54\AA).



- (vi) Since π -electrons ($\pi - e^-$) are free to move throughout the entire layers, graphite is a good conductor of electricity. Its conductivity increases with temperature.
- (vii) It is a soft **greasy**, dark greyish coloured crystalline solid having density 2.5 g mL^{-1}
- (viii) Since it leaves a black mark on paper it is called black lead or plumbago
- (ix) It is thermodynamically more stable than diamond and its free energy of formation is 1.9 kJ less than diamond.

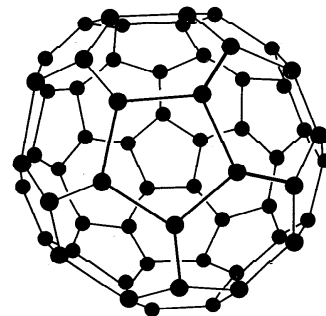


Amorphous :**(c) Fullerenes**

- (i) Discovered by smily & robert curl (Noble prize - 1996)
- (ii) Fullerene normally contain C_{60} with smaller quantity of C_{70}

Structure of C_{60}

- (i) C_{60} is also called buckminster fullerene in honour of robert buckminster fuller.
- (ii) Shape of C_{60} is Soccer ball & C_{70} is Rugby ball.
- (iii) C_{70} & C_{60} having hexagonal & pentagonal unit.

**(B) AMORPHOUS****Coal**

- (a) Naturally form & artificially.
- (b) It is found in different form.

Ex. Peat, Lignite, Bituminous, Anthracite

- (c) Max percent of C = Anthracite Min percent of C = Peat
- (d) Calorific value Max in = Anthracite

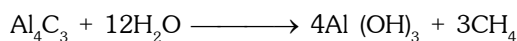
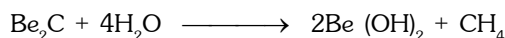
2. CARBIDES

Carbides are of three types according to the type of bonding

(a) Salt like carbides (ionic bonding)

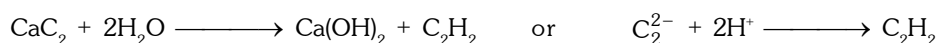
- (i) These are formed by strong electropositive elements of groups 1, 2 and 13
- (ii) These are transparent crystalline substances and do not conduct electric current in the solid state.
- (iii) These are easily hydrolysed by water or dilute acids to give aliphatic hydrocarbons,

Methanides (Methides) : Methanides are the carbides which give methane on hydrolysis. They contain C^{4-} ions.



Acetylides : These are the carbides which yield acetylene on hydrolysis. They contain the ion C_2^{2-}

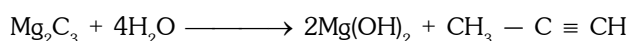
Ex. CaC_2 , BaC_2 and MgC_2



Note: Most of these carbides have ionic NaCl - type of structure.

Allylides : These carbides give methylacetylene or allylene ($CH_3 - C \equiv CH$). On hydrolysis they contain C_3^{4-} ions.

The only example of this class is Mg_2C_3



(b) **Covalent carbides (giant molecular structure)**

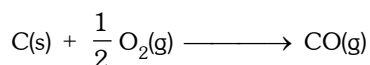
- (i) Covalent carbides are the compounds of carbon with elements having similar electronegativity.
- (ii) These are covalent, polymeric, thermally stable, extremely hard, high melting and technically inert solid.
- (iii) B_4C and SiC are two main covalent carbides.

(c) **Alloy type or interstitial type carbide**

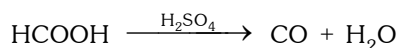
Transition metals like Ti, Zr, Hf, V, Nb, Ta and Mo form these carbides. The metals retain their **close packed lattice** and carbons are incorporated in their interstitial spaces. These carbides are extremely hard and have very high melting points. The carbides of V and Ta are very hard hence they are used for manufacture of high speed cutting tools.

3. CARBON MONOXIDE (CO)**Preparation**

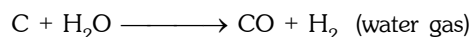
- (a) It is invariably present in automobile exhaust gas.



- (b) Pure CO



- (c) Industrially it is obtained in the form of water gas and producer gas when air (moist) is passed over a bed of white hot coke.

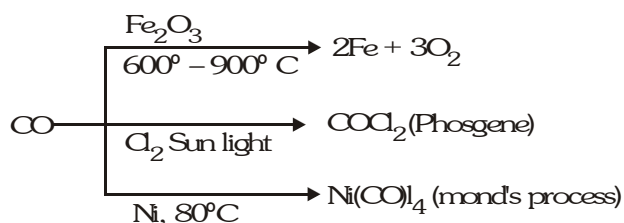
**Properties**

- (a) It is highly poisonous as it combines with haemoglobin to form carboxy haemoglobin which is not capable to absorb oxygen.

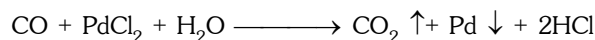
- (b) It burns with blue flame to form CO_2 . This is an exothermic process



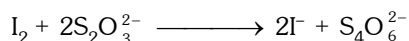
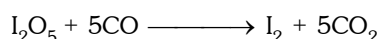
- (c) Chemical reactions

**How to detect**

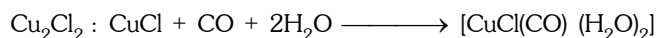
Burns with blue flame CO is passed through $PdCl_2$ solution giving rise to black ppt.



Black metallic deposition

How to estimate

What are its absorbers

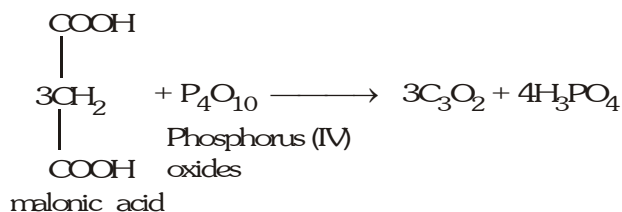


4. CARBON SUB OXIDE



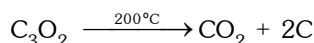
Preparation

By heating malonic acid with phosphorus penta oxide



Properties

- (a) Colourless gas, Boiling point 6°C
- (b) Very readily polymerises to give coloured salts.
- (c) It decomposes at 200°C



5. SILICON (Si)

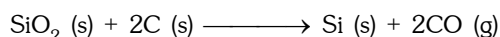
Silicon is the second most abundant (27.2%) element after oxygen (45.5%) in the earth's crust. It does not occur free in nature but in the combined state, it occurs widely in form of silica and silicates. All mineral rocks, clays and soils are built of silicates of magnesium, aluminium, potassium or iron. Aluminium silicate is however the most common constituent of rocks and clays.

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

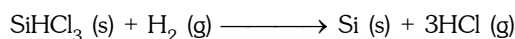
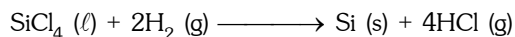
- (a) Feldspar – $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$
- (b) Kaolinite – $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
- (c) Asbestos – $\text{CaO} \cdot 3\text{MgO} \cdot 4\text{SiO}_2$

Preparation

- (a) **From silica (sand) :** Elemental silicon is obtained by the reduction of silica (SiO_2) with high purity coke in an electric furnace.



- (b) **From silicon tetrachloride (SiCl_4) or silicon chloroform (SiHCl_3) :** Is obtained by reduction of highly purified silicon tetrachloride or silicon chloroform with dihydrogen.



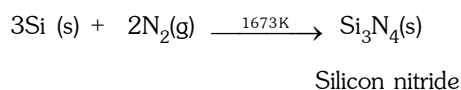
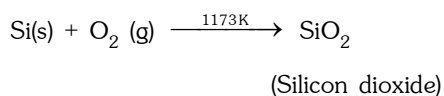
Physical Properties

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

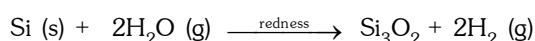
Chemical properties

Silicon is particularly unreactive at room temperature towards most of the elements except fluorine. Some important chemical reactions of silicon are discussed below

- (a) **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.



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

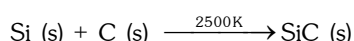


- (c) **Reaction with halogens** : It burns spontaneously in fluorine gas at room temperature to form silicon tetrafluoride (SiF_4).



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

- (d) **Reaction with carbon** : Silicon combines with carbon at 2500 K forming silicon carbide (SiC) known as carborundum.



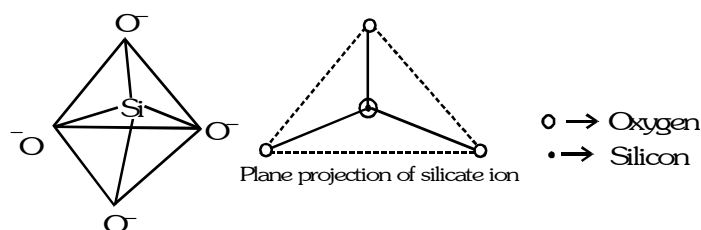
carborundum is an extremely hard substance next only to diamond. It is mainly used as an abrasive and as a refractory material.

Uses

- (a) Silicon is added to steel as such or more usually in form of ferrosilicon (an alloy of Fe and Si) to make it acid-resistant.
- (b) High purity silicon is used as semiconductors in electronic devices such as transistors.
- (c) It is used in the preparation of alloys such as silicon-bronze, magnesium silicon bronze and ferrosilicon.

6. SILICATES

Silicates have basic unit of SiO_4^{4-} , each silicon atom is bonded with four oxide ions tetrahedrally.

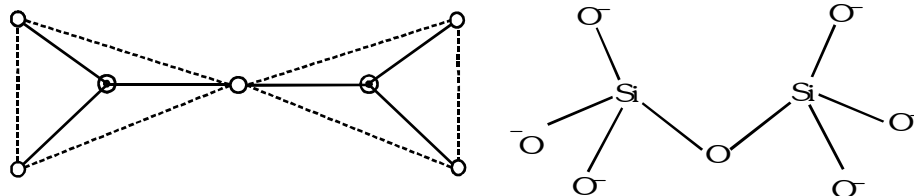


There are following types of silicates

- (a) **Orthosilicates** : These silicates contain single **discrete** unit of SiO_4^{4-} tetrahedral.

Ex. Willemite [Zn_2SiO_4]

(b) **Pyrosilicates**

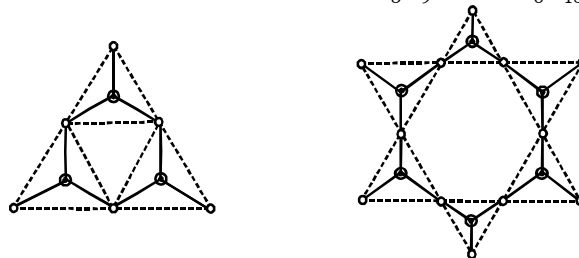


These silicates contain two units of SiO_4^{4-} joined along a corner containing oxygen atom. These are also called as island silicate.

Ex. Hemimorphite $\text{Zn}_3(\text{Si}_2\text{O}_7)\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$, Pyrosilicates ion $\text{Si}_2\text{O}_7^{6-}$

(c) **Cyclic structure** : Cyclic or ring silicate having general formula $(\text{SiO}_3^{2-})_n$ or $(\text{SiO}_2)_n^{2n-}$

Structure and example of cyclic silicates containing $\text{Si}_3\text{O}_9^{6-}$ and $\text{Si}_6\text{O}_{18}^{12-}$ ions are given below

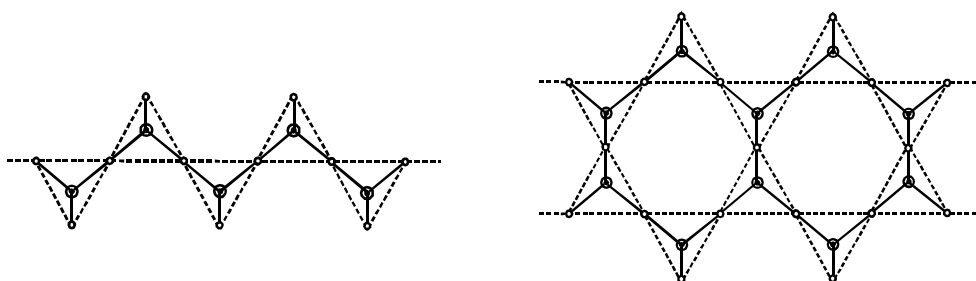


Ex. Beryl $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$

(d) **Chain silicates** : Chain silicates are formed by sharing two oxygen atoms by each tetrahedral. Anions of chain silicate have two general formula.

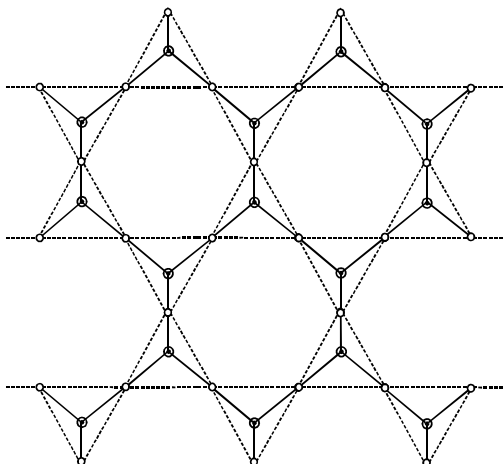
(i) $(\text{SiO}_3)_n^{2n-}$

(ii) $(\text{Si}_4\text{O}_{11})_n^{6n-}$



Ex. Spodumene $\text{Li}_2\text{Al}(\text{SiO}_3)_2$, Tremolite $\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$

(e) **Two dimensional sheet silicates** : In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent SiO_4^{4-} tetrahedral, such sharing forms two dimensional sheet structure with general formula $(\text{Si}_2\text{O}_5)_n^{2n-}$ **Ex.** Talc $\text{Mg}(\text{Si}_2\text{O}_5)_2\text{Mg}(\text{OH})_2$



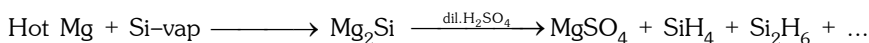
- (f) **Three dimensional sheet silicates** : These silicates involve all four oxygen atoms in sharing with adjacent SiO_4^{4-} tetrahedral.

Ex. Quartz, Zeolites and Ultramarines

7. SILANE

- (a) Only these two are found. SiH_4 & Si_2H_6 (Formula - $\text{Si}_n\text{H}_{2n+2}$).

- (b) Higher molecules are not formed. So, Si can't show catenation property.



- (c) SiH_4 is more reactive than CH_4 . due to following reason

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

C-electronegative than H

Si less electronegative than H

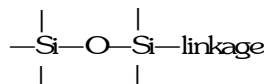
So bond polarity is reversed when Nu^- attacks, so it faces repulsion in C but not in Si

- (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 Nu^- doesn't face any steric hindrance to attack at Si whereas CH_4 is tightly held from all sides.

8. SILICONES

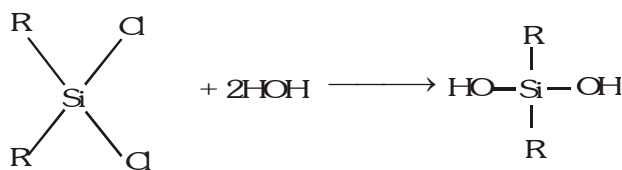
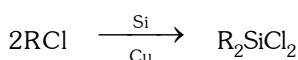
These are organosilicon polymers containing R_2SiO repeating units and empirical formula analogous to ketone (R_2CO)



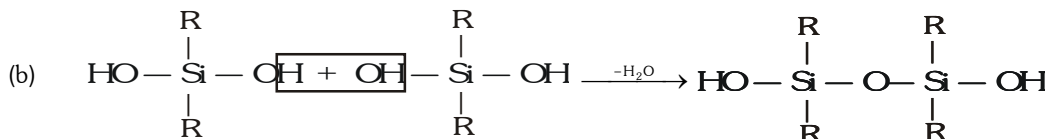
Alkyl substituted : These are formed by hydrolysis of alkyl chlorosilanes and their polymerisation. The alkyl or aryl substituted chlorosilanes are prepared by the reaction of Grignard reagent and silicon tetrachlorides.

Organic polymers containing silicon in them are called as **silicones**.

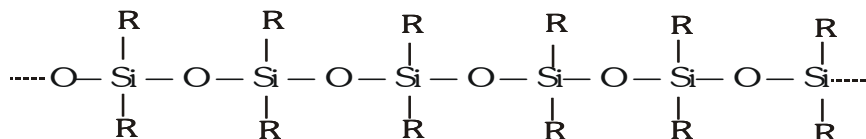
- (a) **Straight chain silicone**



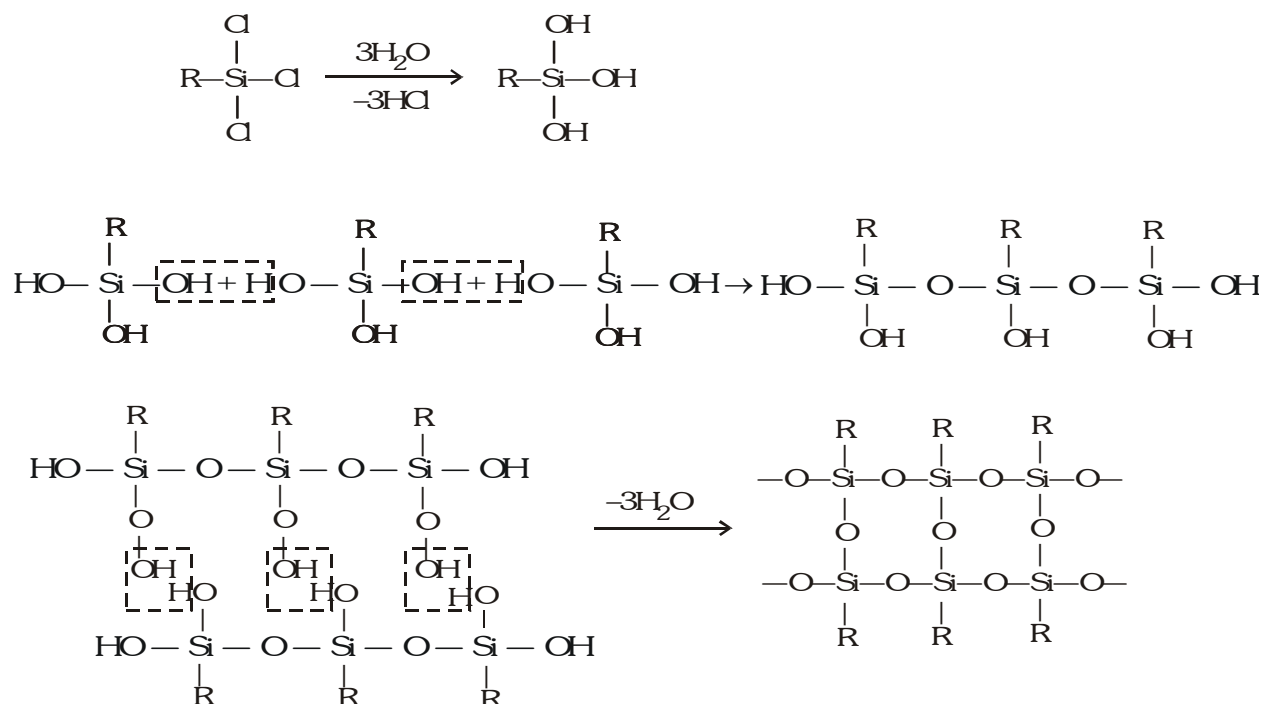
Dialkyldichloro Silane



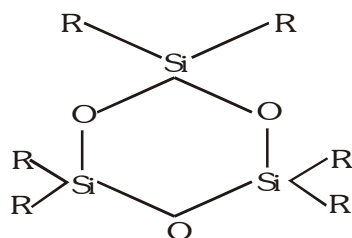
The terminal 'OH' groups which are active, allow the polymerisation reaction to continue and the length of the chain continues to increase



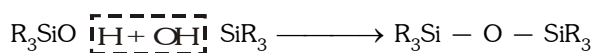
- (c) A complex **cross-linked** polymer is obtained on the hydrolysis of alkyl trichloro silane.



- (d) Cyclic (ring) silicones are formed when water is eliminated from the terminal -OH groups of linear silicones.



R_3SiCl on hydrolysis forms only a dimer



Uses

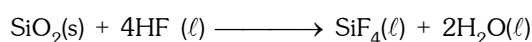
- They are used as greases, varnishes and resins.
- As they are water repellants, they are used for water-proofing.
- They are good electric insulators.

9. SILICA (SiO_2)

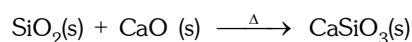
Silica or silicon dioxide occurs in nature in the free state as sand, quartz and flint and in the combined state as silicates like Feldspar $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, Kaolinite $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ etc.

Properties

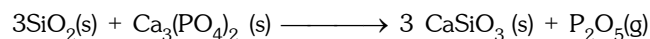
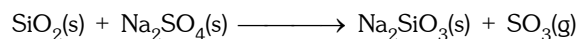
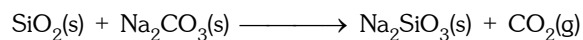
- Pure silica is colourless, but sand is usually coloured yellow or brown due to the presence of ferric oxide as an impurity.
- Silicon dioxide is insoluble in water and all acids except hydrofluoric acid.



- (c) It also combines with metallic oxides at high temperature giving silicates.



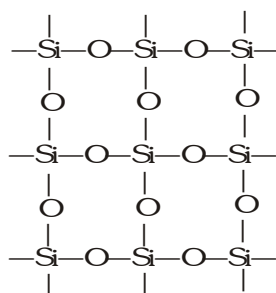
- (d) When silica is heated strongly with metallic salts, silicates are formed and the volatile oxides are driven off as vapours.



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

Structures of Silica

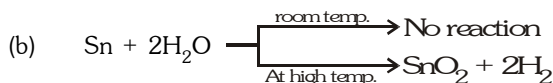
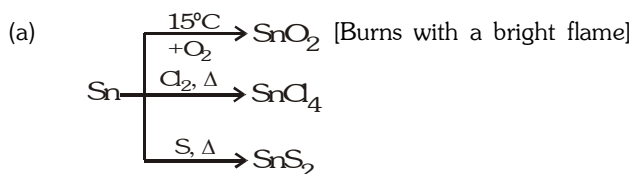
Silica has a three-dimensional network structure. In silica, silicon is sp^3 -hybridized and is thus linked to four oxygen atoms and each oxygen atom is linked to two silicon atoms forming a three-dimensional giant molecule as shown in figure. This three-dimensional network structure imparts stability to SiO_2 crystal and hence a large amount of energy is required to break the crystal resulting in high melting point.



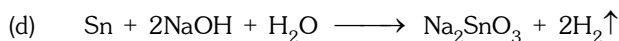
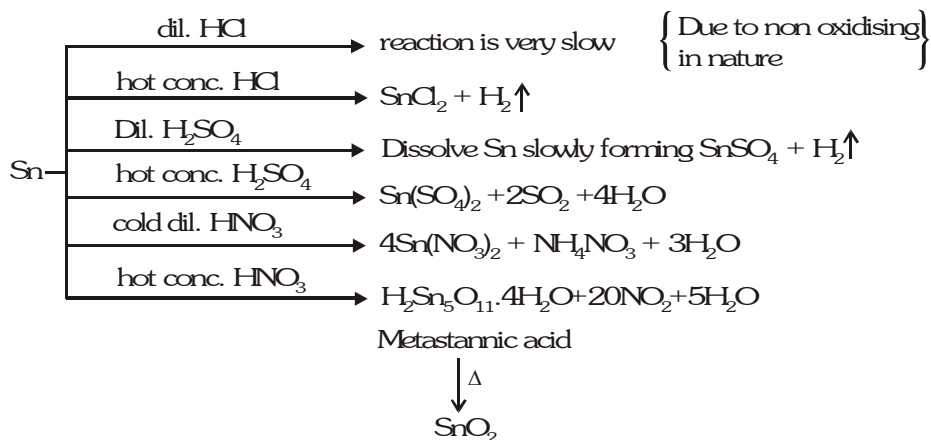
Uses

- Sand is used in large quantities to make the cement.
- 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.
- Powdered quartz is used for making silica bricks.
- 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.

10. COMPOUNDS OF Sn (TIN)/ LEAD



(c) Reaction with acid

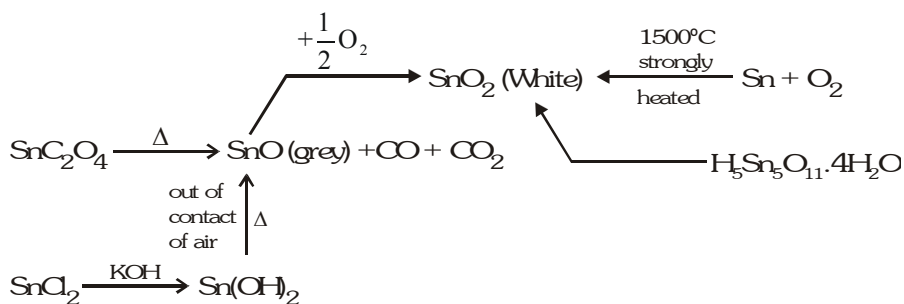


Sodium stannate

Note: KOH [In absence of air] Na_2SnO_2 forms and in contact with air it readily converts into Na_2SnO_3

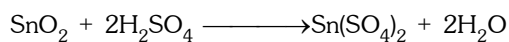
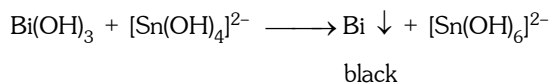
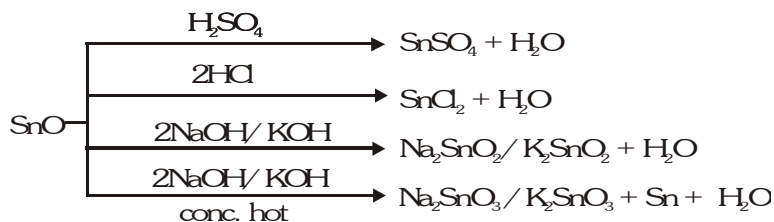
11. SnO (grey) and SnO_2 (white)

Preparation

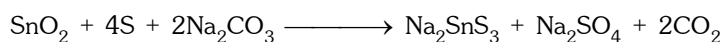
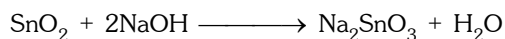


Properties

Both are amphoteric in nature



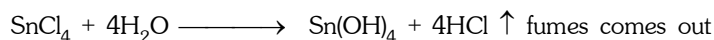
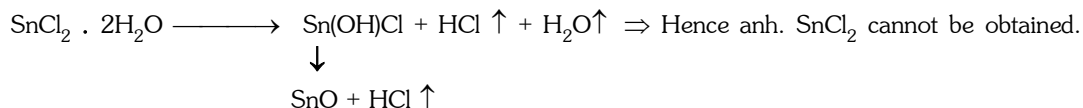
(Soluble only in hot conc. H_2SO_4)



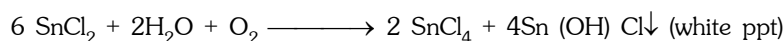
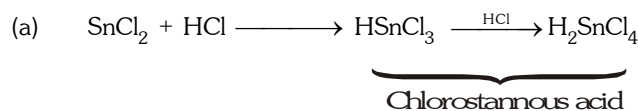
Note : insoluble in all acids even if in aqua regia.

12. STANNOUS CHLORIDE (SnCl_2)**Preparation**

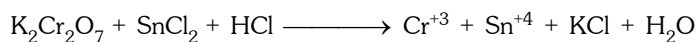
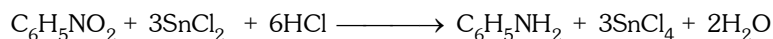
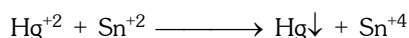
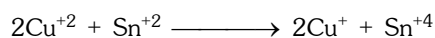
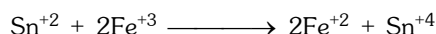
- (b) Anhydrous salt cannot be obtained by heating the hydrated salt as it undergoes hydrolysis and a white solid of tin hydroxy chloride is formed.



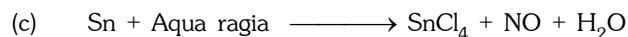
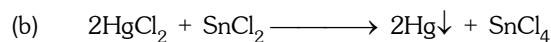
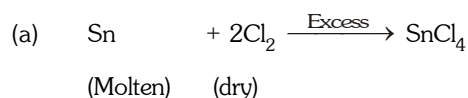
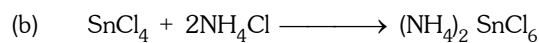
- (c) A piece of Sn is always added to preserve a solution of SnCl_2 .

**Properties**

- (b) Reducing Properties



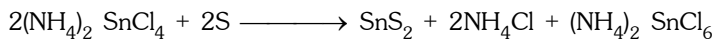
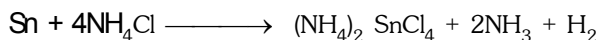
- (c) Readily combines with $\text{I}_2 \Rightarrow \text{SnCl}_2\text{I}_2 \Rightarrow$ This reaction is used to estimate tin.

13. STANNIC CHLORIDE (SnCl_4)**Preparation****Properties**

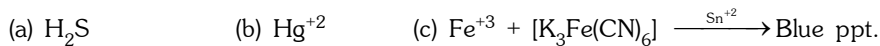
Note: $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ is known as butter of tin \Rightarrow used as mordant.

$(\text{NH}_4)_2\text{SnCl}_6$ is known as 'Pink salt' \Rightarrow used as calico printing.

Mosaic gold : SnS_2 yellow crystalline substance



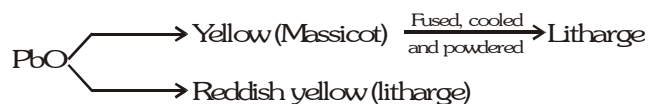
Distinction of $\text{Sn}^{+2}/\text{Sn}^{+4}$



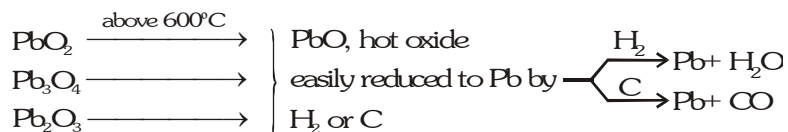
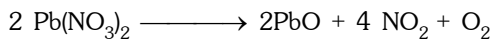
14. OXIDES OF LEAD

(a) **Lead monoxide (pbo)**

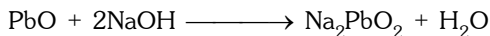
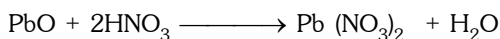
Preparation : It exists in two forms.



Laboratory preparation

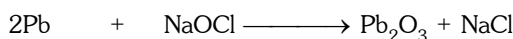


Properties : It is an amphoteric oxide insoluble in water.



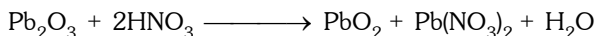
(b) **Sesquioxide (Pb_2O_3)**

Preparation



hot solⁿ. Limited
of NaOH amount

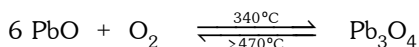
Properties



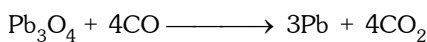
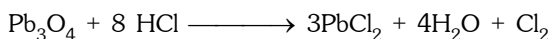
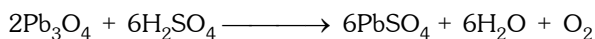
Note: This reaction suggests that Pb_2O_3 contains PbO_2 .

(c) **Red lead (Minium or sindhur) (Pb_3O_4)**

Preparation



Properties

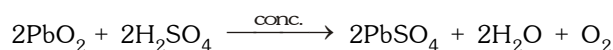


(d) **Lead Dioxide (PbO₂)**

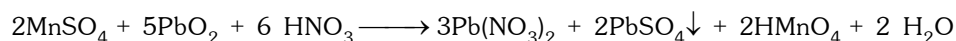
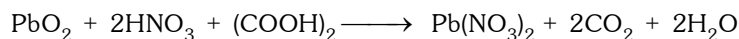
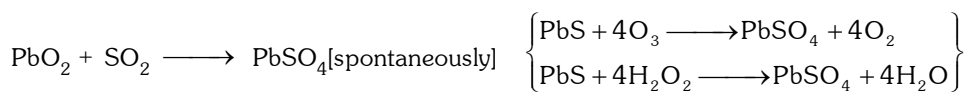
Preparation

- (i) $\text{Pb}_3\text{O}_4 + 4\text{HNO}_3 \longrightarrow 2\text{Pb}(\text{NO}_3)_2 + \text{PbO}_2 + 2\text{H}_2\text{O}$
- (ii) $(\text{CH}_3\text{COO})_2\text{Pb} + \text{Ca}(\text{OH})_2 \longrightarrow \text{Pb}(\text{OH})_2 + (\text{CH}_3\text{COO})_2\text{Ca}$
- (iii) $2\text{Pb}(\text{OH})_2 + 2\text{Ca}(\text{OCl})_2 \longrightarrow 2\text{PbO}_2 + \text{CaCl}_2 + 2\text{H}_2\text{O} + \text{O}_2$
Calcium hypochlorite
- (iv) $\text{Pb}(\text{OH})_2 + \text{CaOCl}_2 \longrightarrow \text{PbO}_2 + \text{CaCl}_2 + \text{H}_2\text{O}$
Bleaching powder

Properties : Insoluble in water and HNO₃, But reacts with (hot conc.) HCl/H₂SO₄ and in hot NaOH/KOH.



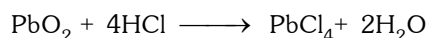
Sodium plumbate



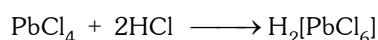
Note: PbO₂ is a powerful oxidising agent.

15. **LEAD CHLORIDE/PLUMBUS CHLORIDE (PbCl₂)**

PbCl₂ Exists as H₂[PbCl₆]

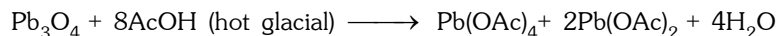


{ice cold conc. saturated with Cl₂}

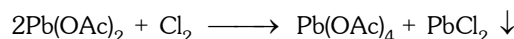


16. **LEAD TETRAACETATE**

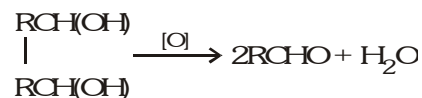
Preparation



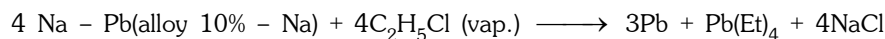
Pb(OAc)₂ is also converted into Pb(OAc)₄ by passing into Cl₂



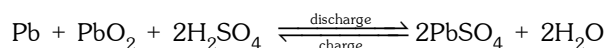
Properties : It is used as oxidising agent in organic chemistry to oxidise 1, 2-diol to aldehydes and Ketones.



17. **TETRAETHYL LEAD**



- It is antiknocking agent.
- Pb is used as a lead storage cell.

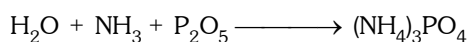
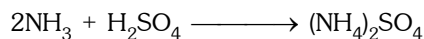


2. AMMONIA (NH_3)

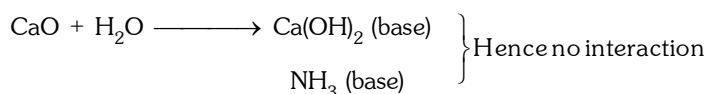
Preparation

- (a) Nitrate or nitrite reduction : $\text{NO}_3^-/\text{NO}_2^- + \text{Zn}/\text{Al} + \text{NaOH} \longrightarrow \text{NH}_3 + [\text{Zn}(\text{OH})_4]^{2-}/[\text{Al}(\text{OH})_4]^-$
- (b) Metal nitride hydrolysis : $\text{N}^{3-} + 3\text{H}_2\text{O} \longrightarrow \text{NH}_3\uparrow + 3\text{OH}^-$
- (c) Haber's process : $\text{N}_2 + 3\text{H}_2 \xrightarrow[200-1000\text{atm}]{450^\circ\text{C}} 2\text{NH}_3$
catalyst Fe/Mo

Note: NH_3 can't be dried by H_2SO_4 , P_2O_5 and anhydrous CaCl_2 because –



Quick lime is used for this purpose



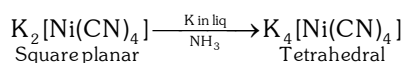
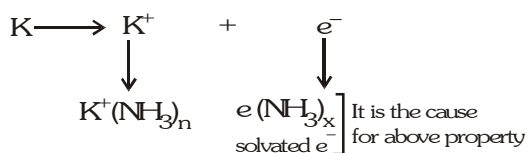
Properties

- (a) It dissolves several electropositive metals like Li, Na, K, Rb, Cs, Sr, Ba etc.

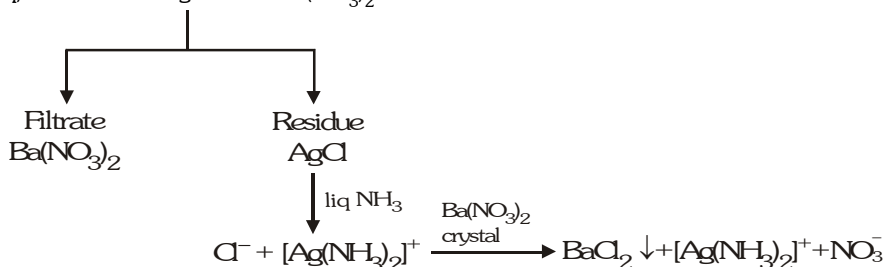
Ex. K in liq $\text{NH}_3 \Rightarrow$ (i) Blue in colour

(ii) Conducts electricity

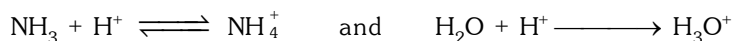
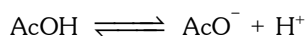
(iii) Having reducing property



- (b) $\text{Ag}(\text{NO}_3) \text{ (aq)} + \text{BaCl}_2 \text{ (aq)} \longrightarrow \text{AgCl} \downarrow + \text{Ba}(\text{NO}_3)_2$

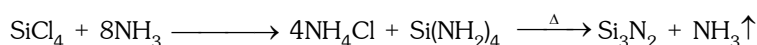
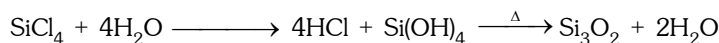


- (c) CH_3COOH is strong acid in liquid NH_3 while in water is weak acid.



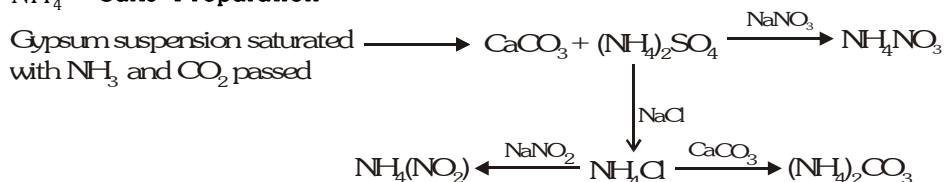
Basisity order $\text{NH}_3 > \text{H}_2\text{O}$

- (d) Hydrolysis and Ammonolysis occurs in a same way.



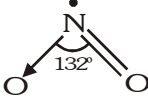
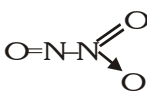
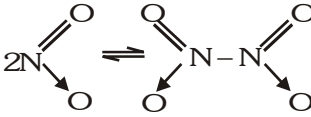
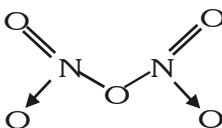
Rate of hydrolysis and Ammonolysis will be affected by the presence of HCl vapour & NH_4Cl vapour respectively.

(e) NH_4^+ - Salts Preparation



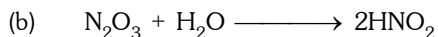
3. OXIDES OF NITROGEN

Preparation and Properties of Oxides of Nitrogen

| Formula | Name | Preparation & Structure | Properties |
|------------------------|--|--|--|
| N_2O | Dinitrogen monoxide (Nitrous oxide) Laughing gas | $\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$ $\text{N} \equiv \text{N} \rightarrow \text{O}$ (sp, Linear polar molecule) | Colourless gas, rather unreactive, diamagnetic neutral to litmus |
| NO | Nitrogen monoxide (Nitric oxide) | (a) $3\text{Cu} + 8\text{HNO}_3 \rightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO}$ (b) $4\text{NH}_3 + 5\text{O}_2 \xrightarrow[900^\circ\text{C}]{\text{Pt}} 4\text{NO} + 6\text{H}_2\text{O}$ | Colourless gas, paramagnetic, Neutral to litmus |
| NO_2 | Nitrogen dioxide Mixed anhydride | $\text{Pb}(\text{NO}_3)_2 \rightarrow 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$  | Brown gas, reactive, paramagnetic, angular and polar $2\text{NO}_2 \xrightarrow{\text{H}_2\text{O}} \text{HNO}_2 + \text{HNO}_3$ |
| N_2O_3 | Dinitrogen trioxide | $\text{NO} + \text{NO}_2 \xrightleftharpoons[\text{Room T}]{\text{Low T}} \text{N}_2\text{O}_3$ $\text{O} = \text{N} - \text{O} - \text{N} = \text{O}$ or  | Dark blue in liquid (-30°C) or solid state, unstable in the gas phase $\text{N}_2\text{O}_3 \xrightarrow{\text{H}_2\text{O}} 2\text{HNO}_2$ |
| N_2O_4 | Dinitrogen tetroxide | $2\text{NO}_2 \xrightleftharpoons{\text{Low T}} \text{N}_2\text{O}_4$  | Colourless, exists in equilibrium with NO_2 both in the gaseous and liquid state, in solid state, N_2O_4 is unstable. |
| N_2O_5 | Dinitrogen pentoxide | $2\text{HNO}_3 + \text{P}_2\text{O}_5 \rightarrow \text{H}_2\text{O} + \text{N}_2\text{O}_5$ $\text{H}_2\text{O} + \text{P}_2\text{O}_5 \rightarrow 2\text{HPO}_3$  | No existence in gas phase, in the solid state exists as nitronium nitrate $[\text{NO}_2]^+ [\text{NO}_3]^-$ |

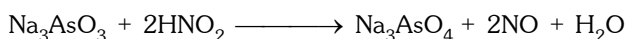
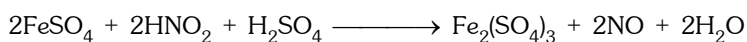
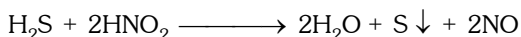
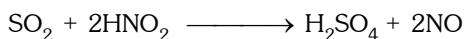
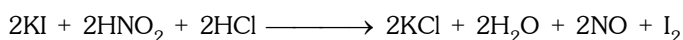
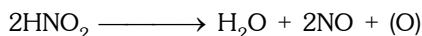
4. NITROUS ACID (HNO_2)

Preparation

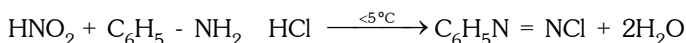
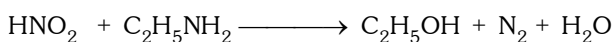
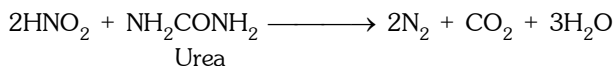
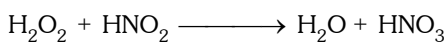
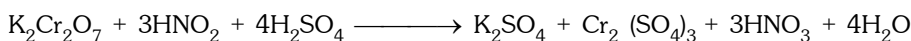
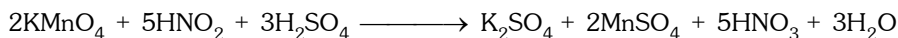
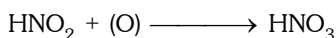


Properties

- (a) **Oxidising property** : Because of its easy oxidation to liberate nascent oxygen, it acts as a strong oxidant



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



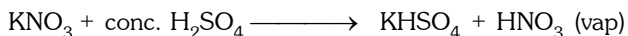
Benzene diazonium chloride

5. NITRIC ACID (HNO_3)

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

Preparation

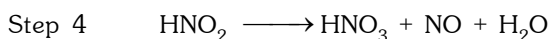
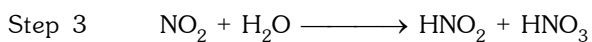
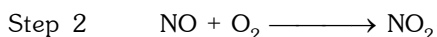
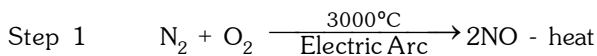
- (a) **Laboratory Method**

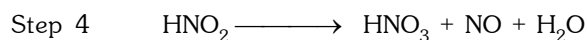
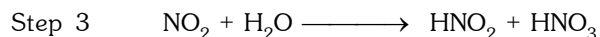
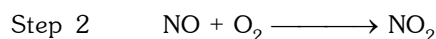
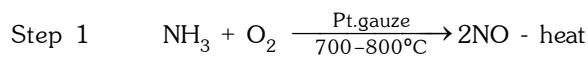


vapours of nitric acid evolved are condensed in a glass receiver.

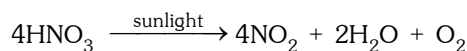
- (b) **Industrial Preparation**

- (i) **Birkeland Eyde Process or arc process**



(ii) **Ostwald's Process****Physical Properties**

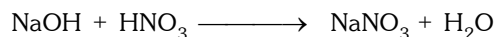
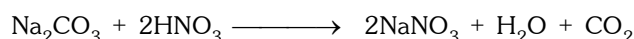
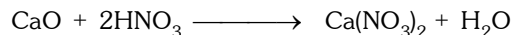
Nitric acid usually acquires yellow colour due to its decomposition by sunlight into NO_2 .



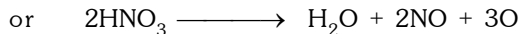
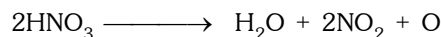
The yellow colour of the acid can be removed by warming it to $60-80^\circ\text{C}$ and bubbling dry air through it. It has extremely corrosive action on the skin and causes painful sores.

Chemical Properties

It is very strong acid and it exhibits usual properties of acids. It reacts with basic oxides, carbonates, bicarbonates and hydroxides forming corresponding salts.

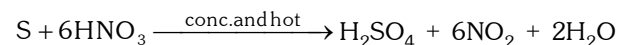


Oxidising nature : Nitric acid acts as a strong oxidising agent as it decomposes to give nascent oxygen easily.

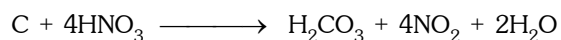


(a) **Oxidation of non-metals :** The nascent oxygen oxidises various non-metals to their corresponding highest oxyacids.

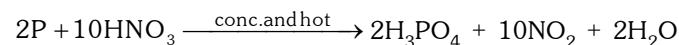
(i) Sulphur is oxidised to sulphuric acid



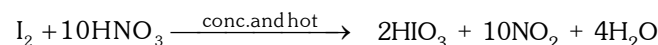
(ii) Carbon is oxidised to carbonic acid



(iii) Phosphorus is oxidised to orthophosphoric acid.

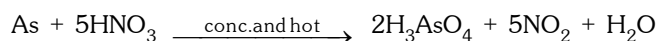


(iv) Iodine is oxidised to iodic acid

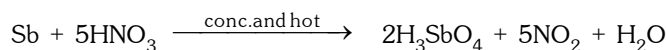


(b) **Oxidation of metalloids :** Metalloids like non-metals also form highest oxyacids

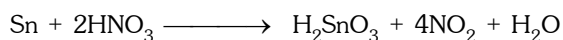
(i) Arsenic is oxidised to arsenic acid



(ii) Antimony is oxidised to antimononic acid

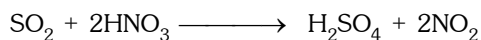


- (iii) Tin is oxidised to meta-stannic acid.

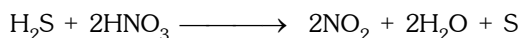


- (c) **Oxidation of compounds**

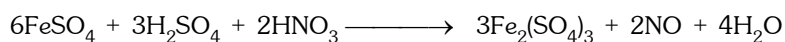
- (i) Sulphur dioxide is oxidised to sulphuric acid



- (ii) Hydrogen sulphide is oxidised to sulphur



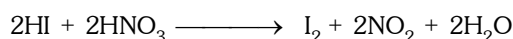
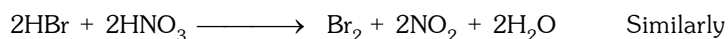
- (iii) Ferrous sulphate is oxidised to ferric sulphate in presence of H_2SO_4



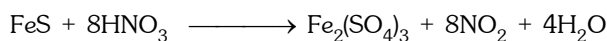
- (iv) Iodine is liberated from KI.



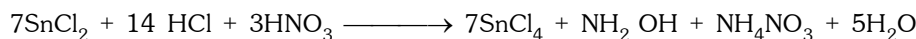
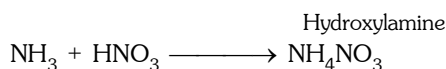
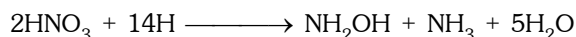
- (v) HBr, HI are oxidised to Br_2 and I_2 , respectively.



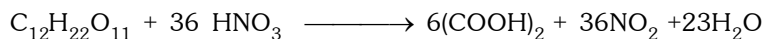
- (vi) Ferrous sulphide is oxidised to ferric sulphate



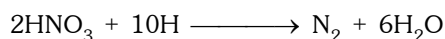
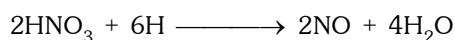
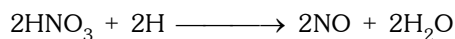
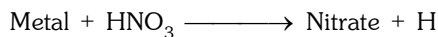
- (vii) Stannous chloride is oxidised to stannic chloride in presence of HCl



- (viii) Cane sugar is oxidised to oxalic acid



Action on Metals : Nitric acid reacts with most of the metals except noble metals like gold and platinum. Towards its reaction with metals, HNO_3 acts as an acid as well as an oxidising agent. Like other acids, HNO_3 liberate nascent H from metals which further reduces the nitric acid into number of products like NO , NO_2 , N_2O , N_2 , NH_2OH or NH_3 according to the following reactions :

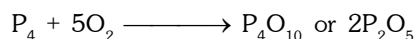


The progress of the reaction is controlled by a number of factors :

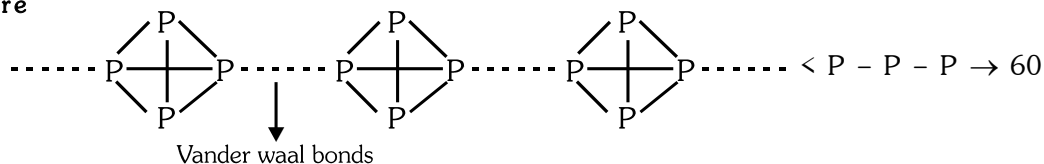
- The nature of the metal
- The concentration of the acid,
- The temperature of the reaction
- The presence of other impurities

Properties

- It has characteristic garlic smell and is poisonous in nature. Persons working with phosphorus develop a disease in which the jaw bones decay. This disease is known as **phossy jaw**.
- In contact with air, it undergoes slow combustion and glows in dark. This property is called **phosphorescence**.
- Its ignition temperature is low (about 30 °C). It readily catches fire giving dense fumes of phosphorus pentoxide. It is, therefore, kept in water.



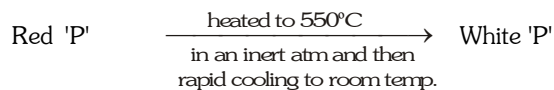
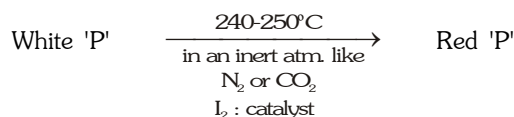
Structure



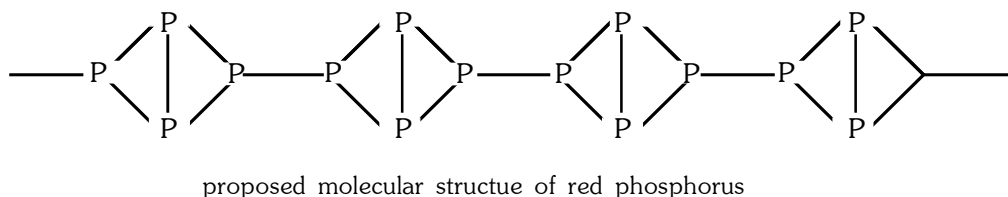
(b) Red phosphorus

Preparation

Red phosphorus is formed by heating yellow phosphorus, between 240–250 °C, in presence of an inert gas.

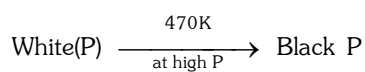


Structure of red phosphorus :- It is regarded as a polymer consisting of chains of P_4 tetrahedral linked together by covalent bond.



(c) Black P

Preparation : This is most stable form of Phosphorus



Black P contain zig-zag & double layered structure.

Order of density & mp

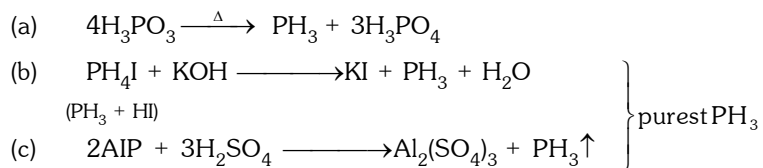
Black > Red > White

Comparison between White and Red Phosphorus

| Property | White phosphorus | Red phosphorus |
|-------------------------------|--|------------------------|
| Physical state | Soft waxy solid. | Brittle powder. |
| Colour | White when pure. Attains yellow colour on standing. | Red. |
| Odour | Garlic | Odourless. |
| Solubility in water | Insoluble. | insoluble |
| Solubility in CS ₂ | 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. |
| Reaction with NaOH | Evolves phosphine. | No action. |
| Molecular formula | P ₄ | Complex polymer. |

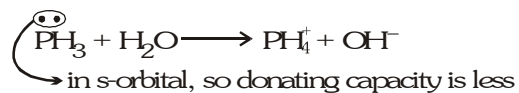
7. PHOSPHINE GAS (PH₃)

Preparation



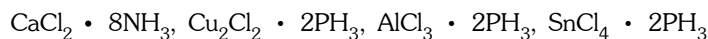
Physical properties

- It is having 'rotten fish' smell.
- It is soluble in CS₂ and insoluble in water.

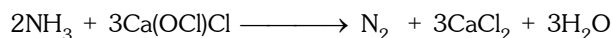
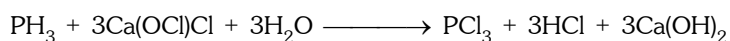


Note : PH₄⁺ is formed with acids.

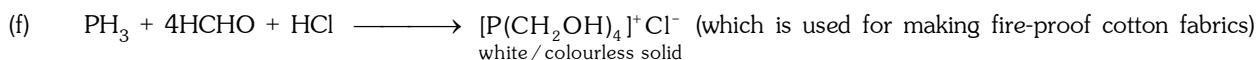
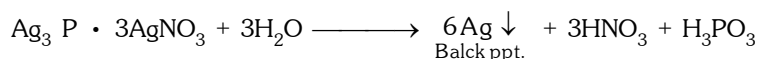
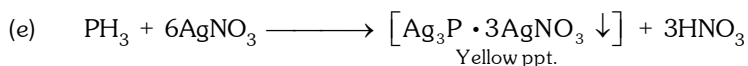
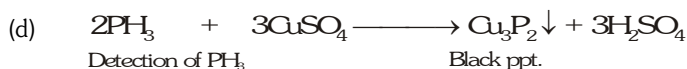
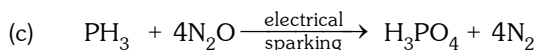
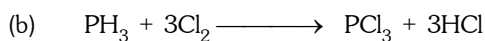
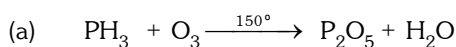
- Like NH₃, PH₃ also can form addition product.



PH₃ can be absorbed by Ca(OCl)Cl.



Chemical properties



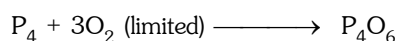
8. OXIDES OF PHOSPHORUS

It forms three important oxides which exist in dimeric forms.

Phosphorus trioxide (P_4O_6)

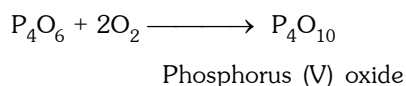
Preparation

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

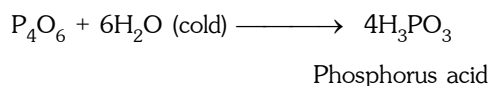


Properties

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



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

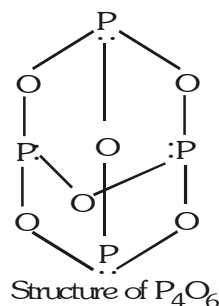


It is, therefore, considered as anhydride of phosphorus acid.

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

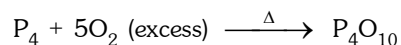
Structure

- (a) Each atom of phosphorus in P_4O_6 is present at the corner of a tetrahedron
- (b) Each phosphorus atom is covalently bonded to three oxygen atoms and each oxygen atom is bonded to two phosphorus atoms.
- (c) It is clear from the structure that the six oxygen atoms lie along the edges of the tetrahedron of P atoms.



Phosphorus (V) oxide (P_4O_{10})

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.



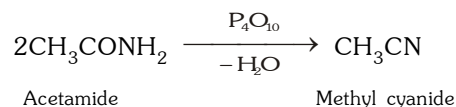
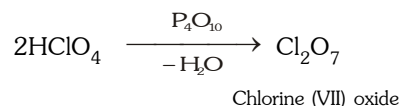
Metaphosphoric acid.

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_4O_{10} is a very strong dehydrating agent and extracts water from many compounds including sulphuric acid and nitric acid.



Structure

- (a) Its structure is similar to that of P_4O_6 .
- (b) In addition, each phosphorus atom forms a double bond with oxygen atom as shown in figure.

